EFFECT OF ADDING GRAPHITE NANO/MICRO PLATELETS ON SALT FREEZE-THAW RESISTANCE OF NANO-MODIFICENT CONCRETE

Submitted by

Ahmad Nawaz

Fall 2016-MS Structural Engineering

00000171820

MASTERS IN STRUCTURAL ENGINEERING

MS Thesis Advisor:

Dr. Rao Arsalan Khushnood

NUST Institute of Civil Engineering (NICE)

School of Civil and Environmental Engineering (SCEE)

National University of Sciences and Technology (NUST)

Islamabad, Pakistan (2019)

This is to certify that

Thesis titled

"Effect of adding graphite nano/micro platelets on salt freeze-thaw resistance of nano-modificent concrete''

Submitted by

Ahmad Nawaz

Fall 2016-MS Structural Engineering

00000171820

Has been accepted towards the partial fulfillment

of

the requirements for the award of degree of

Master of Science in Structural Engineering

____

Dr. Rao Arsalan Khushnood
Assistant Professor
NUST Institute of Civil Engineering (NICE)
School of Civil and Environmental Engineering (SCEE)
National University of Sciences and Technology (NUST),
Islamabad, Pakistan

THESIS ACCEPTANCE CERTIFICATE

Certified that final copy of MS thesis written by **Mr. Ahmad Nawaz,** Registration No. **(00000171820),** of MS Structure 2016 Batch (NICE) has been vetted by undersigned, found completed in all respects as per NUST Statutes/Regulations, is free of plagiarism, errors, and mistakes and is accepted as partial fulfillment for award of MS/MPhil degree. It is further certified that necessary amendments as pointed out by GEC members of the scholar have been incorporated in the said thesis.

Signature______________________________

Name of Supervisor: Dr. Rao Arsalan Khushnood

Date:__________________________________

Signature (HoD)__________________________

Date:__________________________________

Signature (Dean/Principal)____________________

Date:__________________________________

DEDICATION

I Dedicate This Research To

My Parents, Teachers, Friends

And My Loving And Beautiful Spouse

And Children (Sanan Ahmad And Hania Ahmad)

And Especially To My Martyred Cousin

L/NK Saleem Ullah Shaheed (SSG).

ACKNOWLEDGEMENTS

I am grateful to Almighty Allah whose countless blessings gave me strength to complete this research work.

I bestow my sincere thanks to my mentor and advisor Asst. Prof. Dr. Rao Arsalan Khushnood, department of structural engineering, NUST institute of civil engineering (NICE) for his advice, untiring guidance, incredible patience and supervision. He inspired me through his punctuality, professionalism, diligence and sincerity. I am grateful to him for his encouragement and motivation. He always urged me to achieve the best. All credit goes to him for making me hard worker, focused and ambitious.

I extend my gratitude and special thanks to research committee members Dr. Shazim Ali Memon, Dr. M. Usman, Dr. Fawad Ahmed Najam for their guidance during research. I also acknowledge the support of lab staff at NICE Structural engineering lab, NIT Transportation lab and Materials lab UET Taxila. I am grateful to my colleagues Muhammad Tanveer and Imdad Ullah Khan for their sincere help and support during my research work.

Lastly, I am thankful to my elder brother Engr. Saeed Nawaz whom supported me both morally and financially during my studies. Finally, I appreciate the determined support provide by my friends and family as this research work would not have been completed without prayers and enthusiastic encouragements of my parents.

Ahmad Nawaz

ABSTRACT

Concrete is the most consumed material all over the world in construction industry. Though it is more stable than most of the materials, it has still some drawbacks that could be improved. Durability of concrete is main issue nowadays and different materials are added to concrete to improve it especially against frost actions. Nanotechnology has revolutionized the field of materials and present a great opportunity to improve the properties of concrete via successive nano-scaled modifications. Moreover, use of nano-waste particles contributes to add into effectiveness as ecofriendly concrete. Mitigation of nano-flaws will render concrete more robust to be used in environment where it is generally avoided. In this research, GNMP's is induced into cementitious mix to make it more resilient in harsh conditions. Four different dosages of GNMP's by mass of cement, 0.25%, 0.50%, 0.75%, 1.0% were induced in conventional concrete and its effect on salt frost resistance, acid attack, chloride migration, microstructure, porosity, volumetric stability, compressive strength in comparison to control sample were studied. Test result shows that concrete was still durable after 7,14,21 and 28 freeze-thaw cycles. Salt freeze-thaw response was evaluated from scaling and internal structure damage and freeze-thaw resistance was improved. Scanning electron micrographs have verified the crack branching and crack bridging effects of induced GNMP's. GNMP's may offer nucleation sites for hydration products (CSH gel) which make the microstructure dense and impermeable. Compressive strength before and after freeze-thaw exposure was determined and was enhanced with addition of GNMP's. Scaling effect of acid attack was reduced with increase in GNMP's content. Addition of GNMP's has improved chloride permeability resistance of the matrix. Reduction in porosity and making the mix impermeable due to addition of GNMP's was also verified from BET test results. 43% decrement was observed in shrinkage.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

CHAPTER 1

1 INTRODUCTION

1.1 General

Concrete is a multiphase composite material, it derives its properties from the constituent materials i.e. cement, fine aggregates, coarse aggregates and water. The concrete behavior depends on the properties of the materials used, the dosage of its ingredients, the chemical and physical characteristics of the materials and the hardening conditions. Concrete is a multipurpose construction material because it can be used to get an economical, durable and high strength structure. It can be molded in any shape. However, civil engineering infrastructure is still vulnerable to freeze-thaw cycles, which may result in scaling and internal structure damage. Traditional cement based material has their low tensile strength and tendency towards cracking that ultimately affects its strength, durability and safety [1]. Due to freeze-thaw internal cracking mainly arises. Delay in transformation of these cracks as well as enhancement of cement-based material in terms of mechanical and durability properties can be made possible by adding various kinds of microfibers in the matrix [2].

These microfibers may not stop the initiation of cracks but the propagation of micro cracks can be delayed [3]. On the nano scale, nucleation and growth of cracks would be delayed by nano-reinforcement. Likewise, the propagation of cracks to micro level can easily be prevented if their growth at nano scale is controlled [4]. Nano scale fibers have high strength and stiffness, higher aspect ratio and smaller fiber spacing that allow them to hinder the development of micro cracks at nano scale [5]. Addition of nanoparticles will lead to stronger, durable, self-healing, denser microstructure and quick compacting concrete [6].

In order to enhance the frost resistance there could be several solutions including provision of closely space voids to accommodate expansion of water upon freezing and restricting the penetration of water through surface and capillary freezable water by improving microstructure. Air entrainment is most commonly used to enhance the frost resistance of conventional concrete.

Number of technical issues are found in conventional air entrainment like merger of air bubbles in fresh state of concrete, loss of air during pumping [7,13].

Graphite nano/micro platelets could be used as a resource to engineer the pore structure of conventional concrete cementitious systems. With addition of GNMP's, the duration of induction period and the total porosity is reduced. GNMP's reduces the permeability of the mix due to which quantum of water in concrete is reduced significantly. As water amount is reduced, the osmotic pressure caused by water will be reduced and the damage caused by freezing water will also be reduced. GNMP's modifies the structure by packing, improving the interfacial transition zone and intimate bonds with matrix due to van der wall forces [7]. The shape of GNMP's enabled them to block and diverts the micro cracks, thus slowing down the propagation of cracks.

1.2 Nano modificent concrete

Nano modified concrete can be define as the incorporation of suitable nano particles or nano tubes into concrete, thereby producing concrete with improved mechanical, thermal and durability characteristics. Literature available shows that there are possibilities of improving concrete properties through addition of several nano materials including nano silica, carbon nano tubes, nano clay and GNMP's. This research emphasizes the potential effects of GNMP's on concrete.

Nano particles can perform a superb filler effect by refining the intersectional zone in cement and produce more dense concrete. Nano particles also improve the bulk properties known as packing model structure. By acting is good filler their manipulation in the cement matrix provides a nano scale structure. Common discrepancies in concrete microstructure such as micro voids, porosity and deterioration due to alkali silica reaction can be eliminated. Improve strength, durability and fracture toughness of the resultant matrix.

1.3 GNMP's

Graphite nano/micro platelets is a type of carbon based nano particle that is produced from graphite. Natural graphite is a layered compound comprising a series of stacked parallel two-dimensional 2D graphene layers. These grapheme layers can be separated to form thin GNMP's via intercalation and exfoliation. The thickness of GNMP's varies from several to dozens of nanometers which lead to high specific area of GNMP's with a theoretical value of 2630-2695 m^2/g approximately. The structure of GNMP's is shown in Figure 1-1.

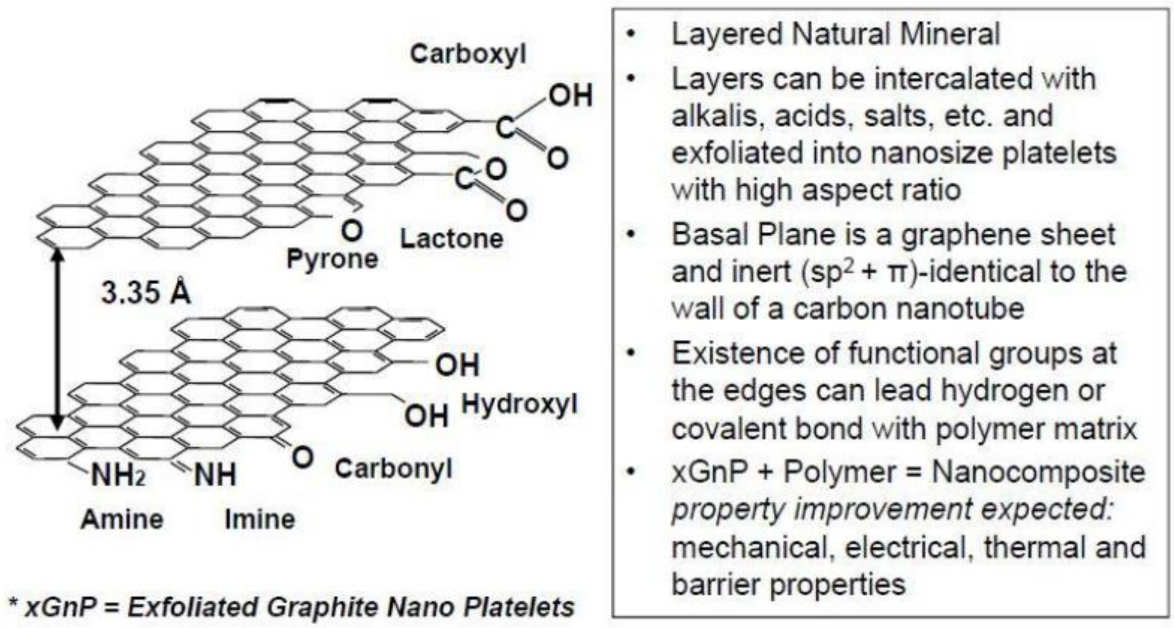


Figure 1-1: Graphite nano-platelets structure

1.4 Merits of graphite nano/micro platelets

GNMP's have high surface area, aspect ratio and thermal conductivity compare to CFs. GNMP's geometric properties helps in controlling defect size and embed in composite. Graphite ano/micro platelets retard the propagation of cracks by diverting the crack path. Matrix reinforced with GNMP's increase the fracture toughness and diffusion resistance.

GNMP's particle induction in matrix is preferred due to some advantages as due to longer size of CFs particle, they may fracture during mixing [Luo 2009]. Also due to entanglement problem lead to poor dispersion of CFs. SEM results shows weak interfacial bonding between matrix and carbon fibers [8].

GNMP's enhances mechanical strength due to high aspect ratio and surface area. The shape of GNMP's helps these particles from entanglement problem. Also the price of carbon nano tubes is much higher than GNMP's. Due to all above reasons, we can prefer to use GNMP's over CNTs in preparing multifunctional cementitious matrix.

1.5 How it effects cementitious composite

1.5.1 Strengthening effect

When load is applied and transferred to interface of GNMP's and matrix, GNMP's interface will carry greater load due to higher elastic modulus which will results in increment in overall strength of mix.

1.5.2 Toughening effect

Concrete failure is delayed due to intrusion of GNMP's which hinders the propagation of cracks by bridging the cracks and hence enhances its toughness.

1.5.3 Small size effect

Material property changes when the size of material is reduced to nano/micro level. The surface area of GNMP's increases as their particles size is reduced to nano/micro scale which results in larger interface. Atoms are arranged along this interface irregularly and when stress causing deformation, these atoms can easily move and energy is absorbed which reduces deformation. Therefore GNMP's reduces the brittleness of cementitious material and increase mechanical property.

1.5.4 Surface effect

When particle size is reduced to nano/micro scale, large surface area and high surface energy is produced due to increase in surface atoms. Due to these properties stronger absorption ability and chemical reactivity is gained compared to other normal materials. Stronger Van Der Waals force of GNMP's particle at the interface make good bonding with cement matrix. They also produce a nucleation site for the cement hydration product which make microstructure denser and enhances strength.

1.5.5 Filler effect

As concrete is porous and non-homogenous system and its porosity has influence on its strength and durability. Mechanical properties of concrete are affected adversely by the pores having size greater than 20nm. Hydrated calcium silicate gel fills hardened cement paste which enhances the strength is a nano material containing millions of gel pores inside [9]. These finding indicates that nano particles like GNMP's can be used as efficient filler to change the microstructure of cementitious material.

1.5.6 Improvement in interfacial transition zone

Hardened concrete consists of three parts i.e. hydrated cement paste, aggregates and interfacial transition zone (ITZ). Role of ITZ is more critical in comparison to other because of different nature. ITZ is a weak component as crack preferentially occurs in it. ITZ is a porous weak zone because cement particles cannot pack effectively around the aggregates, it is known as wall effect phenomena. In cement mortar due to bleeding, water in fresh matrix moves upward and this migration is obstructed when water comes across an aggregate forming water films under the aggregate and the bond between aggregate and cement paste is weakened. As by adding GNMP's, they have large surface area, absorbs large amount of water by which bleeding of cement mortar is reduced and possibility of forming water film is significantly minimized. Due to this the bond between cement paste and aggregate is strengthened and improve the crack resistance of ITZ. 20-40µm is only thickness of ITZ, it nearly occupies 20-40% of total volume of cementitious matrix. With addition of nano materials, ITZ is modified which enhances the properties of matrix.

1.5.7 Crack arresting and particle interlocking

Nano and micro scale cracking is generated internally by applying loads which lead to failure of concrete. Crack arresting and particle interlocking is best way to improve mechanical properties of mix. By adding GNMP's particles, this can be achieved because their large aspect ratio and platelets shape have ability to divert or even block microcracks. Also due to bridging effect of GNMP's can delay crack origination and prevent crack opening. Due to all these effects, a large amount of energy can be absorbed in stress condition, leading to increase strength of the cementitious composites.

1.6 Research objectives

This study focuses on the effect of added GNMP's on salt freeze-thaw resistance of nano modificent concrete in conjunction with acid attack.

The objectives of the current study are:

- To study the mechanical properties of nano modificent concrete with the addition of GNMP's.

- To study the surface scaling due to freeze-thaw in presence of de-icing salt of nano modificent concrete with the addition of GNMP's.
- To identify any internal structure damages in terms of relative dynamic modulus after the exposure to 28 freeze-thaw cycles.
- To compare the compressive strength before and after the exposure to 28 freeze-thaw cycles.
- To compare and evaluate the mass loss after exposure of 14 and 28 days to 5% solution of acid (HCL and H2SO4).
- To determine the chloride resistance of nano modificent concrete.

1.7 Research Tasks

To accomplish research objectives following tasks are performed.

- Literature review
- Test set up which include freeze thaw apparatus, chloride migration test setup, acid attack setup.
- Perform freeze thaw test, chloride migration test and acid attack test
- Evaluate and analyze experimental results
- Conclusions and recommendations

1.8 Research significance

Material properties of NWC are well established against freeze thaw, acid attack and chloride penetration. However, studies on the nano-modified concrete against freeze thaw are scarce in technical literature. In the present pioneering study, material properties of nano-modified mixes are established against freeze thaw after 28 cycles. Freeze thaw test like scaling and internal structure damage was employed. Qualitative microstructural study of morphological changes of freeze thaw treated specimens was also performed using SEM and BET. The data achieved from this research will be used to develop simplified mathematical relationships, which will act as input parameters in computer aided design and analysis.

1.9 Thesis outline

The research undertaken to address the aforementioned objectives is presented in five chapters.

Chapter 1 is a preliminary chapter about the behavior of concrete when exposed to freeze thaw conditions, research objectives and research significance has been discussed.

Chapter 2 describes literature review in detail. A brief literature review about properties of GNMP's in general and when used in cementitious matrix has been provided. Freeze thaw response is also discussed.

Chapter 3 deals with the test setup. It explains which types of equipment are used to evaluate mechanical properties. Furthermore it presents an overview of the test procedure which describes the ways and methods to determine different properties.

Chapter 4 provides evaluation, analysis and discussion for results of material property tests. Results of freeze thaw and shrinkage investigations alongside microstructural study have also been presented. Further simple linear empirical freeze thaw relationships of modified mixes have also been presented. Chloride migration and acid attacks results are also discussed in detail and are also presented in empirical graphs.

Chapter 5 provides detailed conclusions and remarks.

CHAPTER 2

2 LITERATURE REVIEW

2.1 General

Freeze thaw resistance is one of the most vital durability parameters for any type of concrete particularly substantial in cold environments [7]. The water freezes and expands, occupying 9% more volume. Tensile force has been exerted on surrounding concrete and as the tensile force exceeds the material resistance, scaling and cracks arises and deterioration takes place. Excessive damage can be done due to continuous freeze thaw action which may lead to failure of concrete structure.

In order to improve freeze thaw resistance of conventional concrete system, most of research is being carried out globally using conventional air entrainment. No research has been carried out for conventional concrete systems using GNMP's with the intension to improve freeze thaw resistance of such systems.

2.2 Review of carbon based nano material

Nano modificent concrete can be manufactured from carbon based materials like CNTs, CNFs, graphene, graphene oxide and graphite nano/micro platelets (GNMP's). due to low price and easy availability of GNMP's, we preferred to use it. The properties of GNMP's are almost similar to other carbon based alternatives.

2.3 Carbon nano tubes

Nano is a Greek word which means dwarf. Carbon nano tubes belong to family of fullerene in structure. Fullerenes are of two types: spherical or Bucky balls and cylindrical tubes as carbon nanotubes. They have very small diameters that are why they are called nanotubes. They have high strength and elastic modulus [10]. They were first reported by Iijima in 1991[11].

2.4 Application of CNTs

The usage of CNTs after their discovery is growing in every field of engineering along with medicine and environmental sciences [12]. Nowadays, nano materials have been introduced in field of construction industry. Due to high elasticity and strength of CNTs, it makes the cementitious composite more durable and strengthened.

The foremost problem related to CNTs is their excessive value and non-renewable and re-usable characteristics. Though its manufacturing exceeds heaps of heaps consistent with 12 months and its packages are swiftly growing, the commercialization is still a big hurdle. To reduce the fee of manufacturing unique efforts are being put to expand new strategies of training with a view to sooner or later limit their cost. The powerful results of CNTs in production enterprise are immediately linked with their fees. Another most important difficulty that hinders the application of CNTs in production enterprise is their bad dispersion in cementitious matrices which in turn diminishes their proper consequences. Effective dispersion strategies also are needed to be addressed, once the commercialization and powerful dispersion techniques are taken care of out, CNTs applications in construction enterprise will grow in addition.

2.5 Disadvantages of the use of CNTs

Following are the two demanding situations for the usage of CNTs in cement [13].

▪ Strong van der partitions forces being accountable to maintain character CNTs

▪ Inefficient bond linkage between CNTs and cement matrix

2.6 Restraints in the use of CNTs:

For green usage of nanostructures, they have to be dispersed well, dispersion refers to the technique of isolating the bundles into individual flakes inside a matrix.

Proper dispersion is tough to obtain in CNTs and CNFs due to following reasons [14].

▪ Agglomerates are formed due to strong van der Waals forces that exits between CNTs and CNFs

▪ Having excessive element ratio.

2.7 Properties of CNTs and comparison with graphite:

2.7.1 Structure:

The structure of CNT’s are identical as that of Graphite, the handiest difference is that in CNT’s the layers are closed to form a tube like shape at the same time as in Graphite that layers are open. The interlayer distance in MCNT is zero.34-0.36 nm and the C-C bond distance is zero. 14nm that's lesser than that in Diamond indicating that the cloth is more potent than diamond [15].

2.7.2 Synthesis:

When we partly pay attention organic fabric it yields powder like carbon known as soot that's in the structural shape of Bucky ball, nanotube or different structures. With following 3 approaches soot may be produced [15].

EAD (electric arc discharge) 2. LA (Laser ablation) three. CVD (chemical vapor deposition)

2.7.3 Treatment:

Treatment of nano-tubes includes separation of nanotubes from worthless debris in soot. It can be finished with the aid of Ultrasonic tub, chromatography, microfiltration, Annealing and centrifugation etc [15].

2.8 Mechanical properties

Due to high strength and elastic modulus, microfibers such as carbon and steel fibers are used in construction industry. CNTs have high tensile strength and elastic modulus compare to other fibers. Fiber aspect ratio has greater effect on strength. Aspect ratio of CNTs varies from 1000 to 10000 which is much better to be used as a fiber reinforced material [15].

2.9 Graphene and Graphene Oxide (GO):

Graphene is a single layer sp2-bonded carbon sheet, which paperwork a honeycomb crystal lattice. It was invented in 2004 [16]. GOs are received by means of Hummers Method i.e. Processing graphite under intense oxidative conditions, advent of oxygen-containing companies a widespread part of graphene pi-digital community is destroyed in the formation of GO [17]. Oxygen purposeful groups penetrate into the graphite interlayers that cause weakening the interplay among the layers this facilitates in smooth dispersion of GO into aqueous solutions and shape a strong suspension [16].

2.10 Exfoliated graphene Nano platelets (xGnP):

Exfoliated graphene Nano platelets (xGnP) have the same chemical shape as carbon nanotubes (CNT), and their edges are without problem chemically changed for stronger dispersion in polymeric composites. Such nanoplatelets are typically much less than 5nm thick and may be synthesized with lateral dimensions ranging from <1 to a hundred microns [14].

2.11 Applications of (xGnP):

Use of exfoliated graphite flakes could open up many new applications in which electromagnetic defensive, electrical conductivity, excessive thermal conductivity, gas barrier resistance and high fracture longevity are required [14].

2.12 Important observations on including GO (Gong et al., 2014):

- Addition of GO in cement paste complements its degree of hydration
- It decreases the porosity
- It will increase the total pore area of cement paste
- It doubles the gel pore extent
- It refines the pore structure of cement paste
- It increases the tensile and compressive power by using over 40%
- It reduces the workability
- It increases the non-evaporable water content material and calcium oxide in OPC

2.13 Restraints in using GO:

Proper adhesion with cementitious composites is tough to attain because of the Graphitic nature of GO. Due to vulnerable bonding between the cement matrix and flakes, the particles slide out of the cement matrix below a load lower than the strength of individual carbon nano structure [14].

2.14 Dispersion Problem in the use of nano-composites

Dispersion is the process of de-agglomeration. Dispersion can occur either by abrupt splitting of agglomerates into small fragments under high pressure or due to detachment of small fragments at relatively minimum stress [18].

2.15 Factors affecting dispersion

Nano composite behavior of dispersion depends on some important factors i.e. volume fraction, viscosity of matrix, aspect ratio of nano materials, their density and attractive forces [18].

2.16 Dispersion of carbon nanocomposites in cementitious matrix

The dispersion of nano material has great influence on the mechanical properties of mix. Dispersion of carbon based nano materials cannot be achieved within the mix through conventional mixing process. Therefore, to achieve homogenous dispersion of nano materials in cementitious matrix, surfactant action can be used. Physical technique that can be used for dispersion is ultrasonication which can be used in combination with surfactant to get better results. The main problem with carbon based nano material is their agglomeration in cementitious matrix [19] [20] [21]. The proper dispersion of CNTs can lead to increase in compressive strength up to 40% [22].

Following dispersing technique can be used to achieve proper dispersion.

2.16.1 Physical technique

Commonly technique for dispersion is sonication in which particles in solution excited through sound waves. These nano particles start vibration by a process called cavitation. Molecular interaction is disrupted by vibration and lead to mixing [18].

Table 2-1: Different dispersants used

Types of dispersant	Acetone
	Ethnol
	Nitric acid
	Sulphate acid
	Gum

Table 2-2: Types of sonicator

Types of sonicators	Water bath sonicator
	Probe type sonicator

Electrical voltage is converted to mechanical vibrations in ultrasonication technique which are transferred to water or solvent and will lead to formation and collapse of ultrasonic bubbles. The proper dispersion of nano material in solvent does not guarantee the uniform dispersion of nano material in cementitious matrix.

2.16.2 Chemical methods

Use of surfactants:

The dispersion of nano material in liquid medium can be improved by reducing surface tension of water and due electrostatic repulsion between the surfactant particles adsorbed on nano material surface which leads to stable dispersion. In order to get proper dispersion in cementitious mix, it depends upon on optimum concentration of surfactant [18].

Table 2-3: Different surfactants used previously

Surfactant type	Sodium dodecylbenzenesulfonate (SDBS)
	sodium deoxycholate (NaDC),
	Triton X-100 (TX10)
	Gum Arabic (GA)
	cetyl trimethyl ammonium bromide (CTAB),

The dispersion ability of various surfactants was found in the following order: SDBS and TX10 > SDBS > NaDC and TX10 > NaDC > AG > TX10 > CTAB.

Drawback of using the surfactant:

The electrical and piezoresistive characteristics of nano cementitious matrix is affected by using surfactant i.e. lack of nano material connectivity within the mix that is result of blockage by surfactant molecules. To conquer these polymeric surfactants i.e. acrylic acid and methylcellulose has been mentioned to introduce steric repulsion between the nanomaterials, leading to their homogenous dispersion.

2.16.3 Use of cement admixtures:

Polycarboxylate superplasticizer was also found to be an effective dispersant of nanomaterial in mix.

2.16.4 Covalent functionalization

Covalent functionalization is the most common method to enhance the dispersion of nanomaterials in water or polymeric matrices. Carbon nanomaterial can be treated with strong acids to oxidize the surface and such as carboxylic functional groups is created. Proper dispersion of CNTs individually in cementitious mix can be achieved by covalent functionalization using acid mixture [18].

Table 2-4: Types of surfactant

Four different types of surfactants	cation type surfactant, i.e. tetra-decyl-tri-methyl-ammonium bromide
	non-ion type, i.e. poly-oxy-ethylene (40)
	anion type, i.e. sodium-dodecyl-sulfate
	polymer type i.e. poly-carboxylate

2.17 Aspect ratio of nano materials

Aspect ratio of nano materials holds primary importance to achieve unique properties of nano modificent mix like mechanical, thermal and chemical properties. Crack branching, crack bridging and bonding characteristics are affected by aspect ratio of nano material in mix. Short aspect ratio of 0.2wt.% improves flexural strength by 269% whereas for long aspect ratio with 0.1wt.%, the increment in flexural strength was 65% reported [23]. This shows that both concentration and aspect ratio of nano materials have significant effect on properties of nano modificent concrete.

2.18 Microstructure of nano-modified cementitious matrix

Nano materials act as reinforcing and filling material which resulted dense microstructure and porosity is reduced [24]. Mechanical properties are improved by enhancing microstructure. Fly ash modified with CNTs reveal the filling effect of CNTs between the hydration product i.e. ettringite and calcium silicate hydrate (CSH) gel [25]. The composite containing both CNTs and fly ash shows high strength.

Li et al [9] concluded from the microstructure of nano modificent concrete that CNTs act as a bridge across width of crack which transfer the load in form of tensile stresses.

The intrusion of nano material act as reinforcing material, showing strong bond with cement matrix, improving mechanical properties along with failure characteristics.

The crack bridging phenomena enhances the flexural strength of nano modificent concrete [26].

2.19 Porosity reduction in nano-modified cementitious composites

The proper dispersed nano materials improve the porosity of the cementitious composite. By keeping w/c of 0.5 and properly dispersed the 1wt.% of CNTs improve the microstructure by reducing porosity and mesopores [24].

Nano modified cement pastes were cured for 28 days and mercury intrusion porosimetery test was performed and the result shows in table total porosity, total intruded volume of mercury and total surface area of cement. Porosity of the mix is reduced by increasing the amount of MWCNT. 1% intrusion of CNTs shows smallest intrusion and porosity.

Table 2-5: MIP analysis nano modified cement pastes

Mixes	Total intruded volume (cm^3/g)	Total porosity (%)	Total surface area (m^2/g)
PC	0.717	27.14	31.45
0.5% CNTs	0.1494	25.52	25.36
1% CNTs	0.1422	22.73	24.32

Mesopores (size ≤ 50 nm) and macro pores (size ≥ 50 nm), two types of pores are shown in figure [54]. Reductions in mesopores are found in mix containing CNTs.

Baomin wang et al. [27] reported that MWCNTs dispersion in mix reduces the porosity and have uniform distribution of pores.

Sobolkina et al. [22] reported that 0.25% addition of CNTs reduces the porosity but have no significant effect on strength as shown in Figure 2-1. GNPs also reduce the porosity and improve other properties shown in table 2.6 [28].

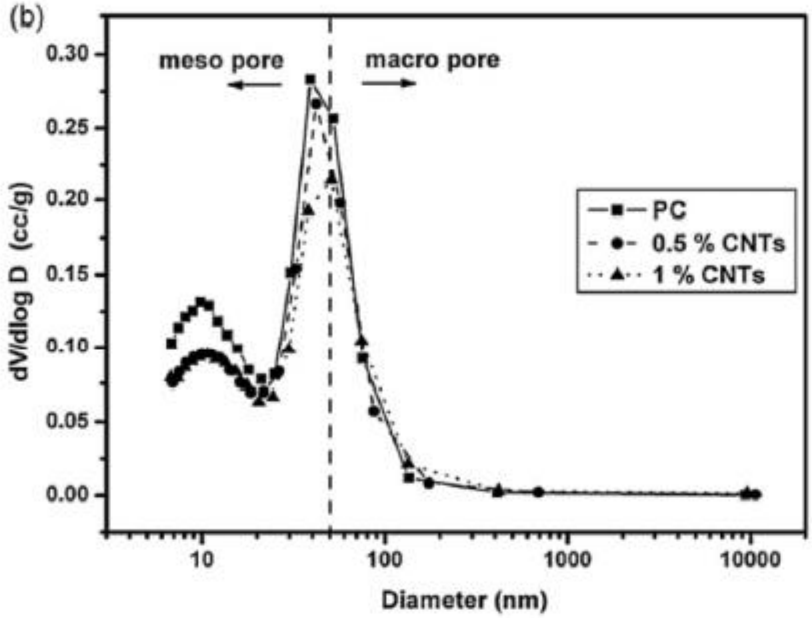


Figure 2-1: MIP analysis of modified cement paste

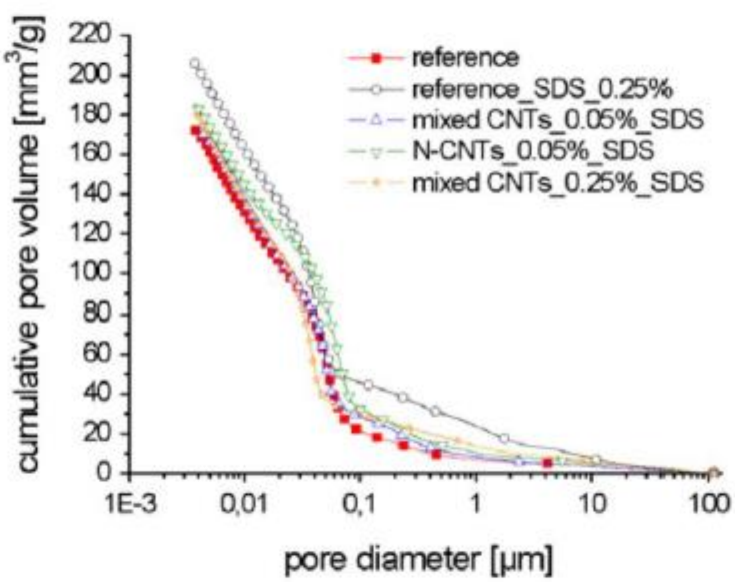


Figure 2-2: MIP analysis showing cumulative pore volume

Table 2-6: Porosity of sample with GNP and CHS

Sample ID	Avg. Pore radius (nm)	Max. pore radius (nm)	Total porosity (%)	Porosity (%) (diameter ≤ 100nm	Porosity (%) (diameter ≥ 100nm)
CEM	10.1	56741.5	17.4	69.4	30.6
0.2_GNPs_3	6.4	54651.2	12.54	82.54	17.8
0.2_GNPs_4	5.2	52564.1	11.48	84.51	15.4
0.2_CBF	7.2	56169.5	14.58	74.56	21.85
0.2_CHS	6.6	55742.4	14.42	77.52	18.74
0.2_CPS	6.5	54852.4	13.54	78.65	18.24

A research investigation shows that nano-modification reduces porosity and improves pore size distribution and strength [29].

2.20 Mechanical properties

Flexural and compressive strength is improved by improving microstructure through addition of CNTs. MWCNTs not only act as a filler but also bridge the cracks, reportedly increase compressive strength 19% and flexure strength by 25% [9].

Table 2-7: Improvement in mechanical properties with addition of CNTs

Concentration of CNTs	Percent improvement in mechanical properties				Researcher
	Tensile strength	Compressive strength	Flexural strength	Fracture toughness	
0.3%	34.28	-	-	-	(Ludvig et al. 2009)
0.5%	19	-	-	-	(Hunashyal 2014)
0.5%	-	19	25	-	(G. Y. Li, Wang, and Zhao 2005)
0.02%	-	11.03	11.23	-	(Kerienė et al. 2013)
0.045-0.15%	-	50	10	-	(Habermehl-Cwirzen, Penttala, and Cwirzen 2008)
0.2%	-	29.5	34.45	-	(J Luo 2009)
0.5%	-	10-20	33	-	(Musso et al. 2009)
0.1%	-	22	-	-	(Bharj et al. 2014)
0.1%	-	-	-40	-	(Tyson et al. 2011)
0.5%	-	-	-	149.23	(Jianlin Luo, Duan, and Li 2009)

Table 2-8: Improvement in mechanical properties with addition of CNFs

Concentration of CNFs	Percent improvement in mechanical properties				Researcher
	Tensile strength	Compressive strength	Flexural strength	Fracture toughness	
0.2%	22-26	-	-	-	(Gay and Sanchez 2010)
0.16%	-	42.7	-	-	(Gao, Sturm, and Mo 2009)
0.2%	-	-	82	270	(Tyson et al. 2011)
0.04%	-	-	46	-	(Peyvandi, Sbia, et al. 2013)
0.048%	-	-	45	-	(Konsta-Gdoutos, Metaxa, and Shah 2010c)

2.21 Concrete durability

However, civil engineering infrastructure is expose to frost attack. Frost attack on concrete is caused due to the freezing of internal moisture. It essentially manifests itself from two aspects [30] [31]; generation of internal cracks and internal frost attack and removal of small pieces from the surface of concrete known as scaling. Scaling is more extensive in salt frost attack [32]. Powers et al [33] [34] [35] research is primarily on fundamental theories of freezing and thawing. Hydraulic theory investigated that movement of water occurs form capillary pores to other pores where osmotic theory says that movement of water occurs form unfrozen to frozen water due to dissolved materials. According to Litvan, water freezes close to outer surface of concrete. The water cannot freezes in capillary pores and remains in top notch cooled circumstance. The tarnsfer of extremely cooled water can reason freeze-thaw damage [36].

Air entraining agent is mostly used to enhance the freeze-thaw resistance of concrete. A total air content 4 to 8% is consider adequate[37]. Frost resistance is increased with addition of air content but the strength of concrete is reduced which has been questioned[38] [39]. Many researchers have concluded that by making the microstructure dense and impermeable, increases the freeze-thaw resistance significantly [38] [39] [40]. Limited study has been done on improvement of freeze-thaw resistance by addition of nano material in the cementitious matrix. Salemi et al used various types of nano media against frost attack [41]. With addition of nano particles, the mix has higher compressive strength and lower water absorption. The mixes containing nano particles after exposed to freeze-thaw have less damage, internal cracks and higher strength. Wang et al. investigated effect of CNTs on freeze-thaw resistance of concrete [42]. Mixes having CNTs show much higher resistance against freeze-thaw than normal concrete. Li et al. also studied that mix having carbon nano tubes CNTs perform better against frost attack[43]. As it is theorized that addition of CNTs in mix reduces porosity, decreases the no. of large pores and also have a bridging effect. Carbon fibers are also investigated against freeze-thaw and found to be much useful than CNTs [44].

Carbon nano tubes and other nano materials have been studied but GNMP's are not introduced against freeze-thaw. In this article we have introduced GNMP's, as they have high aspect ratio, elastic modulus and more surface area than CNTs. GNMP's have shorter length whereas CNTs are longer due to fracture of CNTs may occur. Secondly, poor dispersion may takes place due to entanglement. Also SEM shows that interfacial bond between CF and matrix is weak. Also GNMP's have low cost compare to CNTs. In this study we examine the use of GNMP's to improve the durability of mix. There exist numerous numbers of test methods to evaluate freeze thaw scaling and internal structure damage of concrete. Both surface scaling and internal damage by the same specimen can be determined by slab test. The results of slab test will be presented in this research paper. Other durability test i.e. acid attack and chloride penetration results also have been presented.

CHAPTER 3

3 EXPERIMENTAL PROGRAM

3.1 General

The aim of this chapter is to discuss the procedures and methodologies executed to attain the desired objectives. The detailed procedure from specimens preparation to testing techniques implemented to attain the results has been explained.

For studying and assessing the performance of nano-modified mixes against durability, study on properties of concrete and materials used are required. The mechanical and durability properties thus evaluated were presented in form of graphs and were compared with control mixes. Experimental design, standards, test equipment and procedure are discussed in this chapter.

3.2 Materials and methods

Materials used in experimental study will be discussed in this section.

3.2.1 Materials

3.2.2 Cement

In all types of concrete, Ordinary Portland (OPC) cement was used as a binder. X-ray fluorescence (XRF) was used to obtain the chemical composition of OPC. Physical and chemical properties of binder are mentioned in Table 3-1.

Table 3-1: Physical and chemical properties of cement

Chemical composition	CaO	SiO_2	Al_2O_3	Fe_2O_3	K_2O	MgO	SrO
Content (%)	68.01	15.62	8.63	3.68	0.61	1.30	0.74
Physical properties	Insoluble residue mass %	Specific gravity (g/cm^3)	Specific surface area (m^2/g)	Particle size (d50) (μm)	Loss on ignition mass %		
Content	0.53	3.17	0.84	16.48	2.26		

3.2.3 Fine aggregates

Lawrencpur region sand in saturated surface dry SSD condition was used as a fine aggregate. Fineness modulus of sand was 2.25. Sand was free from clay and other deleterious material. Physical properties of sand are mentioned in Table 3-2.

Table 3-2: Properties of fine and coarse aggregate

Physical properties	Size (mm)	Specific gravity (g/cm^3)	Water absorption (%)	Bulk density (kg/m3)	Los Angles abrasion (%)	Crushing value	Fineness modulus	Maximum size of aggregate (mm)
Coarse aggregate	12.5	2.48	2.66	1558	15.7	23	2.79	12.5
Fine aggregate	-	2.64	1.62	1546	-	-	2.25	-

3.2.4 Coarse aggregate

Gravel utilized was brought from Margalla crushing plants in Taxila, Pakistan. Coarse aggregate were used in SSD condition having maximum particle size of 12.5mm. The properties and sizes are given in Table 3-2.

3.2.5 Surfactant

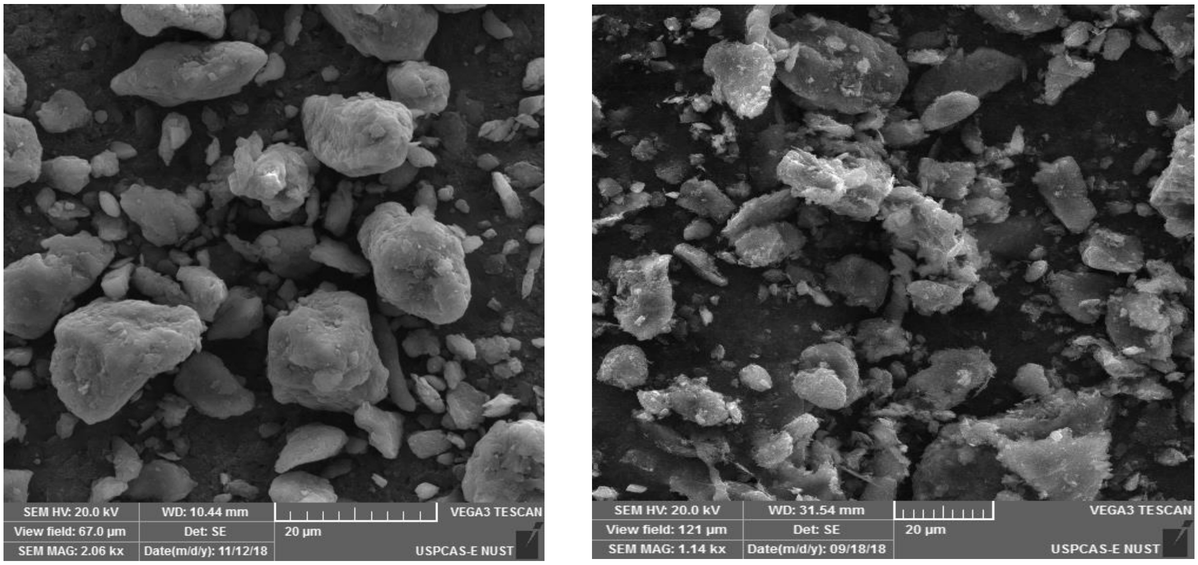
The most important limitation that obstructs the utilization of GNMP's is dispersion of these particles into cementitious matrix and in order to overcome these restriction we have used Acacia gum as an economically feasible alternate for proper dispersion. Acacia Gum is used as an efficient surfactant for better dispersion of nano composites inside the matrix, as reported by previous researchers it behaves as a good surfactant in combination with organic media than other available alternatives, it is natural, easily available and cheap alternative. Its basic function is to lower down the surface tension of water and allowing easier dispersion of carbon nano composites. Particle size analysis results show the mean size of acacia gum to be 4 µm.

Table 3-3: Properties of Acacia gum

Property	Value
Specific Gravity	1.41
BET surface area	36.10(cm^2/g)
Initial setting time	Delayed by 30 min
Final setting time	Delayed by 5 hrs

3.2.6 Graphite nano/micro platelets GNMP's

GNMP's were bought locally in powdered form. SEM images of raw material shows that GNMP's have rough texture, abrasive surface and are long and flaky in shape as shown in Figure 3-1. Particle size varies from micro to nano was also confirmed from SEM images.



(a) (b)

Figure 3-1: SEM image of (a) raw GNMP's (b) Ball milled GNMP's

Laser Granulometry of the raw material (figure 2a) confirms that mean particle size of GNMP's is 7.20µm. 150 minutes ball milling was performed in order to get nano size powder. The jar was filled 25% by volume and powder to milling ratio was 1:20. After ball milling the mean particle size achieved was 6.78µm. Mean particle size was reduced to 6.02micron after sieving at sieve No. 200 and then that GNMP's were used for casting.

SEM images and Laser Granulometry both confirms that particle size of GNMP's ranges from micro to nano scale that's why we named the material as graphite nano/micro platelets. As SEM images also shows that GNMP's have layered and abrasive texture that will helps in physical bonding with cementitious matrix. GNMP's physical properties are shown in Table 3-4.

Table 3-4: Properties of GNMP's

Property	Value
Surface area (m^2/g)	154.0
PSA (mm)	6.02
Specific Gravity	1.62

3.3 Mix proportions and preparation of GNMP's reinforced concrete samples:

Five types of concrete formulation were prepared as summarized in Table 3-5. Controlled formulation prepared was having 0% of GNMP's content and various percentages of GNMP's and AG were added to other four types of formulations. GNMP's were added at a loading rate of 0.25, 0.50' 0.75 and 1% by weight of cement. Acacia gum was added at dosage rate of 0.5% of Graphite nano/micro platelets.

Table 3-5: Composition of concrete samples

Notation	GNMP'S		Acacia gum (AG)	
	%age	Gram	%age	Gram
0P0GNMP's	0	0	0	0
0P25GNMP's	0.25	37.5	0.125	18.75
0P50GNMP's	0.50	75	0.25	37.5
0P75GNMP's	0.75	112.5	0.375	56.25
1P0GNMP's	1.0	150	0.50	75
For each mix 1500g of cement, 1800g of sand, 3750g of Gravel and 750ml of water was used				

For casting concrete specimens water to cement ratio used was 0.5 and 1:1.2:2.5 ratio was used of cement, fine and coarse aggregate. Slight decrease in the slump was observed with addition of nano/micro particles. Uniform dispersion of graphite nano/micro platelets in mixing media and matrix was attained by performing sonication for 45 mins. Size and numbers of sample prepared from each batch are shown in Table 3-6.

Table 3-6: No. and size of samples prepared from each batch

Tests	Sample size	No of samples	ASTM standard
Freeze-thaw test	150mmx150mmx150mm	3	CEN/TS 12390-9
Chloride migration test	150mmx150mmx150mm	3	NT-BUILD 492
Compression test before freeze-thaw	100mmx100mmx100mm	3	ASTM C39
Compression test after freeze-thaw	100mmx100mmx100mm	3	ASTM C39
Acid attack	100mmx100mmx100mm	3 for sulfate attack and 3 for HCL attack	ASTM C-267

First graphite nano/micro platelets and acacia gum were mixed in 1000ml of water and then 45 min of sonication was carried out and in mixing water, the above suspension was added. Then dry mixing was carried out for 3minutes of cement, fine and coarse aggregate. Afterwards GNMP's suspension was added in mixer and was operated for further 2 minutes. Hence the total mixing time becomes 5 minutes. The mix was transferred into cube molds having standard size of 150mm cubes and 100mm cubes as per formulation shown in Table 3-5. Samples were dry cured in molds for 24 hrs. at 20±2 degree C temperature. After that samples were cured in curing tank for 28 days.

3.4 Salt freeze-thaw testing:

3.4.1 Scaling:

According to CEN/TS 12390-9, frost scaling was measured [26]. 150mm cubes were prepared and placed in molds for 24 hrs. After 24±2hrs. the cubes were removed from molds and placed in tap water having temperature of 20±2 °C. When the cubes were 7 days old, they were removed from water and were placed in a climate chamber until the freeze-thaw test starts. At the age of 21 days, 50±2mm thick specimen is sawn from each cube perpendicular to the top surface as shown in Figure 3-2.

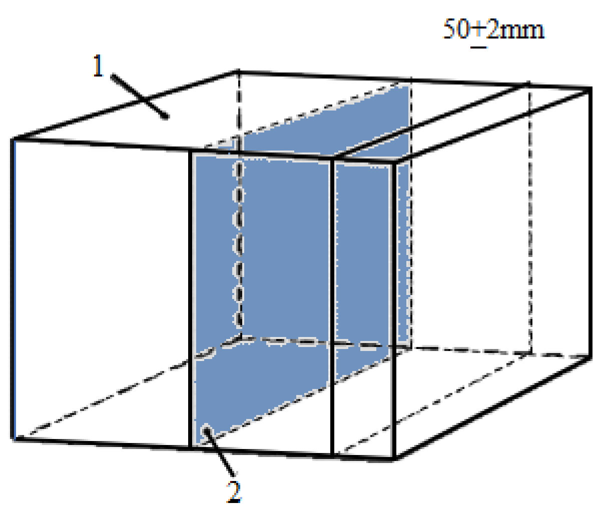
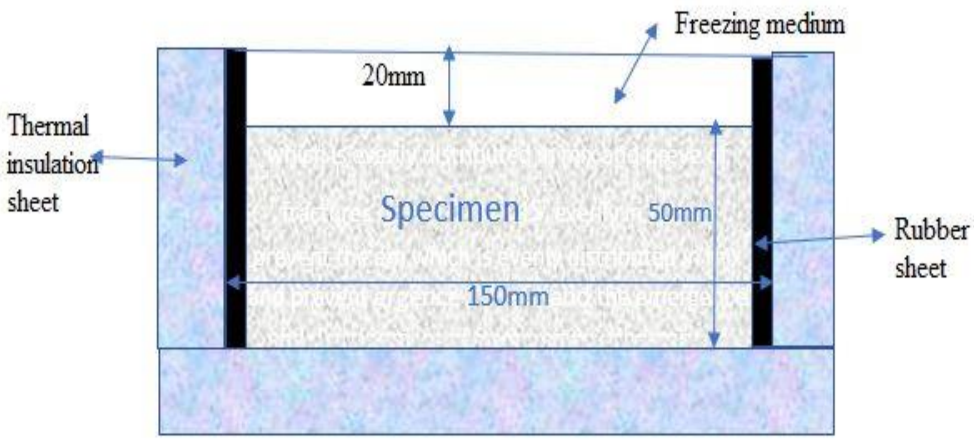


Figure 3-2: Location of test specimen and test surface in sawn cube

1 Top surface at casting

2 Test surface



(a)

(b)

Figure 3-3: (a)The test arrangement of slab test (b) Sample prepared

After sawing, the specimens were washed and without delay bring it to the climate chamber. When the specimens become 25±1 days old, the rubber sheet was glued to all surfaces except test surface. The sawn surface should be used as test surface according to standard. The silicon was placed at the joints between concrete and rubber sheet. The edge of the rubber sheets should be 20mm above the surface. At 28 days, a layer of de-ionized water was poured on the surface up to 3mm. 67 ml of water, gives an approximately 3mm of layer for the surface area of 150mm x 150mm. the saturation was continued for 3 days before freeze-thaw testing. Before the test, the specimen was thermally insulated using insulating sheet except the test surface as shown in Figure 3-3.

Samples were transferred into freeze-thaw chamber and the temperature was maintained through programming as shown in Table 3-7. The scaled material was removed through brush at 7, 14.21 and 28 cycles and were heated up to 105°C in order to fully dry the scaled off material according to CEN/TS 12390-9. Scaled material was weighed and are shown in g/m^2.

Table 3-7: Time and temperature maintained during freeze-thaw cycle

Upper limit		Lower limit	
Time (hours)	Temp (°C)	Time (hours)	Temp (°C)
0	+24	0	+16
5	-3	3	-5
12	-15	12	-22
16	-18	16	-22
18	-1	20	-1
22	+24	24	+16

3.4.2 Internal structure damage:

For internal structure damage measuring, specimen used for scaling was used. ISD was noted at 0, 7, 14, 21 and 28 cycles using UPVT according to CEN/TR 15177:2006 [27]. Ultrasonic equipment was calibrated according to manual. A little amount of sonic grease is applied to contact surface of transducers and marked spots of specimens. The transducers were pressed against the concrete surface until constant minimum value was achieved. RDM was obtained from Equation 1.

$RDM = (to/tn)^2 x100[\%]$ (Equation 1)

Where;

RDM is relative dynamic modulus of elasticity in %

to is initial transit time in microseconds

tn is transit time after n freeze-thaw cycles in microsecond

3.4.3 Compression test before and after freeze-thaw cycles

Compression test was performed on 100mm cubes after 0 and 28 freeze-thaw cycles at loading rate of 0.1kn/sec as shown in figure. Six samples for each formulation were tested, three after 0 freeze-thaw cycles and three after 28 freeze-thaw cycles. The test was performed on total 30 samples and was performed according to ASTM C39 [28].

3.5 Acid attack:

According to ASTM C-267, acid resistance was determined [29]. Three samples of size 100mm x100mm x 100mm were used for each formulation. Two types of acidic solutions were used: 5% sulfuric acid and 5% hydrochloric acid. Cubes were immersed in distilled water for 3 days to full saturate the cubes and weighed. Then concrete cubes were immersed in glass container containing these acidic solutions for 28 days. Containers were kept covered to minimize the evaporation during testing.

After 14 and 28 days of immersion, each specimen was removed, brushed and rinsed in distilled water to remove the scale of material and weight again. Acid resistance was evaluated through measurement of scaled of material from specimen in Weight loss (%) = [(Wo-Wi)/Wo x 100(%)] (Equation 2.

Weight loss (%) = [(Wo-Wi)/Wo x 100(%)]   (Equation 2)

Where Wo is the weight in grams of specimen before immersion in acid solution, and Wi is the weight in grams of specimen after i-days of immersion in acid solution.

(a) (b)

Figure 3-4: Specimen (a) after sulfate attack (b) after HCL attack

3.6 Chloride migration test:

This test was performed according to standard NT-BUILD 492 [30]. This method is applicable for both concrete and mortars. 150 mm cubes were casted and through drilling 50mm thick and 100 mm diameters cylinders were sawn from the cubes. The cores were prepared according to standard as shown in Figure 3-5.

After sawing, the specimens were brushed and washed away. When the specimens were surface dried, for vacuum treatment they were placed in vacuum container. (1-5)KPa pressure was kept in vacuum container. After 3 hours of vacuuming, $Ca(OH)_2$ solution was added to immerse all the specimen. The vacuum was continued for further one hour. After that air was allowed and specimens were kept in solution for further 18 hours.

The apparatus was set up as specified in standard test procedure NT-BUILD 492. 12 liters of 10% NaCl solution was put in catholyte reservoir while anolyte reservoir was filled with 0.3M NaOH. Positive and negative terminal of power supply were connected with anode and cathode respectively. 30V were applied and initial current passed through each specimen were recorded. Initial temperature of anolyte solution was also measured. After specified time, final temperature and current was also recorded.

Specimens were removed from set up and each specimen was cut into half. 0.1M silver nitrate solution was sprayed and the white precipitation appeared which showed the depth of chloride ions. The depth was measured accurately which shows the penetration depth

Chloride migration co-efficient was calculated from Equation 3.

$$Dnssm = \frac{0.0239(273+T)L}{(U-2)t}\left[(xd - \frac{0.0238\sqrt{(273+T)xd}}{\sqrt{(U-2)}})\right] \qquad \text{(Equation 3)}$$

Where:

Dnssm: non-steady-migration co-efficient, x $10^{-12}m^2$/sec;

U: Absolute of applied voltage, V

T: average value of initial and final temperatures in anolyte solution ^{O}C

L: thickness of specimen, mm

Xd: average value of penetration depths, mm

t: test duration, hour

 (a)  (b)

Figure 3-5: (a) Prepared core for chloride migration test (b) Chloride migration test setup

3.7 Microstructural investigation:

Specimens for study were extracted using chisel and hammer. The extracted specimen of approximately 5-10 mm was subjected for SEM and BET. To perform SEM and BET test, samples were oven-dried at 50°C for 24 hrs. Further hydration was stopped by immersing these samples in acetones for 24 hrs. The FEI XL 30 Scanning electron microscope was used. SEM was performed to determine the microstructure, ITZ, crack bridging and crack controlling. BET was used to find out pore diameters and pore volumes. Internal porosity of specimens was also measured to examine the effect of GNMP's reinforcing on the cementitious composites.

3.8 Volumetric stability

Shrinkage test is performed at early age to get an idea regarding volumetric stability of cementitious matrix with addition of particles. 4x6x25 cm fresh mixes were placed in modified version of German Classical "Schwindrinne" channel apparatus at 20-25°C interfaced with software. To avoid movement obstruction and bleeding effect, the edges of moveable plate were greased. In order to get results both of expansion and compression of the cement paste, the measuring probe was pressed up to 50% of its maximum compression. Shrinkage response was recorded for first 24 hours and plotted the shrinkage response with respect to time.

CHAPTER 4

4 RESULTS AND DISCUSSION

4.1 General

As per respective standards/guidelines experimental study were carried out and results obtained are presented in this chapter. This chapter comprises of the effect of graphite nano/micro platelets (GNMP's) on strength and durability of nano modificent concrete. Following experiments were carried out to evaluate different properties.

- Dispersion scheme
- Freeze thaw scaling
- Freeze thaw internal structure damage
- Microstructure study with scanning electron microscopy (SEM)
- Strength (compressive)
- Acid attack
- Chloride migration test
- Microstructure study with BET
- Shrinkage test to evaluate early dimensional stability

All the test were performed in controlled environment in laboratory. The temperature of room was kept 20^{o}C and humidity was maintained greater than 65%.

4.2 Dispersion scheme

Quandary in diffusion of nano media in water is due to the strong Vander wall forces. By including a dispersant and applying external power to break the bonds, the intermolecular interplay of the particle may be reduced and homogenous dispersion of GNMP's can be carried out [31]. Ultraviolet spectroscopy was carried out in 300ml of water for five types of formulation. Solution containing graphite nano platelets, acacia gum and water 150 W, JAC-1505 high energy sonicator was operated at 40 KHz for 45 min to investigate stability of the said solution. Absorbance value at 500 nm wavelength was noted just after the sonication and after 45 minutes of sonication as shown in Figure 4-1. Optimum ratio of GNMP's to surfactant was 1:0.5

revealed from the spectrum result. At 1:0.5 ratio of GNMP's to AG, most absorption can be achieved having maximum uniform dispersion of graphite nano/micro platelets in water.

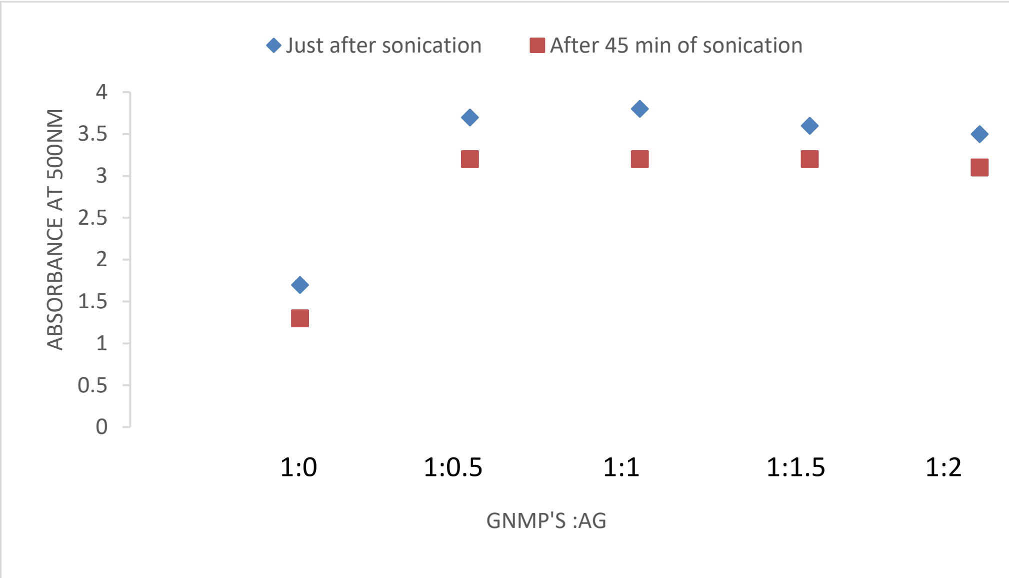


Figure 4-1: Absorbance by UV spectroscopy at 500nm

4.3 Salt freeze-thaw testing:

4.3.1 Scaling:

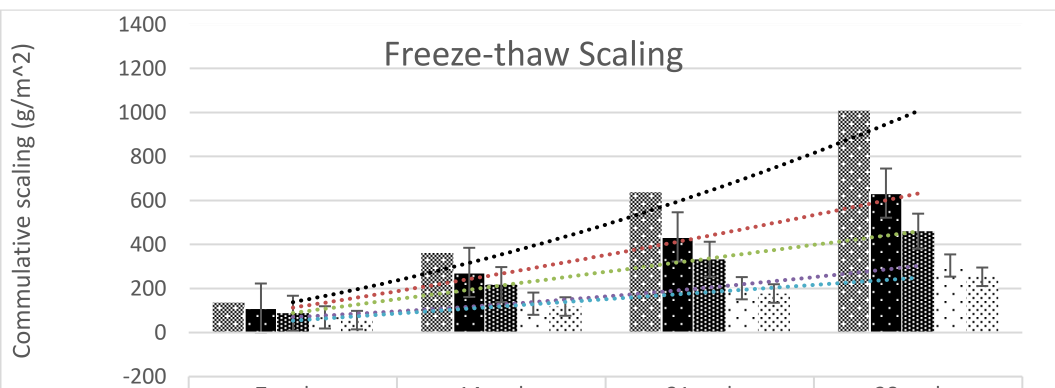
The Slab test procedure CEN/TS 12390-9 was followed to evaluate freeze-thaw scaling of concrete by adding GNMP's. The scaling material was measured at 7, 14, 21 and 28 freeze-thaw cycles. For controlled formulation having 0% GNMP's, exceptionally high scaling was observed which is higher than available scaling limit specified by CEN/TS 12390-9 for concretes (1000g/m^2). Freeze-thaw scaling reduces significantly with the increase in addition of GNMP's as shown in Figure 4-2. Addition of GNMP's has reduced scaling up to 75% by improving microstructure. GNMP's modifies the structure by packing, improving the interfacial transition zone and intimate bonds with matrix due to van der wall forces [20]. The shape of GNMP's enabled them to block and diverts the micro cracks, thus slowing down the propagation of cracks.

SEM results confirm the densification of microstructure through hydration products and diversion and blockage of cracks by hydration products and GNMP's. Figure 4-3 (a) shows less amount of hydration products. Figure 4-3 (b) shows significant amount of increase in hydration products on GNMP,s particles due to nucleation sites which encourages high precipitation of hydration products. Moreover all the particles seem covered with hydration products i.e. CSH gel which reduces the overall porosity. By making the internal microstructure relatively denser, the strength is increased and permeability is reduced due to which less water is absorbed and scaling effect is minimized.

Pore size distribution and air content has great influence over freeze-thaw resistance of cementitious matrix. With addition of graphite platelets, the overall porosity has been reduced significantly i.e. by refining the porosity of capillary pores and increasing the gel micro pores porosity [8]. Refinement in porosity is also verified from BET and SEM results. The finer pore size distribution has both positive and negative affects i.e. decreases the freezable water in matrix but on the other hand also significantly reduces the permeability which causes high internal disruptive pressure of water upon freezing.. As in our case the fine pore size distribution is reduced significantly as shown in BET results and negative effects of finer pore size is minimized.

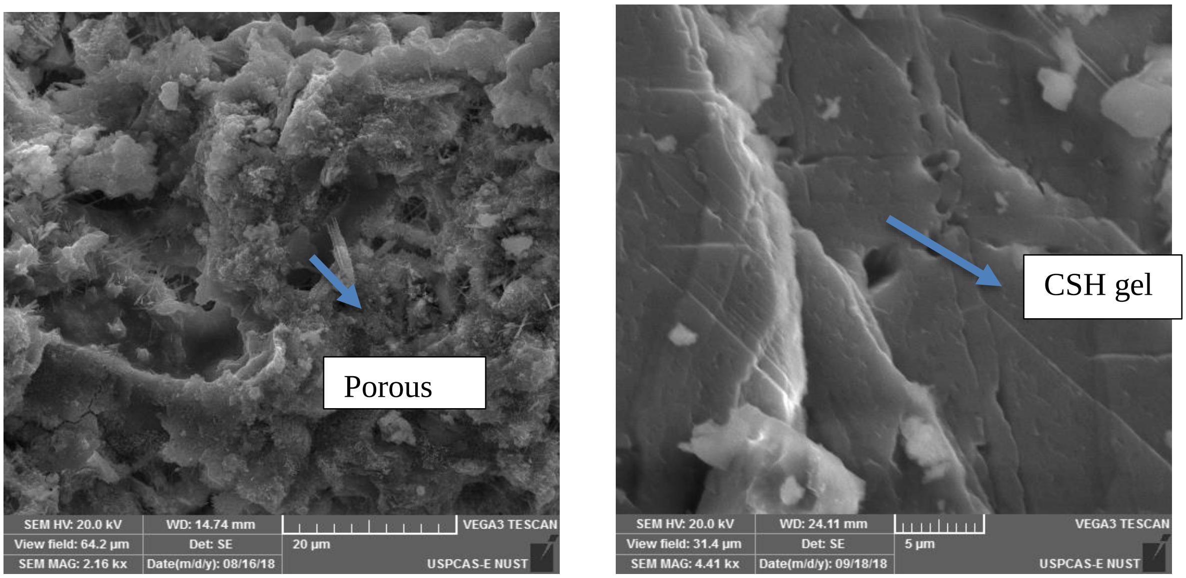
With addition of Nano material from 0-0.3%, the air content increases significantly [22] [21]. As GNMP's we used also contain nano particles which act as air entrainment agents that leads to increase in the air content in matrix occur and reduces the freeze-thaw scaling significantly.

Many other researchers have used Nano material against freeze-thaw and freeze-thaw resistance is improved. CNTs have been investigated and improvement in freeze-thaw resistance is found by refining the porosity, reducing permeability and crack bridging effect [12].



	7 cycles	14 cycles	21 cycles	28 cycles
0P0GNMPs	135.5555556	360.8888889	637.3333333	1008.888889
0P25GNMPs	111.1111111	273.3333333	434.6666667	633.3333333
0P50GNMPs	87.55555556	217.7777778	332.8888889	460.4444444
0P75GNMPs	68.88888889	131.1111111	201.3333333	304.4444444
1P0GNMPs	56.44444444	118.2222222	177.3333333	253.3333333

Figure 4-2: Freeze-thaw scaling



(a) (b)

Figure 4-3: SEM images of (a) 0P0GNMP's (b) 1P0GNMP's before freeze-thaw cycles

4.3.2 Freeze-thaw internal structure damage:

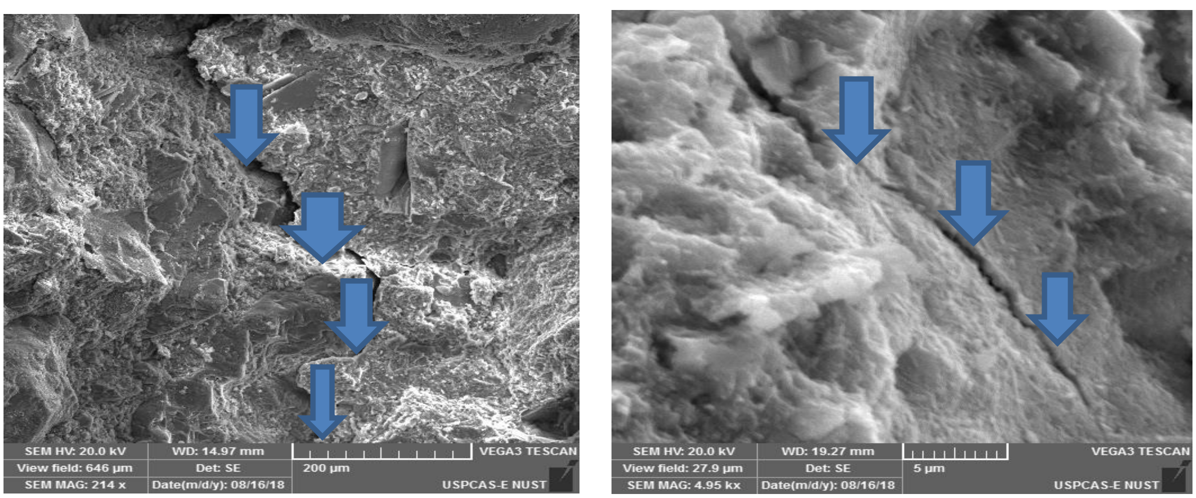
The Slab test procedure CEN/TR 15177 was followed to evaluate freeze-thaw internal structure damage of concrete by adding GNMP's. Internal structure damage was determined by performing ultrasonic pulse transit time test. By obtaining transit time, RDM of elasticity was obtained and results are presented in Table 4-1. ISD was minimized with addition of GNMP's due to the fact that Nano material reduces the capillary pores and increases the gel pores and in general freeze-thaw exposure increases total porosity due to internal micro cracks and maximum pore size remain unaffected. The volume of gel pores influences internal structure damages more because high volume of such pores reduces internal structure damage. Also freeze-thaw action caused more damage in smaller pores. The water in large capillary pores freezes first followed by small capillary pores whereas water in gel pores remain in very cool condition as it freezes below -78 degree C [9].

GNMP's reduces the permeability of the mix due to which quantum of water in concrete is reduced significantly. As water amount is reduced, the osmotic pressure caused by water will be reduced and the damage caused by freezing water will also be reduced. SEM also confirms decrement in damage due to addition of GNMP's. In Figure 4-4(a), the micro cracks are produced due to freeze-thaw action. The cracks developed due to the freeze-thaw action in mix having no GNMP’s causes more deterioration and is bigger. In Figure 4-4(b) the crack indicates smaller deterioration in dense microstructure and GNMP’s platelets is compelling cracks to stop or change its trajectory.

Many researchers have evaluated that low permeability enhance freeze-thaw resistance[9] [8]. Air content is enhanced with addition of graphite nano/micro platelets. The formulation having greater air content, have less internal structure damage [32].

Table 4-1: Relative dynamic modulus of elasticity

Formulation Name	Relative dynamic modulus of elasticity RDM (Average ± Standard deviation)			
	Number of freeze-thaw cycles			
	7	14	21	28
0P0GNMP’s	0.942±0.06	0.895±0.11	0.8170±0.13	0.747±0.07
0P25GNMP’s	0.965±0.12	0.929±0.08	0.875±0.11	0.802±0.03
0P50GNMP’s	0.987±0.10	0.944±0.04	0.891±0.09	0.848±0.009
0P75GNMP’s	0.991±0.05	0.952±0.12	0.915±0.04	0.876±0.02
1P0GNMP’s	0.995±0.07	0.986±0.09	0.959±0.003	0.938±0.01



(a) (b)

Figure 4-4: Scanning electron microscopy of (a) 0P0GNMP's (b) 1P0GNMP's after frost attack

4.3.3 Compression test before and after freeze-thaw cycles

The test result shows that addition of GNMP’s is directly related to increase in compressive strength. Elastic modulus of GNMP’s is much higher than that of concrete due to which compressive strength might be increased. When the load is applied, load is transferred to interface of cement matrix and GNMP’s. GNMP’s interface will carry greater load than cement aggregate interface that results overall increase in strength. Increase in compressive strength may be due to the bridging effect of micro cracks and improving the interfacial transition zone. The concrete failure is mainly related to development of micro cracks. Adding Nano materials limit development of internal micro cracks and increase in compressive strength occur [33].

GNMP’s shows higher load resistance in post cracking. Due to larger surface area of GNMP’s , more hydrates are formed in mix and increasing compressive strength [22]. Up to 0.75% there is significant increase in compressive strength, but after that there is little decrease at 1%. That change in trend may be due to re-agglomeration of high content of GNMP’s producing defective sites [34]. Increase in compressive strength of mortar with addition of GNMP’s is reported [35]. Kumar et al has reported increase in compressive strength with addition of CNTs but at higher content decrease in strength occur due to agglomeration [36]. Many other researchers have also reported increase in compressive strength with addition of Nano materials [37] [38]. 20-50% increase of compressive strength with addition of CF is also reported [33]

From the results we conclude that 0.75% is the optimum GNMP’s content which give maximum compressive strength.

The loss in compressive strength after 28 freeze-thaw cycles for mix having 0% GNMP’s was found to be 35% whereas for 0.75% of GNMP’s, the loss in compressive strength was reduced to 9.5%. This shows that GNMP’s have positive effect on durability of concrete.

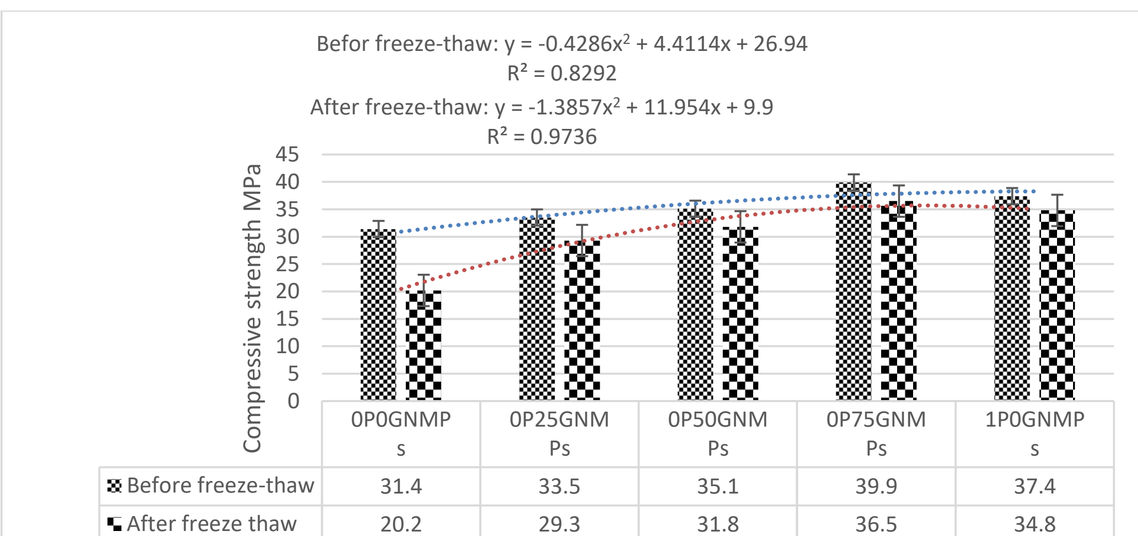
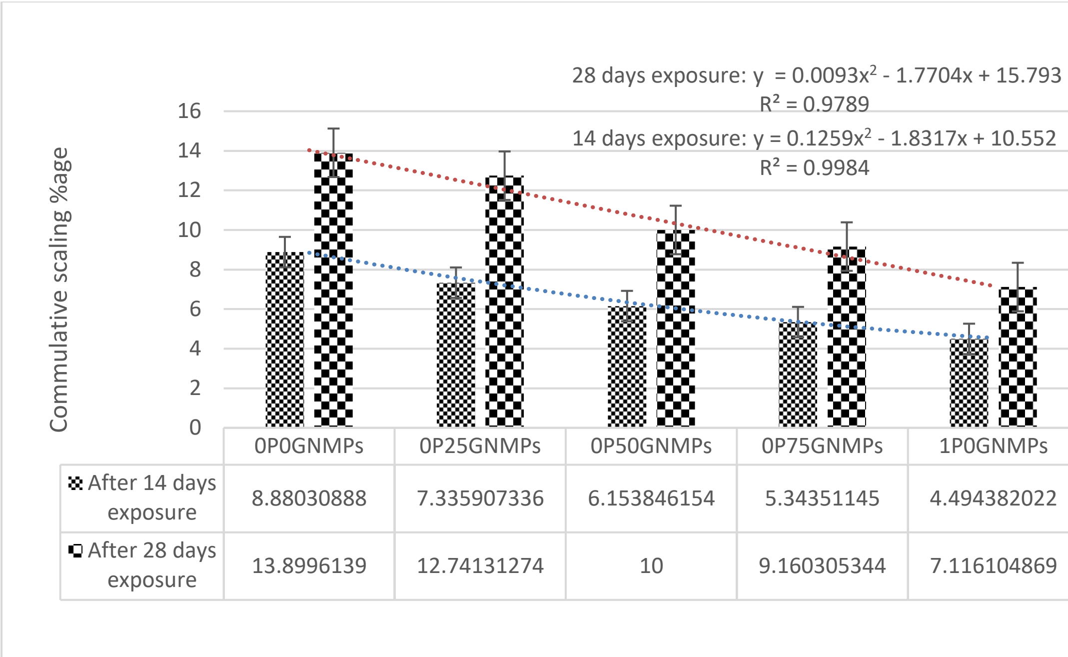


Figure 4-5: Comparison of compressive strength before and after freeze-thaw cycles

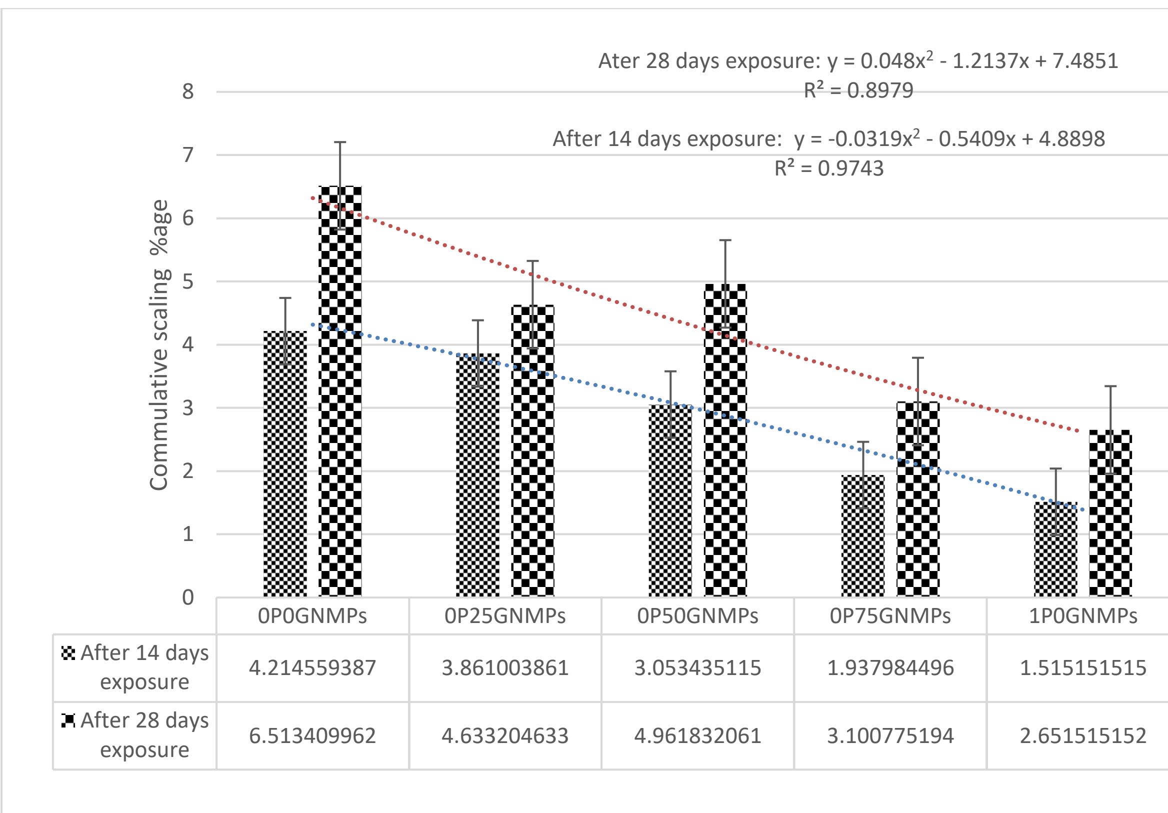
4.4 Acid attack:

Concrete is vulnerable to acid attack because of its alkaline nature. When acid comes in contact with concrete, constituents of concrete get damaged. To evaluate the formulations for its application in acid rich environment, acid attack test was conducted. To evaluate the performance of concrete mixes, samples were placed in sulfuric acid and hydrochloric acid (5% solution) for 14 and 28 days. Resistant were evaluated on basis of weight loss. The result of weight loss of control and GNMP's mixes after exposure are shown in Figure 4-6 and Figure 4-7. The weight loss decreases with increase in GNMP's content for both hydrochloric and sulfuric acid attack. By increasing the percentage of GNMP's the microstructure of mix becomes denser and the permeability is reduced. So the water absorption decreases with increase in GNMP's content in the mix. This shows that by increasing percentage of GNMP's, acid absorption is reduced. This in turn, results less deterioration and weight loss. Hence, the dense microstructure may be related to the decrease in weight loss. The minimum and maximum weight loss after 28 days exposure to HCL were observed for 1P0GNMP's and 0P0GNMP's concrete mixes and were equal to 2.71 and 6.5 % respectively. Similarly for sulfuric acid the minimum and maximum values for 1P0GNMP's and 0P0GNMP's are 7.10 and 13.90 % respectively. From this we conclude that deterioration caused by sulfuric acid was more than hydrochloric acid. Sulfuric acid is known to be more severe and destructive compare to hydrochloric acid. Due to sulfuric acid attack, ettringite is formed which cause expansion and bursting of concrete whereas no product is formed during hydrochloric acid attack[39]. MWCNT have also improved sulfate resistance due to Nano and micro size packing which reduces the porosity and high mechanical properties of Nano material which is evenly distributed in mix and prevent the emergence and development of fractures [40] .



	0P0GNMPs	0P25GNMPs	0P50GNMPs	0P75GNMPs	1P0GNMPs
After 14 days exposure	8.88030888	7.335907336	6.153846154	5.34351145	4.494382022
After 28 days exposure	13.8996139	12.74131274	10	9.160305344	7.116104869

Figure 4-6: Sulfate attack scaling at 14 and 28 days exposure



	0P0GNMPs	0P25GNMPs	0P50GNMPs	0P75GNMPs	1P0GNMPs
After 14 days exposure	4.214559387	3.861003861	3.053435115	1.937984496	1.515151515
After 28 days exposure	6.513409962	4.633204633	4.961832061	3.100775194	2.651515152

Figure 4-7: HCL attack scaling at 14 and 28 days exposure

4.5 Chloride migration test:

The major cause of deterioration in concrete is due to the reinforcement corrosion and the main cause of corrosion is the diffusion of chloride ions. The major effect on durability of structure is due to rate at which chloride ions diffuse. When chloride ions reach the vicinity of bars, the process of corrosion begins. NT-BUILD 492 test procedure is followed to determine the chloride migration coefficient in concrete from non-steady-state migration experiments. The chloride migration coefficient determined by the method is measure of the resistance of tested material to chloride penetration.

The results from chloride migration test confirms that specimens having more amount of GNMP's offer more resistance to chloride penetration as shown in Table 4-2. From chloride penetration depth, migration coefficient values are determined from Equation 3. As already discussed the chloride resistance parameter was to be evaluated by determining migration coefficient shown in Figure 4-8. This is due to the fact that by adding GNMP's, the concrete structure becomes more dense and impermeable. The porosity was reduced due to which rate of diffusion of chloride ion was reduced significantly. Both BET and SEM also confirms the densification and reduction in porosity of matrix. In literature, it is reported that increase or decrease of chloride penetration resistance in concrete depends on the improvement or degeneration of pore structure [41]. Carbon Nano tubes have also improved the chloride penetration resistance because of reduction in porosity and pore size decrement [42]. MWCNT have also improved the resistance due to Nano and micro packing and high mechanical properties of Nano materials which is evenly distributed in mix and prevent the emergence and development of fractures [40] .

Table 4-2: Penetration depth and migration co-efficient

Sample type	Penetration depth (mm)	Migration co-efficient, Dsnm ($10^{-12} m^2/sec$)
0P0GNMP's	22.0	10.29
0P25GNMP's	15.4	7.01
0P50GNMP's	12.8	5.74
0P75GNMP's	9.6	4.18
1P0GNMPS	7.4	3.15

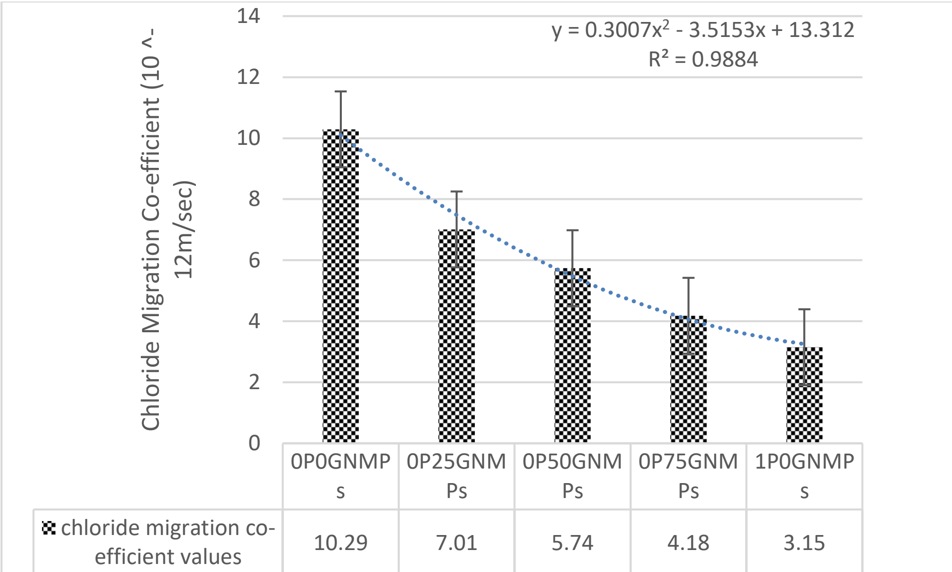
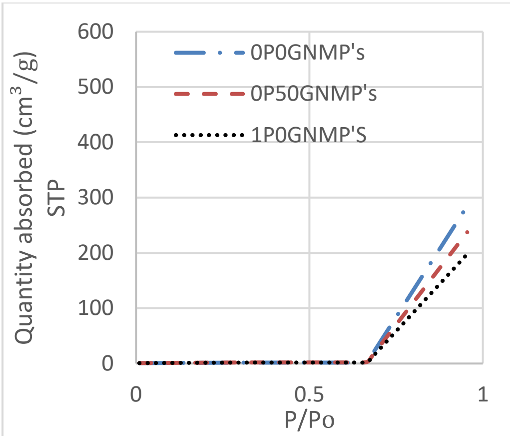


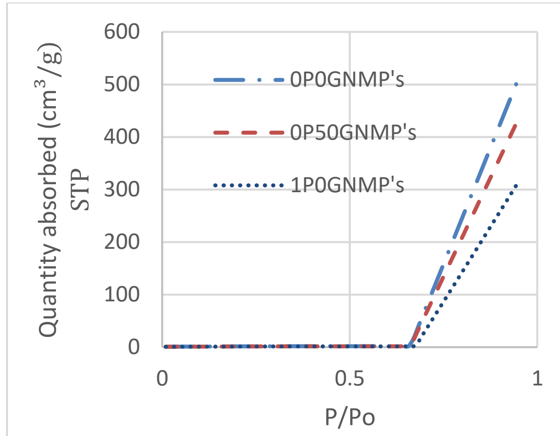
Figure 4-8: Chloride migration co-efficient

4.6 BET Porosimetry:

Bet technique is widely used to determine the specific surface area of porous materials but can also be used as an alternative to MIP to find out the porosity distribution. Mainly the BET results are affected by pre-treatment technique. In pre-treatment method, the free water present in sample is removed by different techniques. Mainly, following three methods are used. (1) Oven drying (2) D-drying (3) Methanol exchange after D-drying which all can results in different results. Decomposition of CSH gel may occur if oven drying is done at high temperatures which may results in collapsing void structure up to some extent. Therefore, the sample was pre-treated at 60 for 24 hours. Maria et al [43] has discussed the above mentioned techniques and their effects on results in detail. Increase in relative pressure shows that larger amount of nitrogen is absorbed in sample which shows that GNMP's intrusion has reduced pore volume of concrete as shown in Figure 4-9. After 28 freeze-thaw cycles, the figure show that the relative pressure of sample is increased but the effect on relative pressure is much less on sample having graphite platelets compared to control sample. Pore size distribution has also been shown in Figure 4-10.

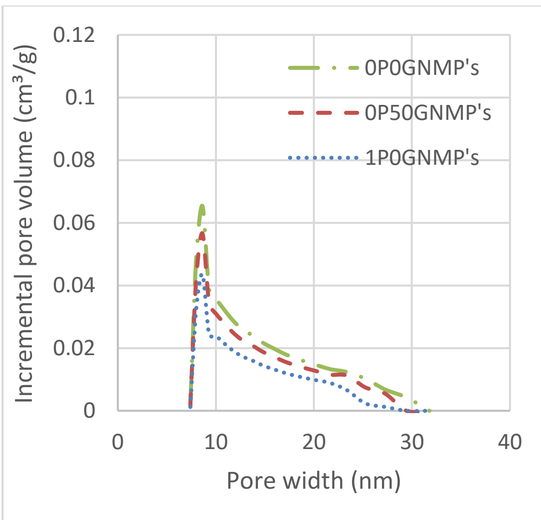


(a)

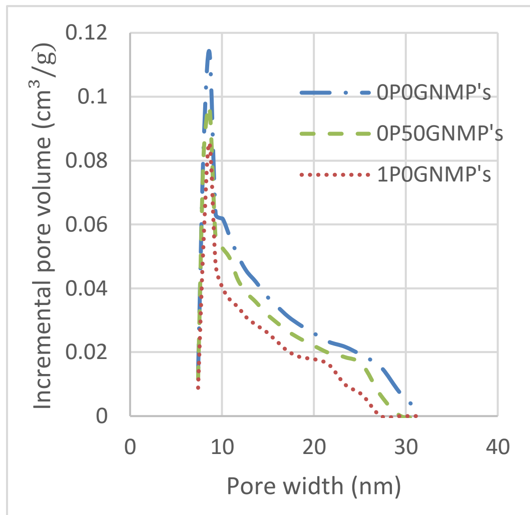


(b)

Figure 4-9: Nitrogen absorption isotherm (a) before (b) after frost attack



(a)



(b)

Figure 4-10: Incremental pore size distribution (a) Before and (b) After frost attack

The

Table 4-3 also shows that pores size and pore volume both are refined with intrusion of graphite platelets before and after frost attack. Pore volume is reduced up to 32 % before and 34 % after frost attack. Improvement in porosity of mix with addition of GNMP's is reported [38]. Other nano materials has also been reported such as CNTS addition has reduced the porosity and refined microstructure [44] [45] [46] [47]. Up to 64 % decrement in porosity is reported by addition of MWCNT [48].

Table 4-3: Comparison of pore size and volume before and after freeze-thaw cycles

Sample type	Before freeze-thaw cycles		After 28 freeze-thaw cycles	
	Pore size Å	Pore volume (cm^3/g)	Pore size Å	Pore volume (cm^3/g)
OP0GNMP’s	1476.47	0.45796	2470.15	0.7896
0P50GNMP’s	1354.62	0.38736	1987.34	0.6542
1P0GNMP’s	1122.56	0.30755	1598.08	0.5214

4.7 Volumetric stability:

Structural engineers are mainly interested in overall shrinkage irrespective of shrinkage mechanism that’s why maximum allowable limit of overall shrinkage is specified in most of design codes. Mix was poured into channel of shrinkage apparatus and early shrinkage was measured for first 24 hours.

The Figure 4-11 shows that the shrinkage values decreases significantly as the concentration of GNMP’s increases. Overall reduction in shrinkage was 43%. The reduction in shrinkage is mainly due to reinforcing action of GNMP’s as it helps in mitigating induced tensile stresses inside the matrix. Due to their smaller sizes tend to fill the pores and reduces shrinkage [49].The bleeding and formation of water films was significantly reduced in cement mortar due to absorption of large amount of water by GNMP’s which have high surface energy and large surface area. Shrinkage and creep are influenced in cementitious matrix by reduction in pores [50]. Addition of CNTs reduces the drying shrinkage is reported [51]. It is also reported that autogenous shrinkage was reduced by addition of CNTs to the paste [50]. It seems that reduction of micro pores by adding GNMP’s helps in decreasing shrinkage of cement paste samples.

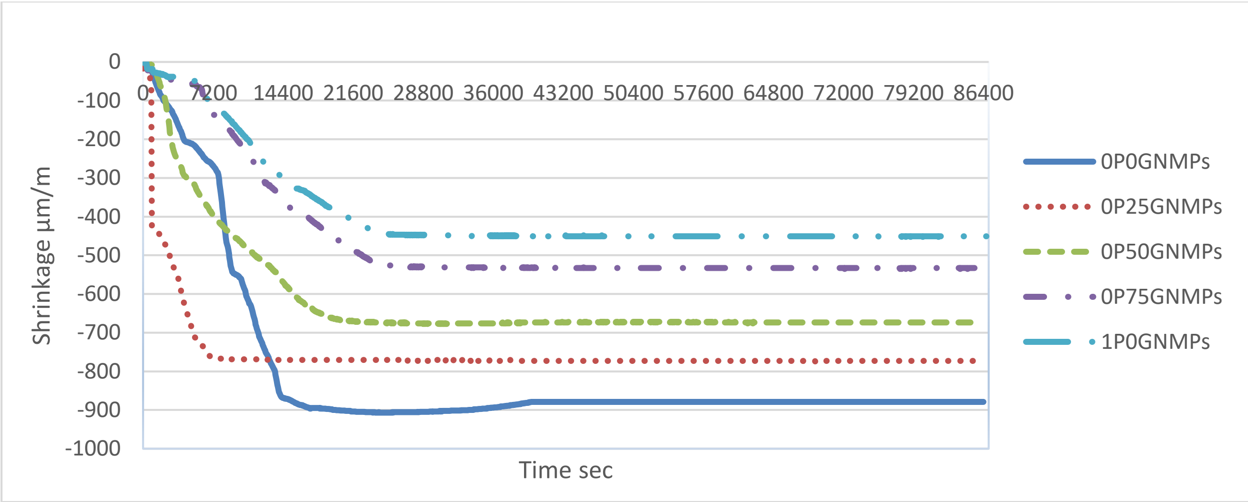


Figure 4-11: Total linear shrinkage of plain and modified mortars

CHAPTER 5

5 CONCLUSIONS AND RECCOMENDATIONS

5.1 Conclusions

The results stipulated in this study report new data on durability performance characteristics of nano modified concrete. Based on results in this study following conclusions were reached.

- In this study, graphite platelets were effectively used in cementitious matrix to enhance its strength, microstructure and durability.
- UV spectrum results shows that graphite platelets to AG ratio of 1:0.5 gives maximum uniform dispersion of graphitic material in water.
- SEM and BET results reveal that porosity is reduced significantly and microstructure is dense, making the mix impermeable.
- A considerable enhancement in compressive strength by induction of well dispersed GNMP’s in cementitious mix. Also the effect of freeze-thaw on compressive strength is reduced from 35% to 7.5% with an addition of 1% graphite platelets.
- The induction of GNMP’s in cementitious concrete matrix also improves salt freeze-thaw scaling resistance in proportion to injected loading of GNMP’s. Salt freeze-thaw scaling was minimized up to 75% with addition of 1% graphite platelets.
- ISD was not visible in concrete systems with standard test method, however, the mix containing 1% GNMP’s offered maximum resistance against change in porosity due to internal damage, shown in BET results. SEM results also shows less internal structure damage compare to control due to crack bridging effect of GNMP’s.
- Shrinkage values were declined up to 43% with maximum addition of 1% of graphite platelets content.
- Acid attack resistance was also increased. Sulfuric acid scaling was reduced from 14% to 7%. Scaling due to HCL attack was also minimized from 6.5 to 2.8 percent.
- Chloride penetration and chloride migration co-efficient both were reduced due to reduction in permeability. Chloride penetration was reduced up to 65 % and migration co-efficient was minimized up to 69%.

5.2 Recommendations

- Use of SRMs and SCMs alongside these nano particles and their effect on freeze-thaw, acid attack and chloride penetration
- Evaluating the effect in SCC, HPC and UHPC mixes.

6 REFERENCES

[1] A. M. Neville, *Properties of concrete*, 5th ed. Harlow, England ; New York: Pearson, 2011.

[2] N. Banthia and J. Sheng, "Fracture toughness of micro-fiber reinforced cement composites," *Cem. Concr. Compos.*, vol. 18, no. 4, pp. 251–269, Jan. 1996.

[3] N. Banthia and N. Nandakumar, "Crack growth resistance of hybrid fiber reinforced cement composites," *Cem. Concr. Compos.*, vol. 25, no. 1, pp. 3–9, Jan. 2003.

[4] F. Babak, H. Abolfazl, R. Alimorad, and G. Parviz, "Preparation and Mechanical Properties of Graphene Oxide: Cement Nanocomposites," *Sci. World J.*, vol. 2014, pp. 1–10, 2014.

[5] E. Hammel *et al.*, "Carbon nanofibers for composite applications," *Carbon*, vol. 42, no. 5–6, pp. 1153–1158, 2004.

[6] W. Zhu, P. J. M. Bartos, and A. Porro, "Application of nanotechnology in construction: Summary of a state-of-the-art report," *Mater. Struct.*, vol. 37, no. 9, pp. 649–658, Nov. 2004.

[7] K. S. Novoselov, "Electric Field Effect in Atomically Thin Carbon Films," *Science*, vol. 306, no. 5696, pp. 666–669, Oct. 2004.

[8] J. Li, P.-S. Wong, and J.-K. Kim, "Hybrid nanocomposites containing carbon nanotubes and graphite nanoplatelets," *Mater. Sci. Eng. A*, vol. 483–484, pp. 660–663, Jun. 2008.

[9] G. Y. Li, P. M. Wang, and X. Zhao, "Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes," *Carbon*, vol. 43, no. 6, pp. 1239–1245, May 2005.

[10] H. Liao, B. Paratala, B. Sitharaman, and Y. Wang, "Applications of Carbon Nanotubes in Biomedical Studies," in *Biomedical Nanotechnology*, vol. 726, S. J. Hurst, Ed. Totowa, NJ: Humana Press, 2011, pp. 223–241.

[11] S. Iijima, "Helical microtubules of graphitic carbon," *Nature*, vol. 354, no. 6348, pp. 56–58, Nov. 1991.

[12] K. S. Ibrahim, "Carbon nanotubes-properties and applications: a review," *Carbon Lett.*, vol. 14, no. 3, pp. 131–144, Jul. 2013.

[13] J. Njuguna, Ed., *Structural Nanocomposites*. Berlin, Heidelberg: Springer Berlin Heidelberg, 2013.

[14] F. Babak, H. Abolfazl, R. Alimorad, and G. Parviz, "Preparation and Mechanical Properties of Graphene Oxide: Cement Nanocomposites," *Sci. World J.*, vol. 2014, pp. 1–10, 2014.

[15] Q. Li, J. Liu, and S. Xu, "Progress in Research on Carbon Nanotubes Reinforced Cementitious Composites," *Adv. Mater. Sci. Eng.*, vol. 2015, pp. 1–16, 2015.

[16] M. Cai, D. Thorpe, D. H. Adamson, and H. C. Schniepp, "Methods of graphite exfoliation," *J. Mater. Chem.*, vol. 22, no. 48, p. 24992, 2012.

[17] L. Tian *et al.*, "Graphene Oxides for Homogeneous Dispersion of Carbon Nanotubes," *ACS Appl. Mater. Interfaces*, vol. 2, no. 11, pp. 3217–3222, Nov. 2010.

[18] S. Parveen, S. Rana, and R. Fangueiro, "A Review on Nanomaterial Dispersion, Microstructure, and Mechanical Properties of Carbon Nanotube and Nanofiber Reinforced Cementitious Composites," *J. Nanomater.*, vol. 2013, pp. 1–19, 2013.

[19] M. S. Konsta-Gdoutos, Z. S. Metaxa, and S. P. Shah, "Highly dispersed carbon nanotube reinforced cement based materials," *Cem. Concr. Res.*, vol. 40, no. 7, pp. 1052–1059, Jul. 2010.

[20] J. Luo, Z. Duan, and H. Li, "The influence of surfactants on the processing of multi-walled carbon nanotubes in reinforced cement matrix composites," *Phys. Status Solidi A*, p. NA-NA, Jul. 2009.

[21] X. Xie, Y. Mai, and X. Zhou, “Dispersion and alignment of carbon nanotubes in polymer matrix: A review,” *Mater. Sci. Eng. R Rep.*, vol. 49, no. 4, pp. 89–112, May 2005.
[22] A. Sobolkina *et al.*, “Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix,” *Cem. Concr. Compos.*, vol. 34, no. 10, pp. 1104–1113, Nov. 2012.
[23] A. Yazdanbakhsh, Z. Grasley, B. Tyson, and R. Abu Al-Rub, “Challenges and Benefits of Utilizing Carbon Nanofilaments in Cementitious Materials,” *J. Nanomater.*, vol. 2012, pp. 1–8, 2012.
[24] T. Nochaiya and A. Chaipanich, “Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials,” *Appl. Surf. Sci.*, vol. 257, no. 6, pp. 1941–1945, Jan. 2011.
[25] A. Chaipanich, T. Nochaiya, W. Wongkeo, and P. Torkittikul, “Compressive strength and microstructure of carbon nanotubes–fly ash cement composites,” *Mater. Sci. Eng. A*, vol. 527, no. 4–5, pp. 1063–1067, Feb. 2010.
[26] G. Sun, R. Liang, Z. Lu, J. Zhang, and Z. Li, “Mechanism of cement/carbon nanotube composites with enhanced mechanical properties achieved by interfacial strengthening,” *Constr. Build. Mater.*, vol. 115, pp. 87–92, Jul. 2016.
[27] B. Wang, Y. Han, and S. Liu, “Effect of highly dispersed carbon nanotubes on the flexural toughness of cement-based composites,” *Constr. Build. Mater.*, vol. 46, pp. 8–12, Sep. 2013.
[28] R. A. Khushnood, “High Performance Self-Compacting Cementitious Materials Using Nano/Micro Carbonaceous Inerts,” *Politec. Torino*, 2015.
[29] S. Xu, J. Liu, and Q. Li, “Mechanical properties and microstructure of multi-walled carbon nanotube-reinforced cement paste,” *Constr. Build. Mater.*, vol. 76, pp. 16–23, Feb. 2015.
[30] M. T. Hasholt, “Air void structure and frost resistance: a challenge to Powers’ spacing factor,” *Mater. Struct.*, vol. 47, no. 5, pp. 911–923, May 2014.
[31] G. Fagerlund, “Contribution to the International Workshop on Fteeze-Thaw and Deicing Salt Scaling Resistance of Concrete Québec August 30-3 I, 1993,” p. 26.
[32] “12.pdf.” .
[33] “power 1.pdf.” .
[34] “power 2.pdf.” .
[35] “BCPS_47178_1946_Journal-of-the-Ameri.pdf.” .
[36] G. G. Litvan, “Phase Transitions of Adsorbates: IV, Mechanism of Frost Action in Hardened Cement Paste,” *J. Am. Ceram. Soc.*, vol. 55, no. 1, pp. 38–42, Jan. 1972.
[37] S. Mindess, J. F. Young, and D. Darwin, *Concrete*, 2nd ed. Upper Saddle River, NJ: Prentice Hall, 2003.
[38] Y. Z. M. D. Cohen and W. L. Dolch, “Non-Air-Entrained High-Strength Concrete--Is it Frost Resistant?,” *Mater. J.*, vol. 89, no. 4, Jul. 1992.
[39] “MnDOT1998-10.pdf.” .
[40] G. Fagerlund, “FROST RESISTANCE OF HIGH PERFORMANCE CONCRETE- SOME THEORETICAL CONSIDERATIONS,” p. 42.
[41] N. Salemi, K. Behfarnia, and S. A. Zaree, “EFFECT OF NANOPARTICLES ON FROST DURABILITY OF CONCRETE,” p. 10.
[42] X. Wang, I. Rhee, Y. Wang, and Y. Xi, “Compressive Strength, Chloride Permeability, and Freeze-Thaw Resistance of MWNT Concretes under Different Chemical Treatments,” *Sci. World J.*, vol. 2014, pp. 1–8, 2014.

[43] W.-W. Li, W.-M. Ji, Y.-C. Wang, Y. Liu, R.-X. Shen, and F. Xing, “Investigation on the Mechanical Properties of a Cement-Based Material Containing Carbon Nanotube under Drying and Freeze-Thaw Conditions,” *Materials*, vol. 8, no. 12, pp. 8780–8792, Dec. 2015.
[44] A. Cwirzen and K. Habermehl-Cwirzen, “The Effect of Carbon Nano- and Microfibers on Strength and Residual Cumulative Strain of Mortars Subjected to Freeze-Thaw Cycles,” *J. Adv. Concr. Technol.*, vol. 11, no. 3, pp. 80–88, 2013.
[45] J.-L. Le, H. Du, and S. D. Pang, “Use of 2D Graphene Nanoplatelets (GNP) in cement composites for structural health evaluation,” *Compos. Part B Eng.*, vol. 67, pp. 555–563, Dec. 2014.
[46] C09 Committee, “Test Method for Compressive Strength of Cylindrical Concrete Specimens,” ASTM International.
[47] *Testing hardened concrete: freeze-thaw resistence.* Place of publication not identified: Euro Comm For Stand, 2006.
[48] “[PD CENTR 15177-2006] -- Testing the freeze-thaw resistance of concrete. Internal structural damage..pdf.” .
[49] C03 Committee, “Test Methods for Chemical Resistance of Mortars, Grouts, and Monolithic Surfacings and Polymer Concretes,” ASTM International.
[50] “nt-build 492.pdf.” .
[51] D. D. L. Chung, “Self-monitoring structural materials,” *Mater. Sci. Eng. R Rep.*, vol. 22, no. 2, pp. 57–78, Mar. 1998.
[52] W. Meng and K. H. Khayat, “Mechanical properties of ultra-high-performance concrete enhanced with graphite nanoplatelets and carbon nanofibers,” *Compos. Part B Eng.*, vol. 107, pp. 113–122, Dec. 2016.
[53] M. S. Morsy, S. H. Alsayed, and M. Aqel, “Hybrid effect of carbon nanotube and nano-clay on physico-mechanical properties of cement mortar,” *Constr. Build. Mater.*, vol. 25, no. 1, pp. 145–149, Jan. 2011.
[54] S. Kumar, P. Kolay, S. Malla, and S. Mishra, “Effect of Multiwalled Carbon Nanotubes on Mechanical Strength of Cement Paste,” *J. Mater. Civ. Eng.*, vol. 24, no. 1, pp. 84–91, Jan. 2012.
[55] G. Y. Li, P. M. Wang, and X. Zhao, “Mechanical behavior and microstructure of cement composites incorporating surface-treated multi-walled carbon nanotubes,” *Carbon*, vol. 43, no. 6, pp. 1239–1245, May 2005.
[56] R. A. Khushnood, “High Performance Self-Compacting Cementitious Materials Using Nano/Micro Carbonaceous Inerts,” *Politec. Torino*, 2015.
[57] S. P. Shah, P. Hou, and M. S. Konsta-Gdoutos, “Nano-modification of cementitious material: toward a stronger and durable concrete,” *J. Sustain. Cem.-Based Mater.*, vol. 5, no. 1–2, pp. 1–22, Mar. 2016.
[58] M. S. Konsta-Gdoutos, Z. S. Metaxa, and S. P. Shah, “Multi-scale mechanical and fracture characteristics and early-age strain capacity of high performance carbon nanotube/cement nanocomposites,” *Cem. Concr. Compos.*, vol. 32, no. 2, pp. 110–115, Feb. 2010.
[59] F. Torabian Isfahani, W. Li, and E. Redaelli, “Dispersion of multi-walled carbon nanotubes and its effects on the properties of cement composites,” *Cem. Concr. Compos.*, vol. 74, pp. 154–163, Nov. 2016.
[60] M. C. Garci Juenger and H. M. Jennings, “The use of nitrogen adsorption to assess the microstructure of cement paste,” *Cem. Concr. Res.*, vol. 31, no. 6, pp. 883–892, May 2001.

[61] A. Sobolkina *et al.*, “Dispersion of carbon nanotubes and its influence on the mechanical properties of the cement matrix,” *Cem. Concr. Compos.*, vol. 34, no. 10, pp. 1104–1113, Nov. 2012.
[62] S. Xu, J. Liu, and Q. Li, “Mechanical properties and microstructure of multi-walled carbon nanotube-reinforced cement paste,” *Constr. Build. Mater.*, vol. 76, pp. 16–23, Feb. 2015.
[63] B. S. Sindu, S. Sasmal, and S. Gopinath, “A multi-scale approach for evaluating the mechanical characteristics of carbon nanotube incorporated cementitious composites,” *Constr. Build. Mater.*, vol. 50, pp. 317–327, Jan. 2014.
[64] T. Nochaiya and A. Chaipanich, “Behavior of multi-walled carbon nanotubes on the porosity and microstructure of cement-based materials,” *Appl. Surf. Sci.*, vol. 257, no. 6, pp. 1941–1945, Jan. 2011.
[65] K. Wille and K. J. Loh, “Nanoengineering Ultra-High-Performance Concrete with Multiwalled Carbon Nanotubes,” *Transp. Res. Rec. J. Transp. Res. Board*, vol. 2142, no. 1, pp. 119–126, Jan. 2010.
[66] W. Meng and K. H. Khayat, “Effect of graphite nanoplatelets and carbon nanofibers on rheology, hydration, shrinkage, mechanical properties, and microstructure of UHPC,” *Cem. Concr. Res.*, vol. 105, pp. 64–71, Mar. 2018.
[67] Z. Liu and W. Hansen, “Freeze–thaw durability of high strength concrete under deicer salt exposure,” *Constr. Build. Mater.*, vol. 102, pp. 478–485, Jan. 2016.
[68] P. K. Mehta and P. J. M. Monteiro, *Concrete: microstructure, properties, and materials*, Fourth edition. New York: McGraw-Hill Education, 2014.
[69] B.-M. Wang, S. Liu, Y. Han, and P. Leng, “Preparation and Durability of Cement-Based Composites Doped with Multi-Walled Carbon Nanotubes,” *Nanosci. Nanotechnol. Lett.*, vol. 7, no. 5, pp. 411–416, May 2015.
[70] M. Zhang and H. Li, “Pore structure and chloride permeability of concrete containing nano-particles for pavement,” *Constr. Build. Mater.*, vol. 25, no. 2, pp. 608–616, Feb. 2011.
[71] L. Lu, D. Ouyang, and W. Xu, “Mechanical Properties and Durability of Ultra High Strength Concrete Incorporating Multi-Walled Carbon Nanotubes,” *Materials*, vol. 9, no. 6, p. 419, May 2016.