STRENGTH AND DURABILITY INVESTIGATION OF CEMENT MORTAR PARTIALLY REPLACED WITH NANOCLAY AND CARBON NANO FIBERS

A Thesis submitted

in partial fulfillment of the requirements for

the award of the degree of

MASTER OF ENGINEERING

IN

STRUCTURAL ENGINEERING

Submitted by:

KUNAL SINGLA

Roll No :- 801322011

Under the guidance of

Dr.Naveen Kwatra
Professor & Head
Department of Civil Engineering

Dr.Shruti Sharma
Associate Professor
Department of Civil Engineering

Thapar University

THAPAR UNIVERSITY, PATIALA
JULY 2015

DECLARATION

The author hereby declare that this dissertation entitled *" **Strength and durability investigation of cement mortar partially replaced with nanoclay and carbon nano fibres** "*, in whole or part has not been used to obtain any degree in this, or any other, institute, except where references have been given in text, it is entirely the author own work. The author conform that the library may lend or copy this upon request for academic purposes.

(KUNAL SINGLA)
REGD.NO. 801322011

CERTIFICATE

This is to certify that the work presented in dissertation entitled ***"Strength and durability investigation of cement mortar partially replaced with nanoclay and carbon nano fibres"*** submitted by **Mr. Kunal Singla** in partial fulfillment of the requirements for the award of degree of **Master of Engineering** in Structural Engineering at **Thapar University, Patiala,** is a bonafide work carried out by the student under our supervision and guidance. The matter embodied in this report has not been submitted anywhere for award of any other degree.

Dr. NAVEEN KWATRA
Professor & Head
Department of Civil Engineering
Thapar University, Patiala

Dr. SHRUTI SHARMA
Associate Professor
Department of Civil Engineering
Thapar University, Patiala

COUNTERSIGNED

Dr. S.S. BHATIA
Dean, Academic Affairs
Thapar University, Patiala

ACKNOWLEDGEMENTS

Time has provided me the cherished opportunity to express my heartfelt gratitude to my guides Dr Naveen Kwatra (HOD) & Dr. Shruti Sharma**,** Associate Professor, Civil Engineering Department, Thapar University, Patiala, who permitted me to carry out research work under their able guidance. I shall ever remain indebted to them for their meticulous guidance, constructive criticism, clear thinking, keen interest, constant encouragement and forbearance right from the beginning of this research to its completion.

I wish to express my sincere thanks to Dr. Naveen Kwatra, Professor and Head CED, Thapar University, Patiala, who has been a constant source of inspiration for me throughout this thesis work.

The cheerful support of my friends and colleagues is sincerely appreciated. Special words of appreciation go to Sh. Ram Simran, Sh. Virender and other laboratory colleagues, who helped me in my experimental work.

I am also thankful to all the staff members of Civil Engineering Department for their full cooperation and help. I would like to pay my sincere thanks to Chemistry Department of Thapar University.

Above all, I thank my parents whose love and affectionate blessing have been a constant source of inspiration in making this manuscript a reality. I render my gratitude to the Almighty who bestowed self-confidence, ability and strength in me to complete this work.

(KUNAL SINGLA)

ABSTRACT

Nanotechnology (nanotech) is the manipulation of matter on an atomic molecular and supramolecular scale . The introduction of nanotechnology represent a revolution that is responsible for the development of high performance and long lasting products and processes within on ideal context of sustainable development. It will affect almost every aspect of one's life. In comparison to other technologies, nanotechnology is mush less well defined and well structured. Nanotechnology is on emerging field by science related to the understanding & control of matter at the nanoscale i.e.dimension between approx 1 and 100 nm. Nanotechnology encompasses nanoscale science, engineering and technology that involve imaging, measuring, modeling and manipulating matter at this length scale. 'Nano' means 1 billionth or 10^{-9}.Use of nanoclay in this field proves to be a great enrichment to the cement mortar to improve its properties. Nanoclay helps to make mortar a multipurpose smart functional material. The use of nanoclay is used to increase the strength and durability of cementitious composites as well as for pollution reduction, Production of thermal insulation materials with a performance ten times commercial current options, Production of cheap corrosion free steel.Production of nanosensors and materials with sensing ability and self- repairing ability

The basic objective of the study is to to investigates the optimized level of reinforcing cement mortar with nano material in small varying proportions &to investigate the effect of carbon nano fiber replacement level on compressive strength of mortar by conducting compressive strength and flexural test. To investigate the effect of carbon nano fiber replacement level on durability by conducting water absorption test and acid resistance test.To investigate the effect of carbon nano fiber replacement level against sulphuric acid and nitric acid attack.

CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 GENERAL

Nanotechnology (nanotech) is the manipulation of matter on an atomic molecular and supramolecular scale. The concepts that seeded nanotechnology were first discussed in 1959 by renowned physicist Richard Feynman in which he described the possibility of synthesis via direct manipulation of atoms. The term "nano-technology" was first used by Norio Taniguchi in 1974. The introduction of nanotechnology represent a revolution that is responsible for the development of high performance and long lasting products and processes within on ideal context of sustainable development. It will affect almost every aspect of one's life. In comparison to other technologies, nanotechnology is mush less well defined and well structured. Nanotechnology is on emerging field by science related to the understanding & control of matter at the nanoscale i.e.dimension between approx 1 and 100 nm. Nanotechnology encompasses nanoscale science, engineering and technology that involve imaging, measuring, modeling and manipulating matter at this length scale. 'Nano' means 1 billionth or 10^{-9}. Therefore, 1 nm is 1-billionth of a meter:

- A sheet of paper is about 100,000 nm thick.
- A strand of human DNA is 25 nm in diameter.
- There are 25,400,00 nm in 1 inch.
- A human hair is approx 80,000 nm wide.
- On a comparative scale, if the diameter of a marble was 1 nm, then diameter of the earth would be 1 m.

There are mainly two ways to approach the nonoscale (i) "top down" approach (ii) "Bottom up" approach or molecular nanotechnology or molecular manufacturing. In which materials are engineered from atoms or molecular components through a process of assembly Figure 1.1 (Sanchez and Sobolev, 2010).

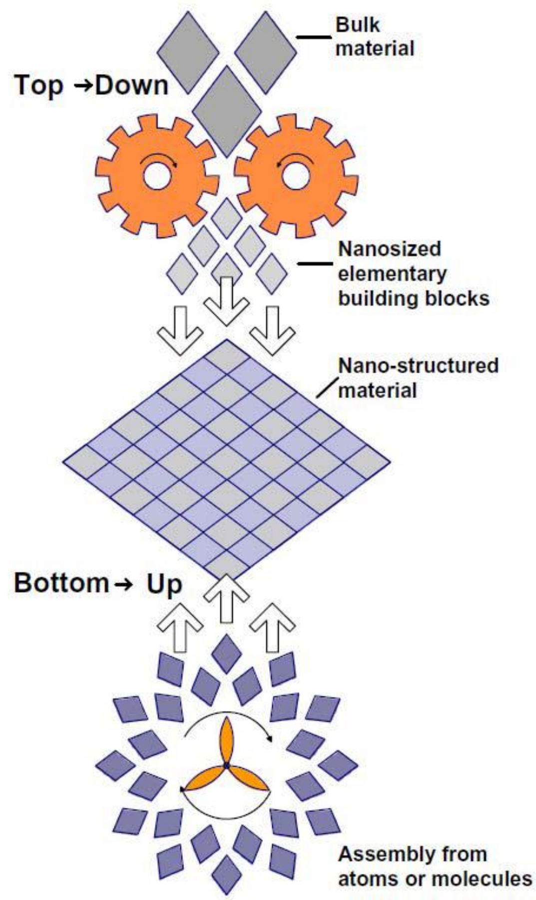


Figure 1.1: The top-down and bottom-up approaches in nanotechnology
(Sanchez and Sobolev, 2010)

The bottom up approach is used for engineering purposes. Nanotechnology is being used for the creation of new materials, devices and systems at molecular, nano and micro-level. Interest in nanotechnology concept for portland cement composites is steadily growing. The most reported research work regarding application of nanotechnology in cement-based materials is either related to coating or enhancement of mechanical and electrical properties. Currently, the most active research areas dealing with cement and concrete are: understanding of the hydration of cement particles and the use of nano-size ingredients such as alumina and silica particles. Knowledge at the nanoscale of the structure and characteristics of materials will promote the development of new applications and new products to repair or improve the properties of construction materials. For example, the structure of the fundamental calcium-silicate-hydrate

(C-S-H) gel which is responsible for the mechanical and physical properties of cement pastes, including shrinkage, creep, porosity, permeability and elasticity. C-S-H gel can be modified to obtain better durability. Cement-based materials containing carbon nanotubes can be used for both strengthening and enhancing electrical and electronic properties of the concrete besides their mechanical properties. Fig 1.2 shows Particle size and specific surface area related to concrete materials

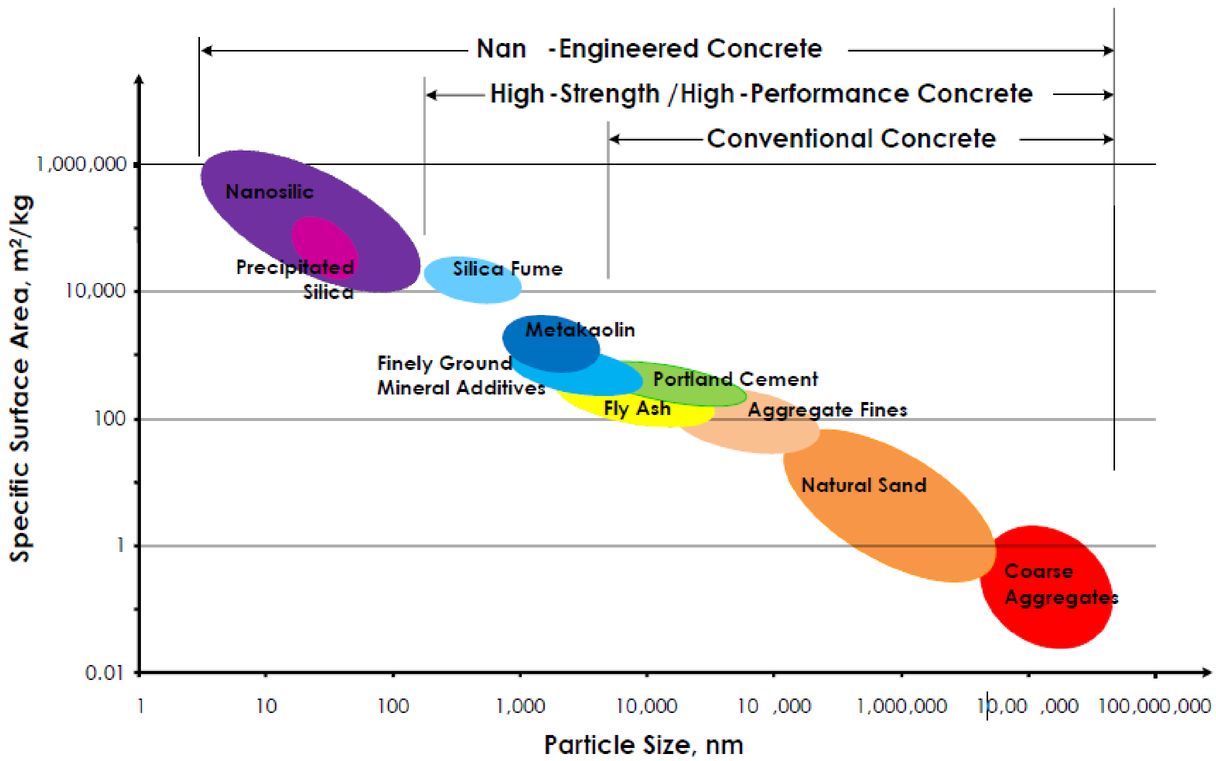


Figure 1.2: Particle size and specific surface area related to concrete materials **(Sobolev, 2005)**

The mechanical behavior of the concrete material depends to a great extent on structural elements that are effective on a micro and nanoscale. The size of the calcium silicate hydrate (C-S-H) phase, the primary component responsible for strength and other properties in cementations system, falls in the few nanometers range. The structure of C-S-H is much like clay, with thin layers of solids separated by gel pores filled with interlayer and absorbed water, this has significant impact on the performance of concrete, because the structure is sensitive to moisture movement. Hence nanotechnology may have the potential to engineer concrete with superior properties through the optimization of material behaviour and required performance to significantly improve mechanical performance, durability and sustainability.

The development of nanotechnology based concrete material require a multidiscipline approach. Consisting of team of concrete material experts; Civil Engineers, chemists, physicists and material scientists, Porro et. al. (2005) presented an overview of have nanotechnology could be applied to concrete technology, emphasizing the multidiscipline approach required for successful breakthrough leading to ultra high performance materials and new multiscale models that enable the opportunities for nanotechnology leading to a new concrete products and materials and also for improving the sustainable and reducing the environmental footprint of concrete based material in the future. He identified the following key breakthroughs in concrete technology that are most likely to result from the use of nanotechnology.

- Development of high performance cement and concrete materials as measured by their mechanical and durable properties.
- Development of sustainable concrete material and structure through engineering for different adverse environment, reducing energy consumption during cement production and enhancing safety.
- Development of intelligent concrete material through the integration of nanotechnology based self-sensing and self-powdered materials and cyber infrastructured technologies.
- Development of novel concrete materials through nanotechnology based innovative processing of cement and cement paste.
- Development of fundamental multiscale model (s) for concrete through advanced characterization and modeling of concrete at the nano -micro, and micro scales.

The development of fibers at the nanoscale has opened a new field of research within concrete. Research by various authors work on reinforcing cementations material using various nanao materials shown that the flexural strength and stiffness of cementation matrices can be significantly increased by adding very low concentration of nano particles as little as 0.025%, 0.050% by wt of cement. Recently in the field of fiber reinforced cement there has been much enthusiasm for the development of hybrid fiber system where two or more types of fiber are combined.

1.2 NANOTECHNOLOGY IN CONCRETE

Nano concrete is defined as a concrete made with portland cement particles with sizes ranging from a few nanometer to a maximum of about 100 micrometers .The Nanoscience and Nanoengineering (nano modification) of concrete are terms that have come into common terms & utilization. This describes two main approaches of application of nanotechnology in concrete researcher (Scrivener et.al. 2008). Nanotechnology creates new possibilities to control and improve material properties for civil infrastructure.

Nanoscience is the study of atom, molecules and objects whose size is on the nanometer scale (1-100 nanometer). Nanoscience deals with the measurement & characteristics of the nano and micro scale structure of cement based materials to broader understanding of how this structure affects macro scale properties and performance through the use of advanced technologies and molecular level modeling. These modeling helps in characteristics the various properties of concrete.

Nano engineering is a quickly emerging field. It is the practice of engineering on the nanoscale that encourage the technique of manipulation of structure at the nanometer scale to develop new generation of customized, multidimensional, multifunctional materials. Cementious products in composites with nano materials have dynamic physical, mechanical performance, durability properties such as low electrical resisting, self sensing capabilities, self cleaning, self healing, self compelling, high performance, high durability, high ductility and control of cracks. Different tpyes of nano materials used in concrete technology are as follows.

1.3 VARIOUS NANO MATERIALS USED IN CONCRETE

1. Iron oxide nano particles(Nano-Fe_2O_3)-Iron oxide nanoparticles have attracted extensive interest due to their super paramagnetic properties but have limited application due to its toxicity**.**
2. Nanosilica.(Nano-SiO_2)-This material with high specific surface area and high proportion of very fine particles consisting of nearly clean $Si0_2$ (99%) .The properties of this material are similar to silica fume; however, they are amplified by higher specific area, hence higher reactiveness.Nano Silica increase the compressive strength of concretes containing large fly ash volume at early age, by filling the pores between large fly ash and cement particles.

3. Carbon Nanotubes (CNTs)- Carbon nanotubes (CNTs; also known as bucky tubes) are allotropes of carbon with a cylindrical nanostructure.They are of two types Single walled carbo nanotubes(SWCNTs), Multi walled carbon nanotubes(MWCNTs).When researchers think of nanomaterial reinforcements for concrete, carbon nanotubes come as the first option. Also the research done so far has shown that single and multi-walled nanotubes can produce materials with toughness unmatched in the man-made and natural worlds.
4. Carbon Nanofibres(CNFs)-They are highly graphitic carbon nanomaterials with excellent mechanical properties, electrical conductivity and thermal conductivity. The individual nanofiber has a hollow core that is surrounded by the cylindrical core.
5. Nano-Aluminium Oxide. (Nano-Al_2O_3)-Nanoaluminium oxide is not as widely used as the other nanomaterials. It is 100% crystalline, non-porous, produced in various sizes ranging from 20nm to 800nm. It reacts with calcium hydroxide to improve strength.
6. Nano-Titanium Oxide. (Nano-TiO_2)- Nanotitanium dioxide has proven very effective for the self-cleaning of concrete by the photocatalytic degradation of the pollutants. The concrete containing the nanoparticles have excellent flexural fatigue performance compared with plain concrete in particular at high stress level.
7. Nanoclay**-** Nanoclay has been used in the cement mortar to make it a real "smart" material.The nanoclays are nanoparticles of layered mineral silicates. Nanoclays are organized into several parts which depend upon its chemical composition and nano-particle morphology, such as montmorillonite, cloisite, bentonite, kaolinite, hectorite, and halloysite.

The nano-materials used in this thesis work are Carbon Nano Fibres (CNF) and Nano Clay (NC) (Cloisite30B) and are discussd below in detail.

1.3.1 NANO CLAY

The extraordinary chemical and physical properties of materials at the nanometer scale enable applications ranging from structural strength enhancement to self-cleaning properties. Consequently, various nanoclay has been used in the cement mortar to make it a real "smart" material.The nanoclays are nanoparticles of layered mineral silicates. Nanoclays are organized into several parts which depend upon its chemical composition and nano-particle morphology, such as montmorillonite, cloisite, bentonite, kaolinite, hectorite, and halloysite.

1.3.1.1 Montmorillonite

Nano-montmorillonite (NM) belongs to general mineral group of clays. The particle shape of montmorillonite is sheet like structure, whose dimensions in two directions far exceed its thickness.It consist of a three layered structure of aluminium which is sandwiched between two layer of silicon. Montmorillonite is the major ingredient of the volcanic ash called bentonite. It has an ability to swell to many times its original weight and volume when it absorbs water

1.3.1.2 Kaolinite

Kaolinite is a clay mineral and also a part of the group of industrial minerals. The chemical composition of Kaolinite is $AL_2Si_2O_5(OH)_4$. It is having a layer of silicate. In Kaolinite one part of the tetrahedral structure connected to the oxygen atoms to one octahedralsheet of alumina octahedral. The rocks that are rich in kaolinite are also known as kaolin or china clay. Kaolinite is a soft, earthy, usually off-white mineral which is produced by the chemical weathering of aluminium silicate minerals like feldspar

1.3.1.3 Halloysite nanoclay

Halloysite nanoclay is one the subcategory of the nanoclay. It is a two-layered aluminosilicate with a hollow nano-tubular structure which is composed of hydrated aluminum oxide and silicon oxide that can be used as a component in coatings and nano-composites. Halloysite nanoclay is usually immediately available in most volumes, including bulk orders. The nanoscale elemental powders and suspensions, as alternative high surface area forms, may be considered.

1.3.1.4 Cloisite

Cloisite is an organically modified montmorillonite with ammonium salt. The chemical formula of montmorillonite is $(Na,Ca)_{0.33}$ $(Al,Mg)_2$ Si_4O_{10} $(OH)_2$ nH_20 having a molecular weight of 540.46. The chemical structure of organic modifier which dimethyl dehydrogenated tallow and the chemical structure is explained as

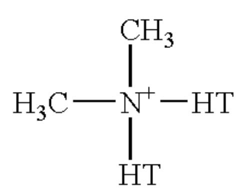


Fig 1.3 Basic structure of Nano Clay (www.google.com)

Cloisite is of different types such as Cloisite 10A, Cloisite 20A, Cloisite 30B, Cloisite Na+

Table 1.1 Physical and chemical properties of different types of Cloisite Nanoclay (www.google.com)

S.No	Density g/cc	Moisture Content	Average Size	Basal Spacing, d_{001}	Colour	Modifier concentration
Cloisite 10A	1.9	<2%	6µm	19.2 Å	Off-white	125meq[a]/100g clay
Cloisite20A	1.77	<2%	6µm	19.2Å	Off-white	95meq[a]/100g clay
Cloisite 30B	1.98	<2%	6µm	18.5 Å	Off-white	90 meq[a]/100g clay
Cloisite Na+	2.86	<2%	6µm	11.7Å	Off-white	92.6meq[a]/100g clay

The type of nanoclay used in the present investigation is Cloisite 30B. The choice of the type of the nanoclay was done on the basis of past published research. A very little focus has been on this type of nanoclay.

1.3.1.5 Advantages of Nano Clay

Cement mortar is the most commonly used construction material on planet. It presents a higher permeability that allows water and other aggressive elements to enter which leads to carbonation and chloride ion attack, resulting in corrosion problems. Use of nanoclay in this field proves to be a great enrichment to the cement mortar to improve its properties. Following are some of the advantages of the using nanotechnology in cement mortar:

- Nanoclay helps to make mortar a multipurpose smart functional material.
- The use of nanoclay is used to increase the strength and durability of cementitious composites as well as for pollution reduction.
- Production of thermal insulation materials with a performance ten times commercial current options.
- Production of cheap corrosion free steel.
- Production of nanosensors and materials with sensing ability and self- repairing ability.

Till date nano clay applications and advances in the construction and building materials fields have been uneven. Exploitation of nanoclay in cement mortar on a commercial scale remains limited with few results successfully converted into marketable products.

1.3.2 CARBON NANOFIBERS

Carbon nano fiber are discontinues highly graphic, highly compatible with most polymer processing techniques and can be dispersed in an isotropic mode.They have excellent mechanical properties, high electrical conducting and high thermal conductivity which can be imported to a wide range of matrices including thermoplastics, thermostat, elastomer , ceramic and metals. Carbon nanofibers also have a unique surface state which facilitates functionalizing and other surface modification technique to tailor the nano fiber to the host polymer or application.

1.3.2.1 Application of Carbon Nano Fibres

- Carbon Nano Fibres helps to make mortar a multipurpose smart functional material.
- The use of Carbon Nano Fibres is used to increase the strength and durability of cementitious composites.
- To increase the compressive strength of concretes by filling the pores between large fly ash and cement particles.
- Carbon Nano Fibres helps in improving the durability properties by improving the pore structure.

1.4 RESEARCH SIGNIFICANCE

Cement based materials are complex materials consisting of several phase. In order to effectively reinforce and improve the response of cementations material to loading crack growth should be reduced at the macro, micro and nano level. This study investigates the reinforcing efficiency of Carbon nano fibers and Nano clay on compressive and durability of cement mortar by partially replacing them with cement according to the assigned percentages.

1.5 OBJECTIVE AND SCOPE OF PRESENT STUDY

- To investigates the optimized level of reinforcing cement mortar with nano material in small varying proportions. Two types of nano material have been used i.e Carbon Nano Fibres and Nano Clay.
- To investigate the effect of carbon nano fiber replacement level on compressive strength of mortar by conducting compressive strength and flexural test.
- To investigate the effect of carbon nano fiber replacement level on durability by conducting water absorption test and acid resistance test.
- To investigate the effect of carbon nano fiber replacement level against sulphuric acid and nitric acid attack.
- To investigate the effect of Nano Clay replacement level on compressive strength of mortar by conducting compressive strength and flexural test.
- To study the micro structure of carbon nano fibres and nano clay using SEM analysis as well as XRD analysis at different compositions.

1.6 ORGANIZATION OF THE THESIS

The thesis comprises of 5 chapters. Each chapter has its own significance in the thesis.

Chapter I: Represent the general introduction of the study background along with objective, scope, and limitation of the study.

Chapter II: Covers a brief literature review variety of strength and durability development of cement mortar containing carbon nano fiber,carbon nano tubes,nano clay etc. at early age and the adverse affects of addition of carbon fibers have been reviewed as well. Papers related to Acid resistance of cement mortar have also been reviewed in this chapter.

Chapter III: The detail of the experiment program materials used and its sources, proportioning of ingredients, specimen preparation and testing procedures are presented.

Chapter IV: Presents experiment results, analysis and relevant discussion.

Chapter V: Summarizes test results and conclusion drawn based on findings of work, limitations and recommendation for further research are also presented.

CHAPTER – 2

LITERATURE REVIEW

2.1 GENERAL

In this chapter the research work concerning to various application and method used for investigation of use of Carbon nano fibers and Nano clay in cement mortar has been studied. This chapter gives a comprehensive review of the work carried out by various researchers in the field of strength and durability development of cement mortar containing nano composite as carbon nanofibers, carbon nanotubes etc. at early age and the adverse effect of over addition of carbon fibers have been reviewed as well. Limited information available in literature on effect of carbon nano fiber and nano clay on strength development of cement mortar including durability & concrete have also been reviewed.

2.2 REVIEW OF LATEST WORK IN THE FIELD

2.2.1 Mechanical Properties

Chang et al. (2007) Studied the material properties of Portland cement paste with the addition of montmorillonite nanoclay. In this case montmorillonite nanoclay have been added at four different proportions i.e. 2%, 4%, 6% and 8% as shown in Fig 2.1. And from Fig.2.1 it is clear that compressive strength of cement paste composite with the addition of montmorillonite nanoclay at different proportions was checked at four ages i.e. 7days, 14 days, 28 days and 56 days. It is clear from the Fig. 2.1 that the optimum value of the compressive strength was obtained at the addition of 0.6% of montmorillonite nanoclay. It is observed from the figure that the maximum percentage of strength increase is about 13.24% which occurs at the age of 56 days.

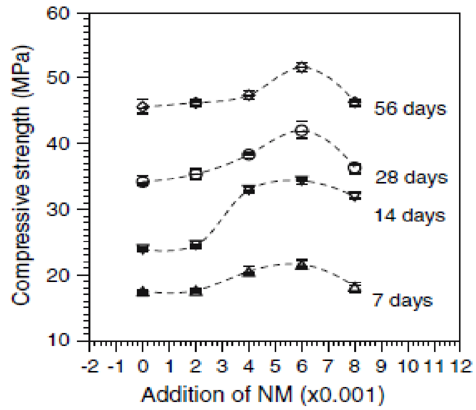


Fig 2.1: Compressive strength of cement paste at various additions of NM and ages **(Chang et al., 2007)**

In this case there is small increase in the compressive strength which indicates that some additional strong bonds may be formed due to the addition of montmorilonite nanoclay from which latter effect can be expected.

Morsy et al. (2008) presented the hybrid effect of carbon nanotube and nanoclay on physico-mechanical properties of cement mortar. In this case CNT is added at different proportions i.e. 0.005%, 0.02%, 0.05% and 0.1% and the proportion of nano-metakaolin in each case remain same i.e. 6%.

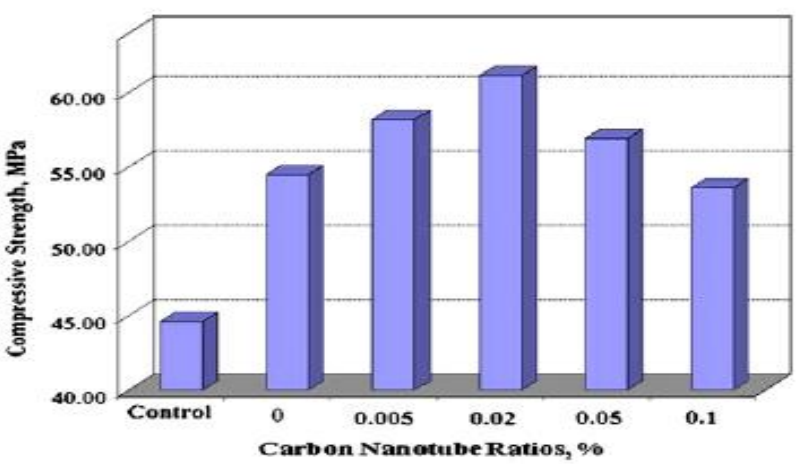


Fig. 2.2: Compressive strength of blended cement mortar containing exfoliated 6%NMK versus CNT's ratio'sat 28 days of hydration **(Morsy et al., 2008)**

From Fig.2.2 it is clear that compressive strength of cement paste composite with the addition of CNT at different proportions and nano-metakaolin at same proportions was checked at 28 days. It is clear from the figure that optimum value of strength obtained at the addition of 0.02% CNT and 6% nano-metakaolin with the replacement of 6% of Ordinary Portland cement.

It is observed from the figure that there is 18% increase in the compressive strength with addition of 0.02% CNT and 6% nano-metakaolin as compared to mortar mix. The nano-metakaolin belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nano-metakaolin acts as a filler and fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of nano-metakaolin with free lime which adds the bonding strength and solid volume which results into higher compressive strength

Konsta and Shah (2009) stated that due to their exceptional mechanical properties, carbon nanotubes (CNTs) are considered to be one of the most promising reinforcing materials for the next generation of high-performance nanocomposites. In this study, the reinforcing effect of highly dispersed multiwall carbon nanotubes (MWCNTs) in cement paste matrix has been investigated. The MWCNTs were effectively dispersed in the mixing water by using a simple, one step method utilizing ultrasonic energy and a commercially available surfactant.Advanced technological aspects of cement based materials have recently focused on developing high-performance cementitious composites, which exhibit high compressive strengths. Carbon nanotubes (CNTs) present several distinct advantages as a reinforcing material for high strength/performance cementitious composites as compared to more traditional fibers. First, they exhibit significant greater strength and stiffness than conventional fibers, which should improve overall mechanical behavior. Second, their higher aspect ratio is expected to effectively arrest the nanocracks and demand significantly higher energy for crack propagation. Thirdly, provided that CNTs are uniformly dispersed, and due to their nanoscale diameter, fiber spacing is reduced. Few attempts have been made to add CNTs as reinforcement in cementitious matrices. Makar et al. investigated the reinforcing effect of 2.0 wt.% CNTs in cement using SEM and Vickers hardness measurements. The results obtained indicated that CNTs may affect the early hydration progress, producing higher hydration rates. Li et al. employed a carboxylation procedure to improve the bonding between 0.5 wt.% MWCNTs and cement matrix and obtained a 25% increase in flexural strength and a 19% increase in compressive strength.

Table – 2.1 Properties of multiwall carbon nanotubes (MWCNTs) (Konsta and Shah,2009)

	Aspect ratio	**Diameter (nm)**	**Length (μm)**	**Purity (%)**	**Surface area (m^2/g)**
Short	700	20-40	10-30	>95	110
Long	1600	20-40	10-100	>97	250-300

The fracture mechanics test results of the average flexural strength of cement paste samples reinforced with short MWCNTs at amounts of 0.048 wt.%, 0.08 wt.% and 0.10 wt.% by weight of cement at the age of 3, 7 and 28 days are presented in Fig. 2.3. In all cases, the samples reinforced with MWCNTs exhibit higher flexural strength than plain cement paste. Samples reinforced with 0.08 wt.% short MWCNTs outperformed all other mixes, exhibiting the largest increase in flexural strength. Generally, the reinforcing effect of the MWCNTs mainly depends on their dispersion within the matrix, which leads to the reduction of the fiber spacing in the nanocomposite. It is observed that samples containing 0.10 wt.% MWCNTs exhibit consistently lower strength than the 0.08 wt.% mixes at all ages. It is possible that effective dispersion of short MWCNTs at a concentration higher than 0.08 wt.% cannot be achieved.

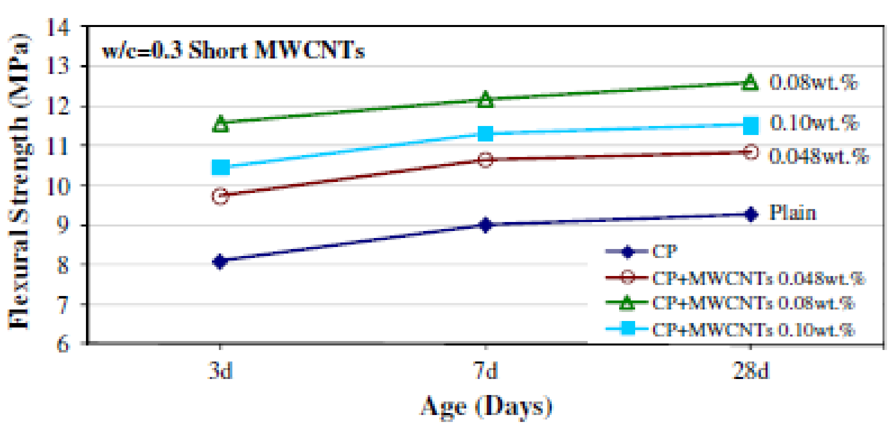


Figure 2.3: Effect of short MWCNTs concentration on the flexural strength of cement paste and w/c = 0.3 **(Konsta and Shah, 2009)**

Figure 2.4 shows the flexural strength results of specimens reinforced with 0.025 wt.%, 0.048 wt.% and 0.08 wt.% long MWCNTs. Similar to the specimens with short MWCNTs, it was observed that in all cases, the samples reinforced with long MWCNTs show improved mechanical performance compared to the plain cement paste. However, contrary to the results obtained with the short MWCNTs, it is observed that samples reinforced with smaller amount of MWCNTs demonstrate higher flexural strength. These results are in good agreement with previous findings.

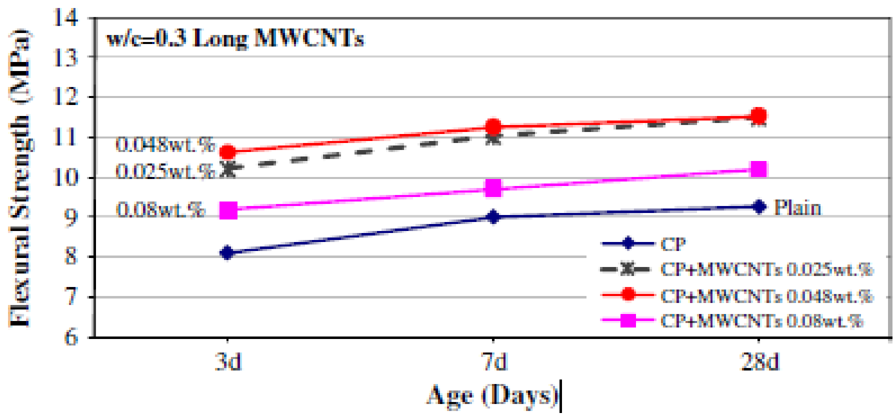


Figure 2.4: Effect of long MWCNTs concentration on the flexural strength of cement paste and w/c = 0.3 **(Konsta and Shah, 2009)**

The flexural strength of the specimens reinforced with MWCNTs shows an increase of 30–40% over plain cement specimens. This increase in the flexural strength seems to be the highest published so far with the lowest concentration of MWCNTs. Until now, the addition of the MWCNTs in cementitious matrices has resulted in either a decrease or smaller increase, up to 25%, of the flexural strength.

Therefore, the development of high-performance cementitious nanocomposites reinforced with multiwall carbon nanotubes was studied. It was found that small amounts of effectively dispersed MWCNTs (0.025–0.08 wt.% of cement) can significantly increase the strength and the stiffness of the cementitious matrix. In particular, lower amounts of long MWCNTs (0.025–0.048 wt.%) provide effective reinforcement, while higher amounts (close to 0.08 wt.%) of short MWCNTs are required to achieve the same level of reinforcement. It was also found that effectively dispersed MWCNTs provide a unique role in cement based materials.

Kawashima et al. (2011) stated is a summary paper on the work being done at the Center for Advanced Cement-Based Materials at Northwestern University on the modification of cement-based materials with nanoparticles, specifically nanoclays, calcium carbonate nanoparticles, and nanosilica. The rheological properties of clay-modified cement-based materials are investigated to understand the influence of nanoclays on thixotropy. The influence of the method of dispersion of calcium carbonate nanoparticles on rate of hydration, setting, and compressive strength are evaluated. And an in-depth study on the mechanisms underlying the influence of nanosilica on the compressive strength gain of fly ash–cement systems is discussed. The motivation behind these studies is that with proper processing techniques and fundamental understanding of the mechanisms underlying the effect of the nanoparticles, they can be used to enhance the fresh-state and hardened properties of cement-based materials for various applications.Calcium carbonate nanoparticles and nanosilica can offset the negative effects of fly ash on early-age properties to facilitate the development of a more environmentally friendly, high-volume fly ash concrete.Nanomodification is the manipulation of the structure at the nanoscale (less than 100 nm) to develop cement composites that exhibit enhanced or novel properties and functions.Carbon nanotubes (CNTs) dispersed by ultrasonication can significantly improve the flexural strength of cement composites by controlling cracks at the nanoscale

The compressive strength gain (1, 3, and 7 d) of 50 mm cube samples were compared for an OPC paste and 30% fly ash–cement pastes with and without a 5% nano$CaCO_3$ addition. All pastes had a w/c = 0.43. The results are shown in Fig. 2.1 At 3 and 7 d, the sonicated sample showed a greater improvement than the blended sample. However, neither reached the strength of the OPC sample. Work on modifying the sonication protocol to improve the stability of nano $CaCO_3$ suspensions is ongoing.

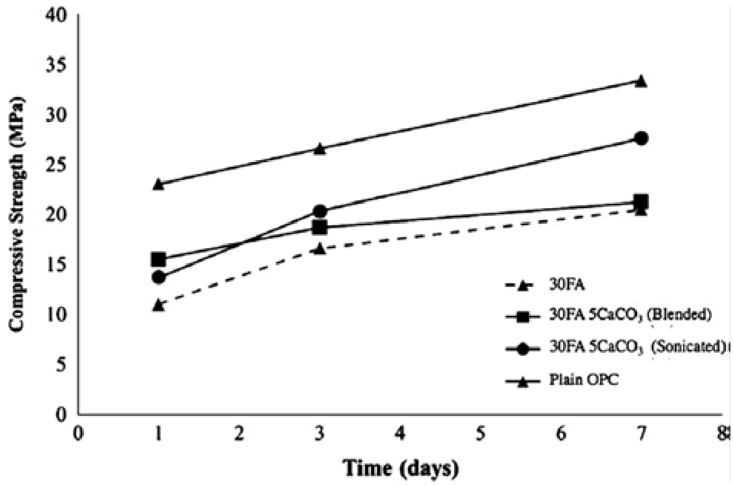


Figure 2.5: Compressive strength gain of 30% fly ash OPC pastes with and without a 5% nano$CaCO_3$ addition, prepared by blending or sonication, compared to plain OPC paste. **(Kawashima et al. 2011)**

The effect of CNS dosage on the slump flow of fly ash–cement mortars is shown in Fig. 2.6. Mortars were prepared with a sand-to-binder ratio of 3 and a w/b = 0.5. River sand with a modulus of 2.8 was used. As expected, fluidity increased with fly ash replacement and decreased with CNS. The greater the amount of CNS, the greater the reduction in fluidity. It is also shown that the fluidity of CNS added fly ash mortars with 40% and 60% of fly ash replacement are higher than that of 20% fly ash replaced mortar. This demonstrates that fly ash can help to increase the workability of CNS-added cement-based materials

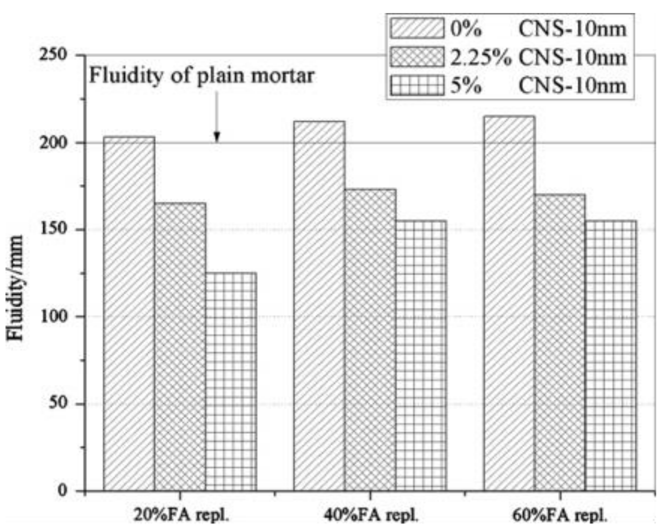


Figure 2.6: Influence of CNS on the slump flow of fly ash–cement mortar w/b = 0.5,cement to sand ratio = 1:3 **(Kawashima and Shah, 2011)**

The compressive strength evolution of CNS-added cement–fly ash mortars is shown in Fig. 2.7 For the 40% fly ash–cement mortar, the addition of CNS significantly increased the strength gain early on – after 7 days, the compressive strength of 5% CNS added fly ash mortar was improved by more than 60%. However, the enhancing effect gradually decreased over time and after 3 months the compressive strength of CNS-added mortar was equal to (CNS-20 nm mortar) or less than (CNS-10 nm mortar) the control fly ash–cement mortar. This implies that nanoSiO_2 has no positive effect on the strength gain of fly ash replaced cement-based material at later ages. To determine why, the hydration and morphology of CNS-modified fly ash–cement systems were closely examined.

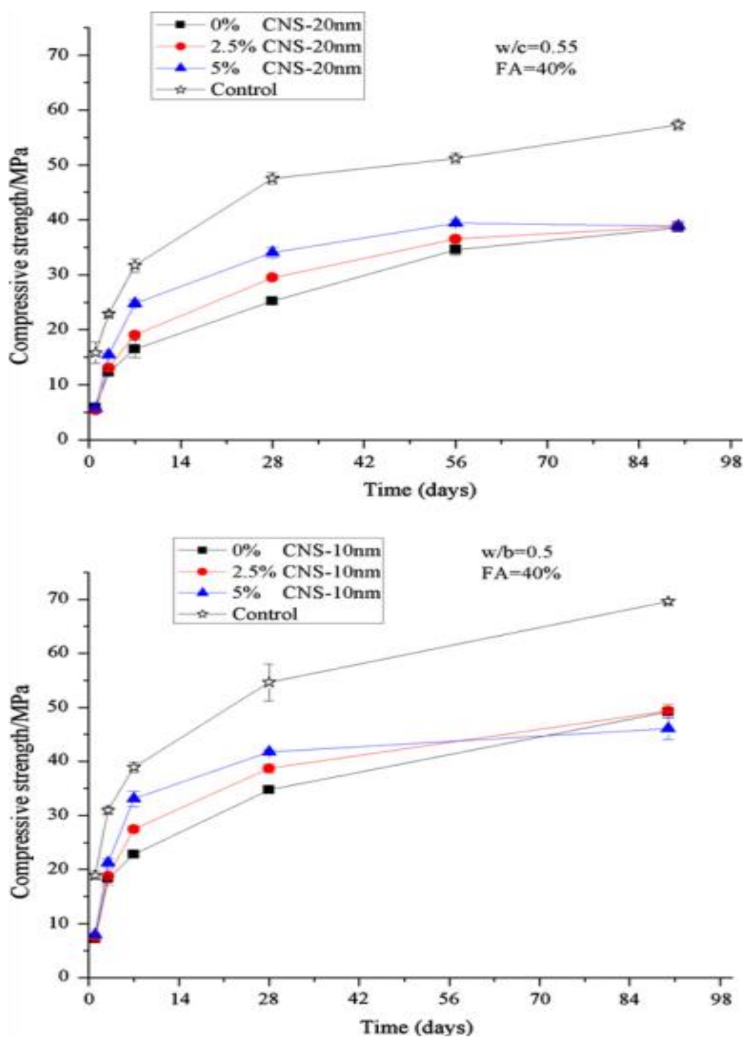


Figure 2.7: Effect of CNS on the compressive strength of fly ash mortar **(Kawashima and Shah, 2011)**

Tyson et al (2011) presented on carbon nanotubes (CNTs) and carbon nanofibers (CNFs) are quickly becoming two of the most promising nanomaterials because of their unique mechanical properties. The size and aspect ratio of CNFs and CNTs mean that they can be distributed on a much finer scale than commonly used microreinforcing fibers. As a result, microcracks are interrupted much more quickly during propagation in a nanoreinforced matrix, producing much lower crack widths at the point of first contact between the moving crack front and the reinforcement. In this study, untreated CNTs and CNFs are added to cement matrix composites in concentrations of 0.1 and 0.2% by weight of cement. The nanofilaments are dispersed by using an ultrasonic mixer and then cast into molds. Each specimen is tested in a custom-made three-point flexural test fixture to record its mechanical properties; namely, the Young's modulus, flexural strength, ultimate strain capacity, and fracture toughness, at 7, 14, and 28 days.

Five batches of cement paste were produced. These included a reference sample of plain cement paste, two batches of cement paste with CNTs at 0.1 wt% and 0.2 wt% by weight of dry cement, and two batches with CNFs at 0.1 wt% and 0.2 wt%. Table 2.2 summarizes the composition of the five batches. These batches were labeled to indicate the components and their concentrations. The letter "F" represents CNFs, "T" represents CNTs, and "1" and "2" indicate filament dosages of 0.1 wt% and 0.2 wt%, respectively. All five batches had a water to cement ratio of 0.40, and the batches containing CNTs or CNFs had a surfactant (i.e superplasticizer) to cement ratio of 0.005.

Table – 2.2 Mix design of the test specimens (Tyson et al., 2011)

Test specimens	**Water/cement ratio**	**CNFs:% weight of cement**	**CNTs:% weight of cement**
Reference	0.4	0	0
F1	0.4	0.1	0
F2	0.4	0.2	0
T1	0.4	0	0.1
T2	0.4	0	0.2

Fig. 2.8 shows the displacement at failure (i.e., peak displacement) for each batch at 7, 14, and 28 days. In Figs. 2.8, the bar represents the mean value, and the top and bottom error bars represent the third and first quartile, respectively. The addition of both CNTs and CNFs improves the peak displacement of cement paste. The greatest increase in peak displacement occurs with the addition of CNFs. A maximum increase of 150% was observed when using a concentration of 0.2 wt% CNFs. For the displacement at failure, both concentrations of CNFs outperformed CNTs. This is most likely attributed to the higher aspect ratios of the CNFs (i.e., approximately 1,000 for CNFs; 150 for CNTs), which makes CNFs more effective as reinforcements because of their larger interaction with the cement matrix. Another reason for the CNFs to outperform the CNTs is the enhanced dispersion achieved when using the CNFs. The average peak stress (i.e., average flexural strength) results are shown in Fig. 2.8. The largest increase of 82% is found at 7 days for CNFs. In many cases, the addition of CNTs shows a decrease in strength. The Young's modulus shows the same general trend as the strength. As shown in Fig. 2.8, the average modulus is less than the reference sample at both 7 and 14 days.

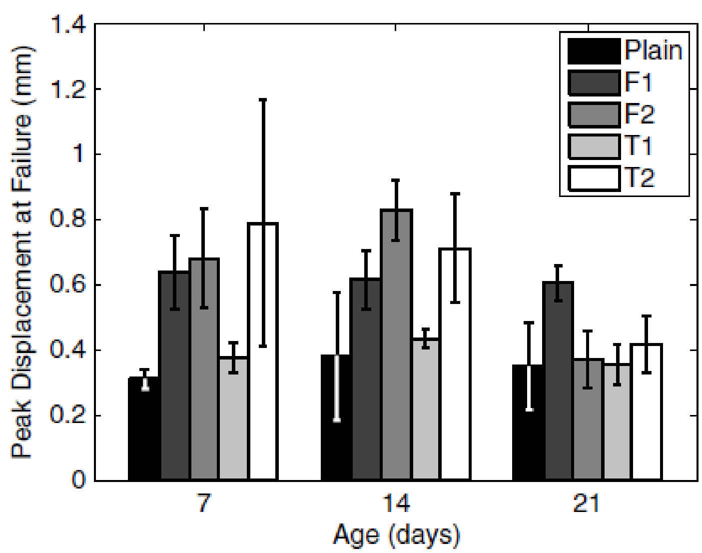


Figure 2.8: Effect of the CNFs and MWCNTs on the strain capacity of cement paste **(Tyson et al., 2011)**

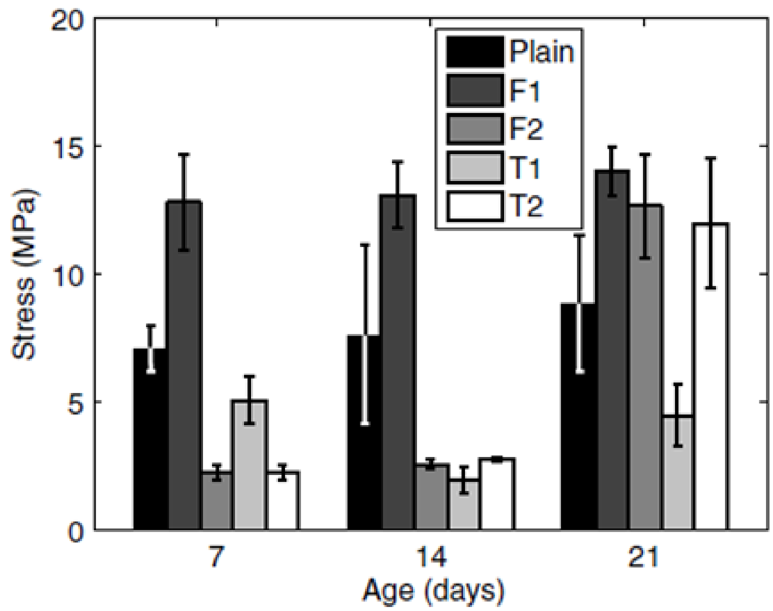


Figure 2.9: Effect of the CNFs and MWCNTs on the ultimate strength of cement paste **(Tyson et al., 2011)**

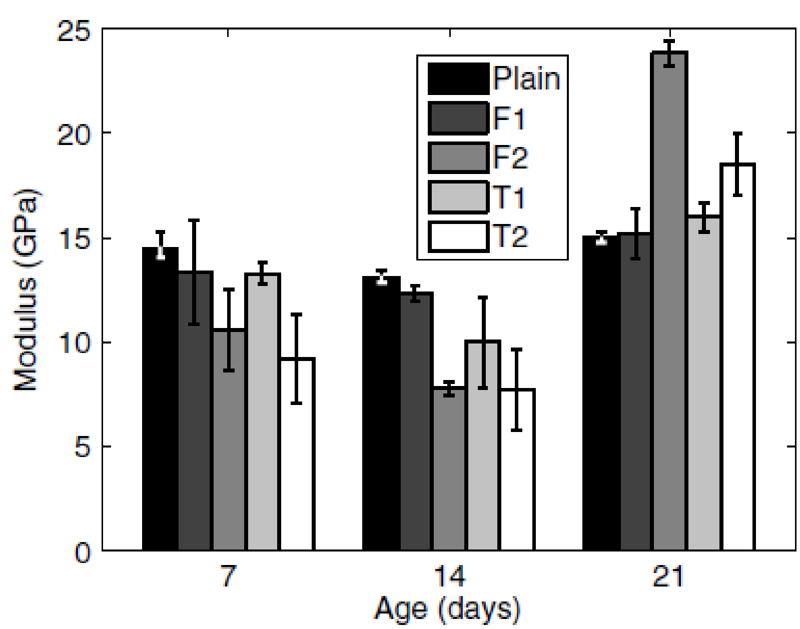


Figure 2.10: Effect of the CNFs and MWCNTs on the elastic modulus of cement paste **(Tyson et al., 2011)**

Metaxa et al . (2011) studied that have aimed at improving the low tensile strength, stiffness, and toughness of cementitious materials. This study also aims to show that all of these characteristics can be greatly improved by the addition of ladder scale reinforcement at the nano and micro scale. Carbon nanofibers (CNFs) as well as polyvinyl alcohol (PVA) microfibers were used as reinforcement. The mechanical properties of the nanocomposites were investigated by fracture mechanics three-point bending test. The microstructure and the morphology of nanocomposite samples were studied using an ultra high resolution scanning electron microscope (SEM). The results clearly illustrate that the incorporation of nanofibers and microfibers greatly improves the flexural strength, Young's modulus, and toughness of the cement matrix. In the work presented here, the characteristics of cement paste containing ladder scale reinforcement using carbon nanofibers (CNFs) and PVA microfibers were investigated. Scanning electron microscopy (SEM) was employed to investigate the nanostructure of the nanocomposites.

Table 2.3 presents the results of all mixtures tested at the age of 3, 7, and 28 days. Comparing the results of plain OPC with nanocomposites reinforced with CNFs, it is observed, that at all ages an increase in flexural strength, Young's modulus and toughness up to 40%, 75% and 35%, respectively, is achieved with the incorporation of CNFs. Typical load-CMOD curves of the 28 days response of plain cement paste and cement paste with CNFs are presented in Fig. 2.12. It is impressive that a concentration as low as 0.048wt% of cement CNFs can impose such a high increase in the Young's modulus. During the early stages of loading, nanofibers provide the material with the ability to carry higher load at the same CMOD. To better understand the effect of CNFs on the nanostructure of cement paste, SEM was employed. Figure 2.12 shows SEM images of the fracture surface of the nanocomposites at a scale of 500 nm (0.02 × 10–3 in). Initially, it is observed that mostly individual CNFs can be identified on the fracture surface. This indicates that good dispersion was achieved. It can also be seen that CNFs appear to be embedded into the hydration products, showing that good bonding between the nanofibers and the matrix was also achieved. Good bonding enables the load transfer between the matrix and the nanofibers which results to the improvement of the overall strength of the nanocomposite. A good illustration of CNFs acting as bridges between nanocracks and pores is also shown.

Table 2.3 Flexural Strength, Young's Modulus and Toughness of Cement Paste at 3, 7, and 28 days of Hydration (Metaxa and Shah, 2011)

	3 days			7 days			28days		
Mixture	MOR, MPa (ksi)	E, GPA (ksi)	T, Nxmm (Ib x in x10^2)	MOR, MPa (ksi)	E, GPA (ksi)	T, N x mm (Ibx in x10^2)	MOR, MPa (ksi)	E, GPA (ksi)	T, Nxmm (Ibx in x10^2)
Plain OPC (CP)	3.9 -566	5.6 -812	1.8 -1.6	4.9 -711	7.4 -1073	2.1 -1.9	5.5 -798	8.8 -1276	2.3 -2
CP + CNFs	5.6 -812	9.9 -1436	2.5 -2.2	6.5 -943	11.9 -1726	2.7 -2.4	7.2 -1044	13.2 -1914	2.8 -2.5
CP + micro PVA	4.1 -595	6.5 -943	61.5 -54.4	5.4 -783	8.1 -1175	66.2 -58.6	5.8 -841	8.9 -1291	68.2 -60.4
CP + CNFs +micro PVA	5.8 -841	10.4 -1508	61.8 -54.7	6.6 -957	12.7 -1842	67.7 -59.9	7.3 -1059	14.6 -2118	72.7 -64.3

Note: MOR = flexural strength; E = Young's modulus; and T = toughness.

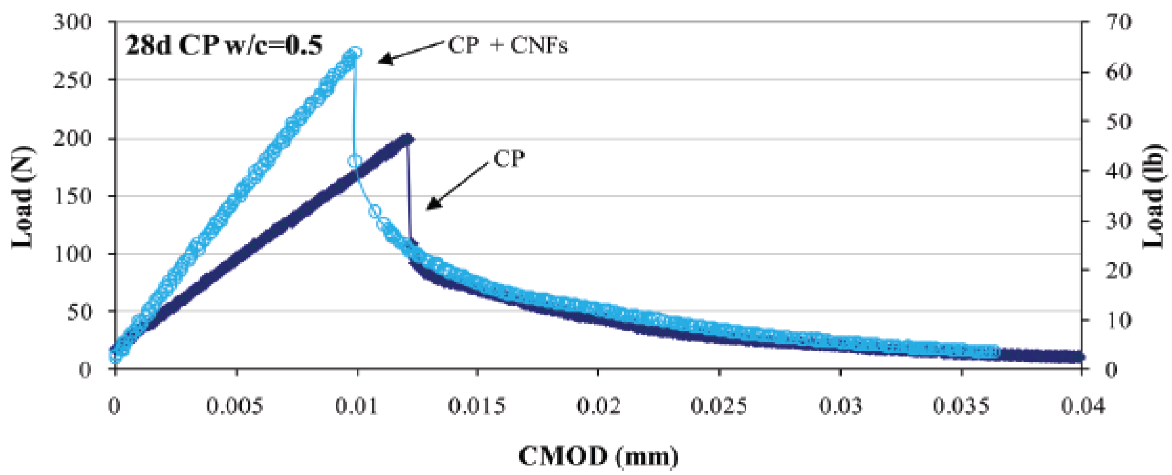


Figure 2.11: Typical load-CMOD curves of 28 days plain cement paste and cement paste reinforced with CNFs. **(Metaxa and Shah, 2011)**

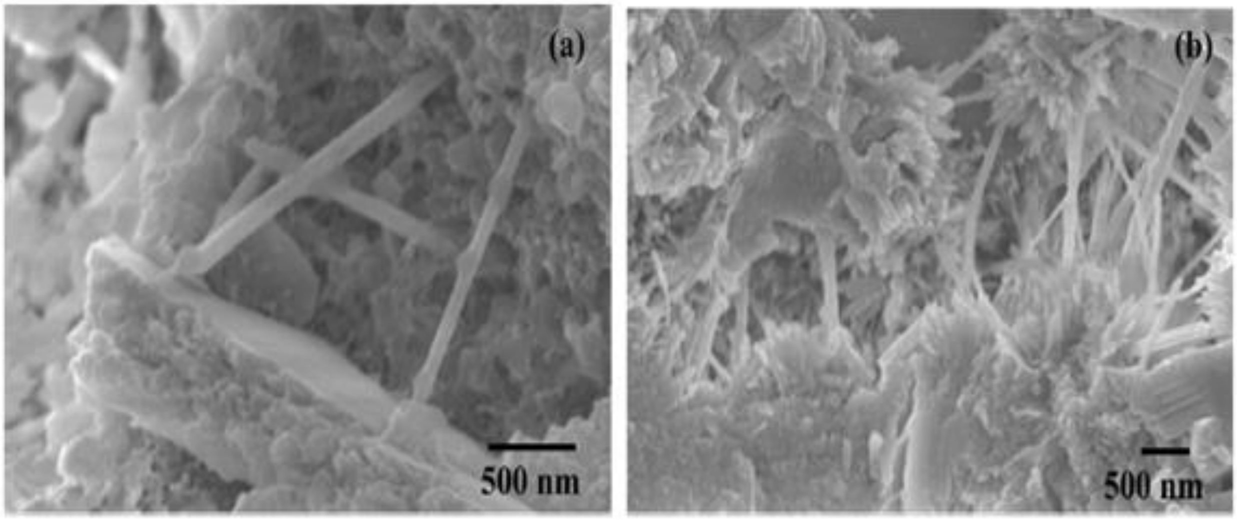


Figure 2.12: SEM images of fracture surface of cement nanocomposites reinforced with NCFs **(Metaxa and Shah, 2011)**

Mo et.al. (2013) stated that Fiber research in concrete construction is an ongoing field and the use of carbon nanofibers (CNF) is examined. Fibers improve brittle materials such as concrete by enhancing tensile strength, ductility, toughness, and conductivity. Short-fiber composites are a class of strain sensor based on the concept of short electrically conducting fiber pull-out that accompanies slight and reversible crack opening. Despite the fact that nanotechnology is a relatively recent development in scientific research, the introduction of the concept is credited to Nobel Prize winner Richard Feynman from his 1959 lecture, “There’s Plenty of Room at the Bottom”.Feynman considered the possibility of direct manipulation of individual atoms as a powerful form of synthetic chemistry. Decades later, Feynman’s concept morphed into the field of nanotechnology. Fibers arrest these cracks by forming bridges across them. With increasing tensile stress, a bond failure eventually occurs, and the fiber will pull out of the concrete allowing the crack to widen. Fig. 2.13 shows the bridging action of fibers across micro and macrocracks in concrete.

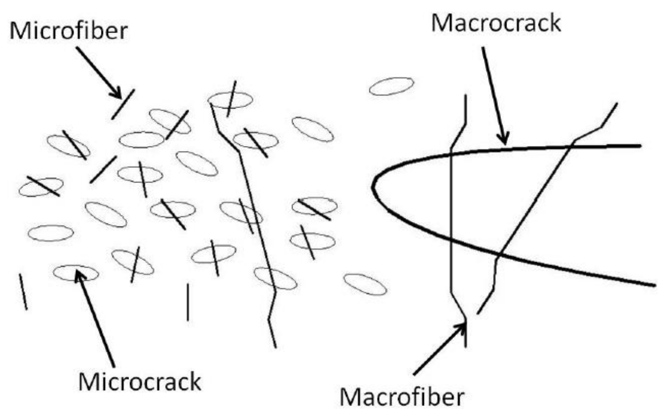


Figure 2.13: Bridging Action of Fibers Across Micro and Macrocracks **(Mo et.al. 2013)**

The majority of nano reinforced composite research has been completed on polymers containing CNT or CNF. One of the main reasons for this is because uniform dispersion is difficult in cement-based materials. Well dispersed CNF results in uniform calcium-silicate-hydrate (CSH) gel formation, which improves the structural and electrical properties of the concrete. CNT and CNF are inherently hydrophobic and are attracted due to Van der Waals forces, causing the fibers to tend to agglomerate hindering their dispersion in solvants.

The CNF mixture is then slowly added to the mixer to gain a homogenous mix. The fresh concrete was used to create cylinders that were tested in compression. After the test, pieces of the cylinders were observed under a scanning electron microscope (SEM). The SEM showed significant CNF clumping in specimens made of normal CNF concrete and uniform distribution in SCC containing CNF, as shown in Figs. 2.14 and 2.15, respectively.

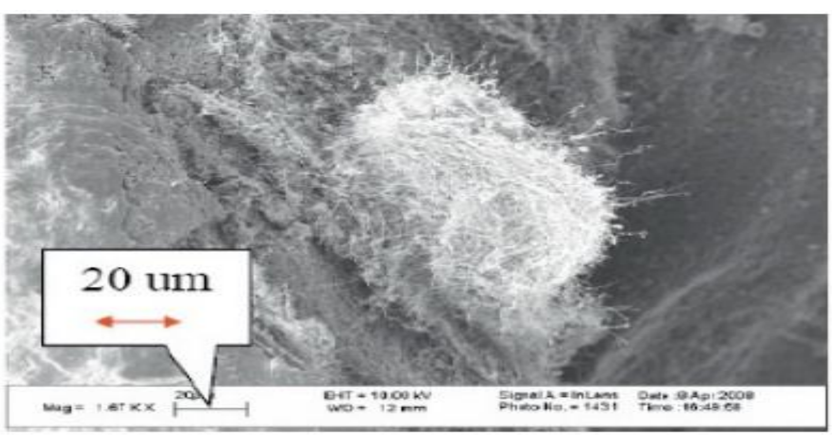


Figure 2.14: Scanning Electron Microscope Image of CNF Clump in Normal Cement (1670x Magnification) **(Mo et.al., 2013)**

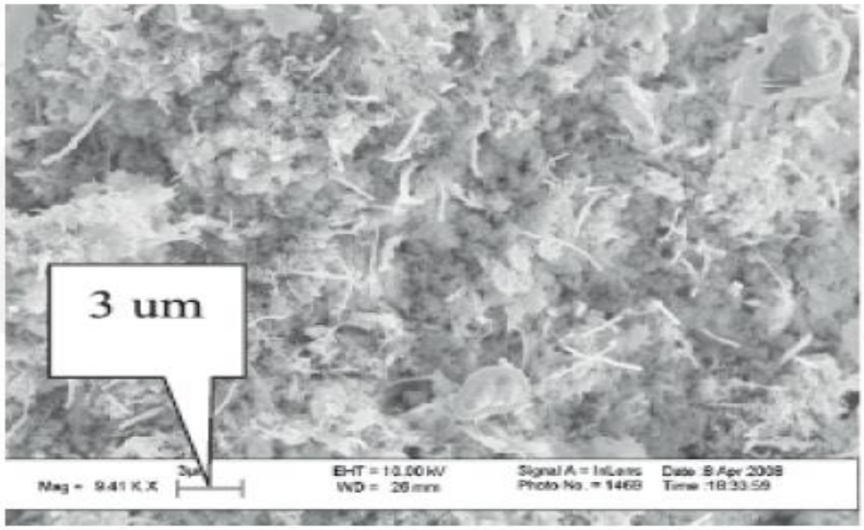


Figure 2.15: Scanning Electron Microscope Image of Well Dispersed CNF in a Uniform Self-Consolidating Cement (9410x Magnification) **(Mo et.al., 2013)**

2.2.2 Durability Properties

Turkel et al. (2007) Studied the Influence of various acids on the physico–mechanical properties of pozzolanic cement mortars. Solutions of hydrochloric, nitric and sulfuric acid with the concentrations of 0·05, 0·075, 0·100, 0·125 mol/L (M) were used in experiments. The pH values of the solutions are presented in table 2.9. The pH values of acid solutions had been reached the neutral value *(*pH ∼= 7±2*)* in 12 days and 14 days initial approximate pH values of 1, for pozzolanic and Portland cement mortars respectively. For this reason, the solutions were renewed at every two weeks. The temperature of the solutions was 20 ± 2◦C during a period of 120 days.

Table2.4. The Ph of the Aggressive Solutions (Turkel et al., 2007)

	Concentrations and pH values of inorganic acids			
Acid type	0·05(M)	0·075(M)	0·100(M)	0·125(M)
Hydrochloric	1·3	1·2	1	0·9
Nitric	1·2	1·1	0·9	0·8
Sulfuric	1·2	1·0	0·9	0·8

The mortar mixes have been prepared with the same river sand for two different types of cement. The cement:sand and water:cement ratios were 1:3 and 1:2 respectively for all specimens. A total of 156 mortar specimens were cast into 50mm cube molds including control mixes. The mortar samples were cured 24 hours at 20 ± 2◦C and relative humidity above 80 %. The specimens were cured in lime-saturated water after demolding. After 28 days of curing, the specimens were dried in an oven at 105^{c}and the initial weights were measured. Then the specimens were stored into solutions of hydrochloric, nitric and sulfuric acids with four different concentrations. For each acid and concentration, six specimens were subjected to each solution. After exposure to acids, the specimens were washed in order to remove the porous layer of the corrosion products such as soft and crystallized acidic materials or calcium salts. Then specimens were dried in an oven at 105◦C. Loss in weight of the specimens was measured weekly during the testing period of 120 days. Compressive strength of the control (non-exposed) specimens after 28 days of their hardening in water and the test specimens subjected to solutions of acids for 120 days were determined. The compressive strength values of specimens were calculated by using the original cross-sectional area of the original cubes.

Average loss of weight of mortars in various acidic solutions within 120 days of testing period is presented in table 2.10. The test results represent the average value of six specimens.

Table2.5 Loss of weight of cement mortars after 120 days in various inorganic acid solutions (Turkel et al. 2007)

		Concentrations (M)							
Acid type	Time (days)	0·05		0·075		0·100		0·125	
		M1	M2	M1	M2	M1	M2	M1	M2
HNO3	30	0·75	0·70	0·60	0·63	0·62	0·89	1·21	1·29
	60	1·70	2·35	2·08	2·67	1·68	2·42	2·59	3·90
	90	2·75	3·40	3·25	3·47	3·20	3·78	4·69	5·24
	120	3·40	4·15	3·98	4·43	4·72	5·48	6·24	7·25
HCl	30	0·68	0·65	1·50	2·23	1·04	1·33	1·67	1·27
	60	1·56	1·88	2·71	3·64	2·34	2·69	2·94	4·54
	90	2·57	3·25	3·52	4·91	4·64	5·20	4·25	6·75
	120	3·28	3·94	4·91	6·23	5·47	6·60	6·45	7·80
H2SO4	30	0·30	0·53	0·32	0·44	0·36	0·40	0·53	0·66
	60	0·89	1·11	0·83	1·22	1·37	1·66	1·12	1·70
	90	1·42	1·89	1·48	2·07	2·18	3·44	2·52	2·93
	120	2·04	2·98	3·16	3·58	3·55	4·83	4·22	4·94

The action of HCl and HNO3 on cement hydration products, in particular $Ca(OH)^2$ and the resulting products are presented in the following chemical equations:

$Ca(OH)^2 + 2HCl \rightarrow CaCl_2 + 2H_2O$ (1)

$Ca(OH)^2 + 2HNO^3 \rightarrow Ca(NO_3)^2 + 2H_2O$ (2)

From equations (1) and (2) it can be seen that, consumption of $Ca(OH)^2$ results with formation of salts of $CaCl^2$ and $Ca(NO_3)^2$. By the help of water, these soluble salts may easily be transported to the outer parts of mortars. In this situation, continuous reactions increase the porosity of cement paste and increased pore volume speed up the rate of reaction.In case of H_2SO_4 attack, the evaluation of deleterious reactions can be divided into two parts (Equations 1 and 2). At the first stage, deterioration of $Ca(OH)^2$ resulted with expansive gypsum formation. The gypsum then reacts with C_3A in aqeuous environment and forms a more expansive product called 'ettringite'. In this study, due to the low C_3A content of cements, mortars were less susceptible to the attack of H_2SO_4.

$Ca(OH)_2 + 2H_2SO_4 \rightarrow CaSO_4 \cdot 2H_2O$ (gypsum)

$3CaSO_4 + 3CaO.Al_2O_3.6H_2O + 25H_2O \rightarrow 3CaO \cdot Al_2O^3 \cdot 3CaSO_4 \cdot 31H_2O$ (ettringite)

The results revealed that there is a meaningful relationship between the loss of weight and loss of compressive strength for the mortar specimens produced by both cements. The coefficients of correlation has been determined as 0·76, 0·82 and 0·87, respectively for three types of acid (hydrochloric, nitric and sulfuric) attacks during 120 days of testing periods as seen in Figure 2.18

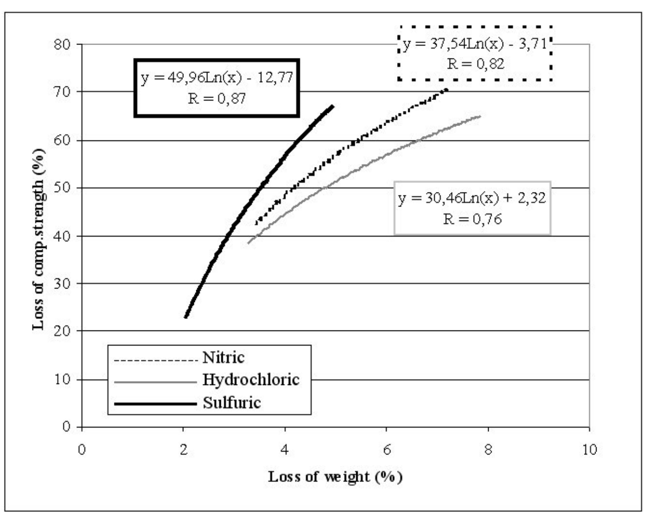


Figure 2.18 Loss in compressive strength of cement mortars made from both cements in relation to loss in weight after 120 days of exposure to solution.(Turkel et al. 2007)

Hewayde et al. (2007) Studied concrete admixtures for sulphuric acid attack. Five admixtures including silica fume, metakaolin, organic corrosion inhibitor (OCI), Caltite and Xypex were used in the experimental programme as listed below.

(a) Five levels of silica fume (6, 8, 10, 12 and 15% by mass of cement) and six levels of metakaolin (2, 4, 6, 8, 10 and 15% by mass of cement) were used as partial replacement for type 50E cement.

(b) Five levels of OCI (3, 4, 5, 6 and 7 litres/m^3 of concrete) were used as an addition.

(c) Four levels of Caltite (20, 25, 30 and 35litres/m3 of concrete) were used as partial replacement for mixing water.

(d) Three levels of Xypex (1, 2 and 3% by mass of cement) were used as partial replacement for Type 50E cement.

(e) Two levels of a binary Xypex–silica fume mixture—2% Xypex C8%silica fume and2%Xypex C 10%silica fume—were used as partial replacement for Type 50E cement. The results of chemical and physical analyses of the five admixtures.

Concrete mixtures

Fourteen 75 mmx150 mm(3 in.x 6 in.) concrete cylinders from each of the 26 concrete mixtures were made and cured as per standard specifications .Nine of the 14 specimens from each mixture were used to determine the compressive strength at 7, 28 and 120 days (three specimens tested at each date). Four specimens from each mixture were used for the sulphuric acid test programme. Small samples were taken from the remaining specimen for each mixture to carry out porosity tests. All specimens were removed from the plastic moulds 1 day after casting and transferred to a curing room.The concrete specimens used for the porosity and sulphuric acid test programme were kept in the curing room for 28 days, whereas those used for the compressive strength tests were cured until testing.

Sulphuric acid baths

Four polyvinyl chloride (PVC) containers with dimensions of 700 mmx700 mmx 400 mm were constructed to carry out sulphuric acid tests (Fig. 2.19). Each pair of containers was connected by a 25 mm (1 in.) diameter PVC pipe and filled with sulphuric acid with a designated concentration. The first two containers contained 7% by volume of sulphuric acid , whereas the remaining two containers contained 3% by volume of sulphuric acid.

Fig2.19 Set-up for sulphric acid exposure tests Hewayde et al.(2007)

- The Figure 2.20 also shows the mass loss of concrete specimens made with OPC (Type10 cement) and exposed to similar conditions, tested as part of an earlier study.At the end of the test period, control specimens made with Type 50E cement experienced mass losses of 28.0 and 19.2% due to immersion in 7% and 3% sulphuric acid solutions, respectively. The corresponding mass losses of the control specimens made with Type 10 cement were 28.4 and 18.3%, respectively. Comparing the trend of mass loss against time for the two mixtures indicates that both concrete types deteriorated at similar rates, exhibiting comparable trends of mass loss against time in both concentrations of sulphuric acid. Thus, partial replacement of OPC with slag did little to enhance the resistance of concrete to attack by aggressive sulphuric acid solutions.

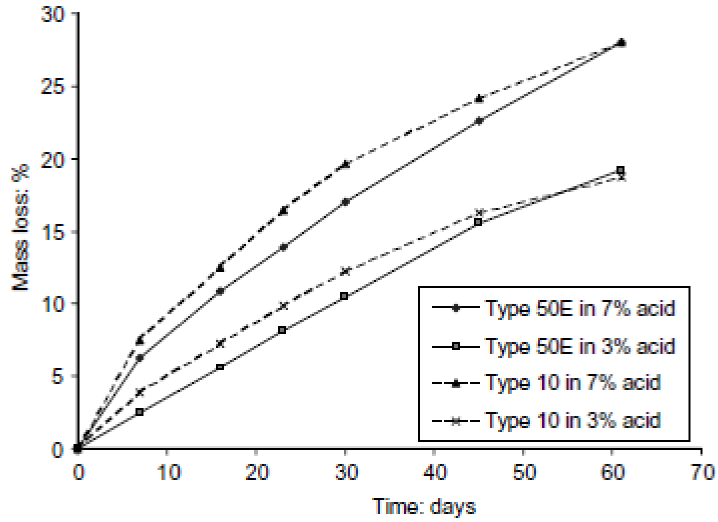


Fig2.20 Mass loss of concrete specimen made with type 10 and type 50 cements due to immersion for 61 days in 7% and 3% sulphuric acid Hewayde et al.(2007)

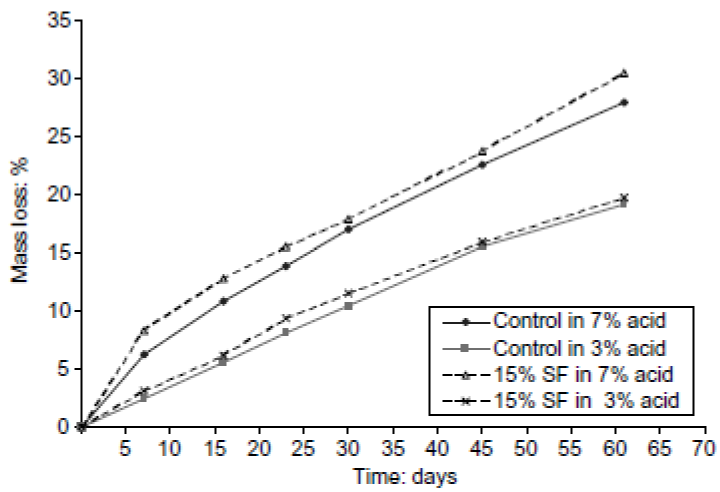


Fig2.21 Mass loss due to immersion in 7% and 3% sulphuric acid solution plotted against time for control and 15% silica-fume modified specimens Hewayde et al.(2007)

- It can be observed that irrespective of the replacement dosage, the presence of silica fume in the concrete mixture had a minor effect on the resistance to the 7% H_2SO_4 solution. For concrete specimens exposed to the 3% H_2SO_4 solution, silica fume dosages less than 10% offered a marginal reduction in the mass loss of concrete specimens. The effect of using 15% silica fume as partial replacement for Type 50E cement on the rate and amount of mass loss during the 61-day test period is shown in Fig. 2.21

- The effect of various dosages of metakaolin on the mass loss of concrete specimens immersed for eight weeks in sulphuric acid solutions. A reduction of 38% and 25% in mass loss of concrete specimens due to immersion in sulphuric acid solutions with concentrations of 7% and 3%, respectively was achieved as a result of incorporating 15% metakaolin. The enhancement in resistance of concrete specimens to sulphuric acid was found to be proportional to the percentage of metakaolin and was more pronounced at the higher concentration of sulphuric acid (7%). the use of 15% metakaolin as partial replacement for Type 50E cement significantly reduced both the rate and amount of mass loss of concrete specimens subjected to sulphuric acid in comparison with that of control specimens.

Bajza and Pavlik (2011) found out that the degree of aggressivity of an acid is dependent on the chemical character of anions present. The strength of the acid, its degree of dissociation in solution and, mainly, the solubility of the salts formed are dependent on the chemical character of the anion Organic acids react with hydrated and anhydrous compounds of the cement paste to give mainly calcium salts. Depending on their solubility, these salts may precipitate or may be dissolved in solution.The concrete is a strongly basic environment with a pH greater than 13. In contact with an acidic solution, the chemical equilibrium of the cement hydrates is destabilized. A variation of pH value means a change in the solubility of the various compounds, which can influence the stability of cement-basedmaterials. In contact with an acetic acidic solution (representing liquid manure composition), the concrete will undergo an acido-basic reaction leading to the formation of soluble to very soluble salts in water. The stability of the different hydrates is variable. Consequently, the porosity of the material and the corrosion of the rebar embedded in degraded concrete will increase, the mechanical strength will drop, and, in the long term, can result in the total collapse of the structure.

Fattuhi and Hughes (2012) used the same test procedure as discussed in above paper but 1% and 3% sulfuric acid solutions. They found that the deterioration of the specimens measured by means of weight loss increased with a corresponding increase in cement content. Depending on the acid concentration, increasing the volume fraction of cement from 10% to 17% caused an increase in weight loss with a factor 2 in a 1% sulfuric acid solution and an increase in weight loss with almost a factor 3 in a 3% sulfuric acid solution.

Bohm (2012) was the first to put forward the movable boundary layer diffusion model which could forecast the speed for sulfuric acid to erode concrete and specified the parameters affecting the speed. This movable boundary layer diffusion model is applied to study sulfuric acid eroded mortar and concrete and to forecast thickness of eroded layer (calcium sulfate), and it has been verified by test.

Yuan et al. (2013) found that concrete with a high water cement ratio has larger and more pores than that with a low water cement ratio. These pores play the role of a capacity to absorb expansion caused by the production of gypsum. Therefore concrete with a high water cement ratio has a higher capacity to absorb the expansion of production reaction of gypsum than that with a low water cement ratio, that is to say, concrete with a low water cement ratio erodes earlier than that with a high water cement ratio.

2.3 CLOSING REMARKS

In this chapter, the experimental details of various tests and the methodology for investigating effect of carbon nano fiber and nano clays on mechanical, chemical composition and micro-structure properties have been discussed , it is very clear from the review of literature that addition of carbon nano fibres and nanoclay in vary proportions, with their high surface, have improved the compressive, flexural and split tensile strength and other properties such as SEM, XRD of the cement mortar. In the following chapter, the experimental study carried out in this research using carbon nano clay and nanoclay as addition to cement mortar have been elaborated in detail.

CHAPTER 3

EXPERIMENTAL PROGRAM & METHODOLOGY

3.1 GENERAL

The experimental program of the research has been designed to investigate the effect of partial replacement of cement with carbon nano fiber and nano clay in varying proportion in cement mortar .The effect on the mechanical, durability and the micro structure property by the addition of two types of nanomatrial has been studied. Cement mortar samples with cement sand ratio as 1:3 have been prepared. CNF has been separately added in liquid form in varying proportion as replacement of cement by weight of 0%, 0.0125%, 0.025%, 0.50%, 0.065%, 0.075% CNF respectively and further another nanomaterial NC has been separately studied by replacing a part of cement 0.5%, 1%, 2% 4% 6% by weight w/c was kept as 0.39 for both the nanomaterial replaced cement mortar.

3.2 MATERIALS USED

3.2.1 Ordinary Portland Cement

Ordinary Portland Cement (43 Grade) have been used conforming to IS:8112-1989 of BIS (Reaffirmed 2005). Cement available in the local market is used in the research and cement used in all tests conducted is from the same batch. Physical properties are given in Table 3.1.

Table – 3.1 Physical properties of ordinary Portland used

Physical Property	Results obtained	IS 8112:1989
Normal Consistency	26%	–
Initial setting times (minutes)	110	Not less than 30
Final setting times (minutes)	235	Not less than 600
Fineness (Percentage)	1.5	10% max.
Specific gravity	3.12	3.15 max.
Compressive strength (N/mm^2)		
3 days (average)	30.4	23 N/mm^2
7 days (average)	35.98	33 N/mm^2
28 days (average)	44	43 N/mm^2

3.2.2 Fine Aggregate

Indian standard sand of three grades obtained from Tamil Nadu Ennore source has been used throughout the research work. The size specification as well as technical details provided by supplier are shown in Table 3.2 compatible with the requirement of IS: 650-1991.

Table – 3.2 Size of Indian Standard Sand Enncore

Sr. No.	Grade	Size specification of Indian standard sand Ennore
1	Grade I	2mm to 1 mm
2	Grade II	1mm to 0.5mm
3	Grade III	0.5mm to 0.09mm

3.2.3 Water

Tap water has been used for both mixing and curing conforming to IS : 456-2000

3.2.4 Carbon Nano Fiber

Carbon nanofibres were procured from M/s Intelligent Material Private Ltd., Panchkula (India) Nanoshel LLC (Wilmington DE) – USA. The samples are highly purity milled fiber with 99% with pure carbon fibers dried from temperature batch graphitization process. Nanoshel carbon nano fibers are hydrophobic and will consequently not disperse well in water. Surfactants such as Triton – X100 have proven to be helpful in dispersing and maintaining the CNFs in a stable suspension. The material properties of carbon nano fiber as furnished by supplier are given in Table 3.3.

Table – 3.3 Material properties of carbon nano fiber (Manufactures Specification)

Sr. No.	Parameters	Nanoshel carbon nano fiber	Nanoshel carbon micro fiber	Remak
1	**Carbon content (%)**	99%	99%	Min. 95%
2	**Specific gravity**	–	1.65	
3	**Bulk density**	24.9 lb/ft^3	–	
4	**Length**	20-30 micro mtr.	90-110 micro mtr.	
5	**Dia**	< 200 nm	< 8 -10 micro mtr.	
6	**Colour**	Black	Black	

3.2.5 Nanoclay (Cloisite 30B)

Cloisite 30B used in this work has been obtained from Connell Bros, Mumbai, Maharashtra. It is white in color as shown in Fig. 3.1. Specifications of Closite 30B provided by supplier are detailed in Table 3.4

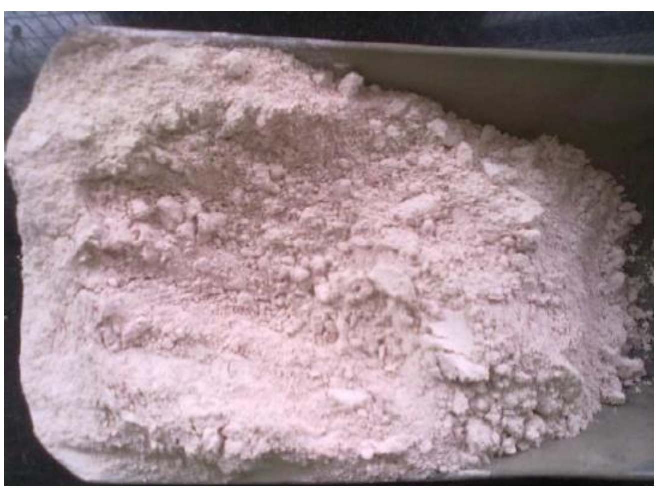


Fig.3.1: Cloisite 30B sample used

Table 3.4: Specifications of Closite 30B (Manufactures Specification)

Properties of Cloisite 30B	
Density	1.98g/cm^3
Moisture content	<2%
Average size	6μm
Basal Spacing, d_{001}	18.5Å
Colour	Off-White
Modifier concentration	90meq^a/100g clay

Cloisite 30B nanoclay has extreme fineness of the nanoclay and very high amorphous silicon dioxide content makes Cloisite 30B nanoclay extremely reactive pozzolanic material. As the Portland cement in mortar begins to react chemically, it releases calcium hydroxide. The Cloisite 30B nanoclay reacts with this calcium hydroxide to form additional binder material called calcium silicate hydrate (CSH), which is very similar to the calcium silicate hydrate formed from Portland cement. It is an additional binder that gives improved properties to the cement mortar.

3.2.6 Acid Resistance

Acid resistance of cement mortar and modified cement mortar with CNF was investigated by checking for chemical attack by sulphuric acid and nitric acid. Sulphuric acid acid used in this experiment was 98.99% concentrated as obtained by Chemical Engineering Department of Thapar University. Concentrated sulphuric acid has been used for investigating durability of cement mortar. 70.6×70.6×70.6 mm cubes have been casted with varying proportion of CNF and checked against acid penetration. Nitric acid acid used in this experiment was 78% concentrated as obtained by Chemical Engineering Department of Thapar University. Concentrated sulphuric acid has been used for investigating durability of cement mortar. 70.6×70.6×70.6 mm cubes have been casted with varying proportion of CNF and checked against acid penetration.

3.4 TESTS CONDUCTED

3.4.1. Mechanical Properties

The compressive strength test has been performed on cubes according to (IS:4031:Part6) to determine compressive strength at various ages. Mix the cement and sand in dry condition with a trowel for 1minitues and then add water. The quantity of water shall be (p/4+3)% of combined weight of cement and sand where, p is the % of water required to produce a paste of standard consistency. Add water and mix it until the mixture is of uniform colour. The time of mixing is between 3-4 minutes. Immediately after mixing the mortar, place the mortar in the cube mould and compact with the help of the rod. The mortar shall be prodded 20 times in about 8 sec to ensure elimination of entrained air. If vibrator is used, the period of vibration shall be 2 min. Then place the cube moulds in room temperature for 24 hours. After 24 hours remove the cubes from the mould and immediately submerge in clean water till testing. Take out the cubes from water just before testing. Testing should be done on their sides without any packing. Test should be conducted for 3 cubes and report the average value as the test result for 3 days 7day and 28 day compressive strength. For compression test standard 70.6×70.6×70.6mm mortar cubes with varying proportions of CNF/NC has been casted and the load is applied at the rate specified of 70kN/min.

The flexural strength test have been performed on mortar beams according to (IS:4031:Part6) to determine the flexural strength at various ages. Mix the cement and sand in dry condition with a trowel for 1minitues and then add water. The quantity of water shall be (p/4+3)% of combined weight of cement and sand where, p is the % of water required to produce a paste of standard consistency determined earlier. Add water and mix it until the mixture is of uniform colour. The time of mixing shall be between 3-4 minutes. Immediately after mixing the mortar, place the mortar in the mould and prod with the help of the rod. The mortar shall be prodded 20 times in about 8 sec to ensure elimination of entrained air. If vibrator is used, the period of vibration shall be 2 mint. Then place the moulds at room temperature for 24 hours. After 24 hours remove the beams from the mould and immediately submerge in clean water till testing. Take out the beams from water just before testing. Testing should be done on their sides without any packing. Test should be conducted for 3 beams and report the average value as the test result for 7day 14 day and 28 day compressive strength. In this experimental study for flexural strength 40×40×160 mm mortar beams were casted with varying proportions of CNF/NC and the load is kept at 2.65 KN/min.

3.4.2 Durability Tests

Water Absorption Test (ASTM C642) 70.6×70.6×70.6 mm mortar cubes have been casted with varying proportion of CNF. Firstly dry weight of mortar cubes have been carefully taken in weighing mnachine and then mortar cubes have been keept in oven at a temperature of 100 to 105 °C for not less than 24 h. After removing from the oven each specimen is allowed to cool in dry air to a temperature of 20 to 25 °C. Weight of the mortar cubes is taken after drying in oven If the specimen is comparatively dry when its mass is first determined, and the second mass closely agrees with the first, consider it dry. If the difference between values obtained from two successive values of mass exceeds 0.5 % of the lesser value, return the specimens to the oven for an additional 24-h drying period, and repeat the procedure until the difference between any two successive values is less than 0.5 % of the lowest value obtained. Immerse the specimen, after final drying, cooling, and determination of mass, in water for not less than 48 h and Surface-dry the specimen by removing surface moisture with a towel, and determine the mass**.** Difference in the mass can be calculated by subtracting the two values hence percentage water absorption can be calculated for different samples.

Acid Resistance Test have been conducted by refering Turkel et al., (2007) .The proportioning of the cement mortar mix is 1:3 as per IS: 4031 (Part 4) 1988. 70.6×70.6×70.6 mm mortar cubes have been casted with varying proportion of CNF. The specimens are cured in tap water after demolding. After 28 days of curing, the specimens are dried in an oven at 100-105˚C and the initial weights are measured. Then the specimens are immersed into solutions of nitric and sulphuric acids. After exposure to acids, the specimens are washed in order to remove the porous layer of the corrosion products such as soft and crystallized acidic materials or calcium salts. And again specimens are dried in an oven at 105˚C. Loss in weight of the specimens have been measured at 7, 14, 21, 28 days respectively.

Average loss of mass for each mix is carefully taken after 7, 14, 21, 28 days. Percentage mass loss is calculated after each reading and is plotted on a graph. Loss of mass shows loss of cementenious products. Molarity of the acids both sulphuric acid and nitric acid was maintained at 0.1 Molar and a constant pH between 0.9- 1 is maitainted throughout the experiment by using a pH meter .Required amount of acid have been added at regular intervals to maintain the pH of the system. Generally pH of the solution becomes neutral after 8-12 days so proper care should be taken to maintain the acidity of the solution.

Mechanism: Damage of concrete due to sulphuric acid and nitric acid can generally be characterized by the following reactions Turkel et al., (2007).

Sulphuric acid

$Ca(OH)_2+H_2SO_4 \rightarrow CaSO_4.2H_2O$ (1)

$CaSiO_2.2H_2O+H_2SO_4 \rightarrow CaSO_4+Si(OH)_4+H_2O$. (2)

$3CaO.Al_2O_3.12H_2O+3(CaSO_4:2H_2O)+14H_2O \rightarrow 3CaO.Al_2O_3:3CaSO_4:32H_2O$ (ettringite) (3)

Nitric acid

$Ca(OH)_2+2HNO_3 \rightarrow Ca(NO_3)_2+2H_2O$ (4)

The primary reaction product manifested on the concrete surface is gypsum that is associated with volume expansion (factor of 2.2) (Turkel et al. 2007) compared to the volume of reactants, which can induce tensile stresses in concrete, resulting in cracking. If not washed out, the accumulation of gypsum on the surface of concrete may slow down the corrosion rate due to surface sealing . Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite, which has more volume increase up to a factor of 7 (Turkel et al. 2007) than that of gypsum, thus leading to more micro- and macro-cracking. In addition, sulfuric acid decomposes the cementitious matrix by decomposing calcium silicate hydrate (C–S–H), thus contributing to strength loss. $Ca(NO_3)_2$ is a soluble salts that may easily be transported to the outer parts of mortars. In this situation, continuous reactions increase the porosity of cement paste and increased pore volume speed up the rate of reaction.

3.4.3 Characterization Techniques

3.4.3.1 X-Ray Diffraction (XRD)

X-ray investigation in the powder form samples were characterized by X-ray diffractometer with CuK_α radiation for the identification of existing phases, crystal structure, lattice parameter of the crystalline solids. The sample is irradiated with monochromatic X-rays and the counters record the reflected radiation. The X-ray diffraction pattern were recorded using Bruker's diffractogram with CuK_α (λ=1.54Å) obtained from Cu target using an inbuilt Ni filter. The 2 values for XRD patterns, in the range of 10º-90º. The X-ray diffraction peaks were identified using Powder Diffraction Files (PDF).

3.4.3.2 Scanning Electron Microscopy (SEM)

SEM is conducted to study the micro-structure properties of the samples. The samples which are already casted and cured for 3 days, 7 days and 28 days are used for the compressive strength test have been used in this experiment. This test is used to identify the changes which had occurred inside the micro-structure and also to identify the formation and deformation of the phases.

3.5 SAMPLE PREPARATION

The proportioning of the cement mortar mix are in the ratio 1:3 as per IS: 4031 (Part 4) 1988. Carbon Nano Fiber in liquid form have been properly mixed in the cement mortar. Dry powdered mixing was done for 30 minutes in case of Nano Clay for the proper dispersion of nanoclay in the cement mortar.

3.5.1 Sample Casted

Table – 3.5 Specimen detail

Specimen	Specification (mm)	Test conducted
Mortar cubes	70.6 x 70.6 x70.6	Compressive Strength
Mortar beam	40 x 40 x 160	Flexural Strength

Table – 3.6 Samples for micro structural properties and chemical analysis

Specimen	Test conducted
Powder retained at respective days of curing	XRD
Broken piece of sample at respective days of curing	SEM

3.6 EXPERIMENTAL PROGRAMME AND METHODOLOGY

3.6.1 Carbon Nano Fibres

Mechanical properties tests and durability tests have been performed to investigate the effect of partial replacement of carbon nano fiber with cement in 0%, 0.0125%, 0.025% 0.065% 0.050%, 0075% proportions. In mechanical properties, compressive strength have been investigated at the ages of 3 days, 7 days and 28 days, while flexural strength have been investigated at the ages of 7 days, 14 days, 28 days. In case of compressive strength the loading rate is taken as 70 kN/min and in case of flexural strength, the loading rate is taken as 2.65 kN/min. In addition to that water absorption and acid resistance test test have been done at age of 28 days for CNF.

The proportion of cement mortar is standard 1:3 where 1 parties cement and 3 parties standard sand. Nomenclature is given in Table 3.6 of mixes prepared with varying proportion of CNF.Mix proportion for flexural and compression test samples are given in Table 3.7 and Table 3.8

Table – 3.6 Details and nomenclature of cement mortar samples modified with CNF

% addition of CNF in cement mortar (by wt. of cement)	Nomenclature for CNF samples
0% CNF / plain CM	CM (Control)
0.0125% carbon nano fibres	CNF M_1
0.025% carbon nano fibers	CNF M_2
0.050% carbon nano fibers	CNF M_3
0.065% carbon nano fibers	CNF M_4
0.075% carbon nano fibers	CNF M_5

Table – 3.7 Mix proportion for CNF modified Samples (Compression and Durability)

Sr. No.	Designated Mix No.	Cement (g)	Standard sand (g)	Water (ml)	CNF (ml)
1	**CM_1**	200	600	78	Nil
2	**CNF M_2**	199.975	600	75.5	2.5
3	**CNF M_3**	199.95	600	73	5
4	**CNF M_4**	199.9	600	68	10
5	**CNF M_5**	199.875	600	65.5	12.5
6	**CNF M_6**	199.85	600	63	15

Table – 3.8 Mix proportion for CNF modified Samples (Flexural Testing)

Sr. No.	Designated Mix No.	Cement (g)	Standard sand (g)	Water (ml)	CNF (ml)
1	**CM_1**	160	480	62.4	0
2	**CNF M_2**	159.98	480	60..40	2
3	**CNF M_3**	159.96	480	58.4	4
4	**CNF M_4**	159.92	480	54.4	8
5	**CNF M_5**	159.9	480	52.4	10
6	**CNF M_6**	159.88	480	50.4	12

3.6.2 Nano Clay

Mechanical properties tests have been performed to investigate the effect of partial replacement of nano clay with cement in 0%, 0.5%, 1% 2% 4%, 6 % proportions. In mechanical properties, compressive strength is investigated at the ages of 3 days, 7 days and 28 days, while flexural strength is investigated at the ages of 7 days, 14 days, 28 days. In case of compressive strength the loading rate is taken as 70 kN/min and in case of flexural strength, the loading rate is taken as 2.65 kN/min.

The proportion of cement mortar is standard 1:3 where 1 parties cement and 3 parties standard sand. Nomenclature is given in Table 3.9 of mixes prepared with varying proportion of NC. Mix proportion for flexural and compression test samples are given in Table 3.7 and Table 3.8

Table – 3.9 Details and nomenclature of cement mortar samples modified with Nano clay

% addition of NC in cement mortar (by wt. of cement)	Nomenclature for NC samples
0% NC / plain CM	CM (Control)
0.5% Nano clay	NC N_1
1% Nano clay	NC N_2
2% Nano clay	NC N_3
4% Nano clay	NC N_4
6% Nano clay	NC N_5

Table – 3.10 Mix proportion for NC modified Samples (Compression and Durability Tests)

Sr. No.	Designated Mix No.	Cement (g)	Standard sand (g)	Water (ml)	NC (mg)
1.	**CM1**	200.00	600	78	Nil
2.	**NC N2**	199	600	78	1
3.	**NC N3**	198	600	78	2
4.	**NC N4**	196	600	78	4
5.	**NC N5**	192	600	78	8
6.	**NC N6**	188	600	78	12

Table – 3.11 Mix proportion for CNF modified Samples (Flexural Testing)

Sr. No.	Designated Mix No.	Cement (g)	Standard sand (g)	Water (ml)	Amount of nano clay (mg)
1.	**CM**	160.00	480	62.40	0
2.	**NC N_1**	159.20	480	62..40	.8
3.	**NC N_2**	158.40	480	62.40	1.6
4.	**NC N_3**	156.80	480	62.40	3.2
5.	**NC N_4**	153.60	480	62.40	6.4
6.	**NC N_5**	150.40	480	62.40	9.6

3.6.3 Chemical Composition and Micro Structure of Cement Mortars

The chemical composition of the samples are investigated using X-Ray diffractometer analysis (XRD) with Cu-radiation. In addition to this 30 kV and voltage of 40 mV was used with diffraction intensity in the rage of 10-80°. The micro structure of the cement mortar samples are examined by using scanning electron microcopy (SEM) analysis which is used to identify the changes which occur in the microstructure including the formation and deformation of phases in the cement mortar sample.

3.6.4 Methodology

All specimen have been casted according to the mix proportion in Table 3.7, Table 3.8, Table 3.10, Table 3.11. For these mix proportions required quantities of material have been weighed. Standard values of size 70.6 × 70.6 × 70.6 mm have been used for compressive strength and durability test. In addition to that size of 40 × 40 × 160 mm have been used for flexural strength as per (IS:4031:Part6). The mixing procedure adopted as follows:

- Before casting the mould should be properly cleaned and oiled. The screw should be tightened properly in the perfect dimension before casting. Care should be taken that no gap should be left in the mould so that mortar start coming out.
- The three grade of standard sand should be weighed with perfect accuracy along with cement.
- Clean appliances were used for mixing and portable was used in preparing the cubes & beams.
- The cement and standard sand were dry mixed in a tray for about 10 minutes. A uniform mix was obtained.
- The material for each batch was mixed separately and the quantity of cement, standard sand and water used was cement (200gm), sand (600gm) and water $\left(\frac{P}{4}+3\right)$ percentage of combined mass of cement and sand, where P is the percentage of water required to produce a paste of standard consistency determined.
- Place on a non porous plate, a mixture of cement and standard sand. Repeat the procedure by using CMF also.

- Dry material have been mixed with a trowel for one minute and then with water as well as dispersed CNF and CMF in liquid form. Until the mixture was of uniform colour.
- The time of mixing in any event be not less than 3 minutes. If time taken to obtain the uniform colour exceed 5 minutes than reject the mixture and entire operation was repeated with a fresh quantity of cement, sand, water .
- The casting immediately followed mixing the top surface of the specimen have been scrapped to remove excess material and achieve smooth finish. The specimen have been removed from moulds after 24 hours and cured in water till testing as per requirement of test.

3.7 CLOSING REMARKS

In this chapter, the experimental details of various tests and the methodology for investigating effect of carbon nano fiber and nano clay on mechanical, durability, chemical composition and micro-structure properties have been discussed. In the following chapter the experimental results obtained is presented and discussed.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 GENERAL

This chapter represent details of the results and analysis of the experimental work carried out in the study by addition of carbon nano fiber and nano clay in cement mortar for the various percentages. The results and analysis for carbon nano fibres and nano clay have been discussed saparetely. Results and discussion of tests such as compressive strength, flexural strength, water absorption, acid resistance test using sulphuric acid and nitric acid along with micro structural analysis using SEM as well as chemical compression with XRD has been discussed in details.

4.2 MICROSTRUCTURE ANALYSIS

4.2.1 Scanning Electron Microscopy

4.2.1.1 Carbon Nano Fibres

SEM have been carried out at the ages of 3 days, 7 days and 28 days for control mix and for 0.05% CNF modified cement mortar. The test samples have been obtained from central part of specimen.

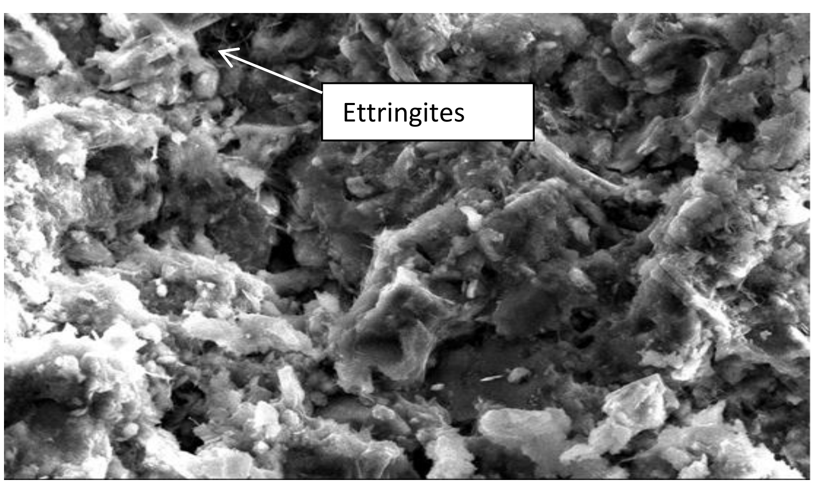


Figure 4.1(a): SEM micrograph OPC (3 days hydrated) showing Ettringites

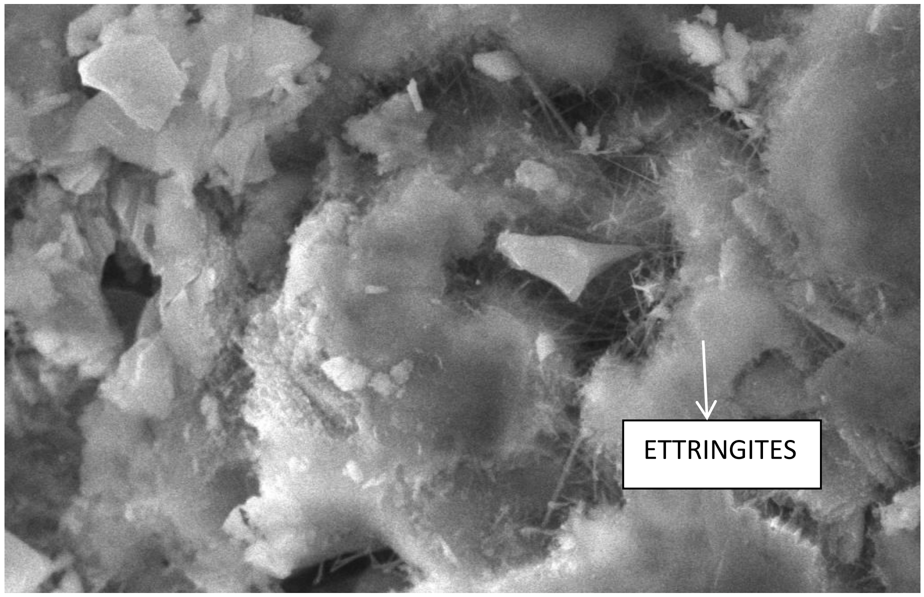


Figure 4.1(b): SEM micrograph of OPC 43 grade (7 days hydrated) showing ETTRINGITES

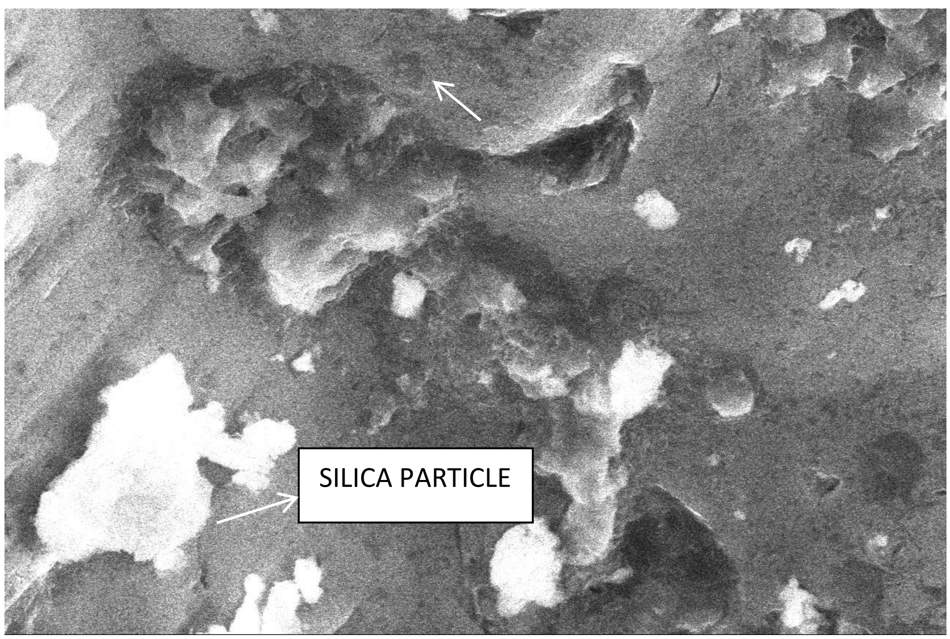


Figure 4.1(c): SEM micrograph of OPC control sample (28 days hydrated) Showing SILICA PARTICLE

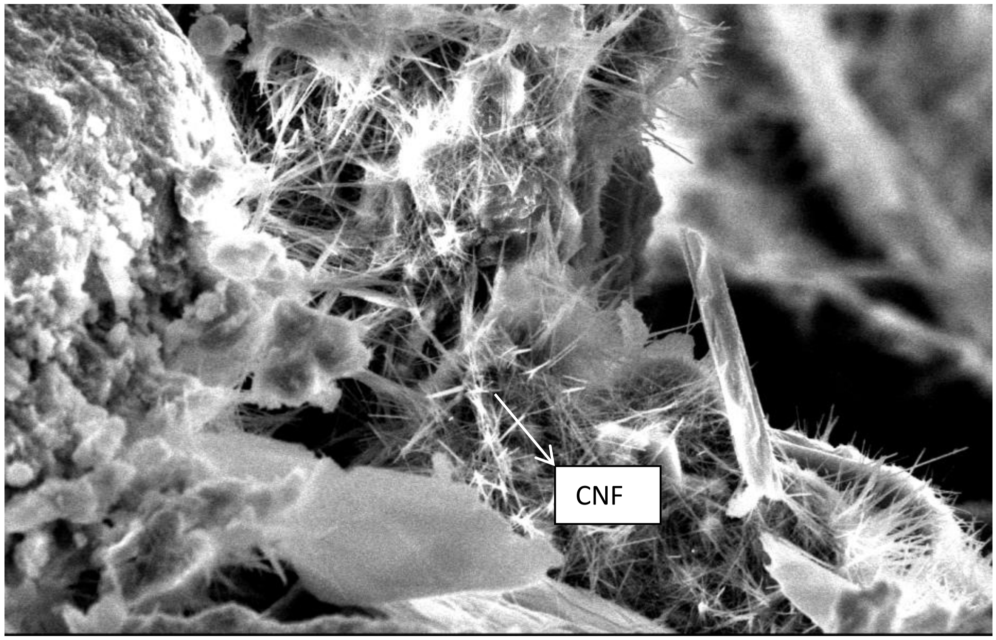


Figure 4.1(d): SEM micrograph of CNF 0.05% (3 days hydrated) showing CNF

Figure 4.1(e): SEM micrograph of CNF 0.05% (7 days hydrated) showing CH

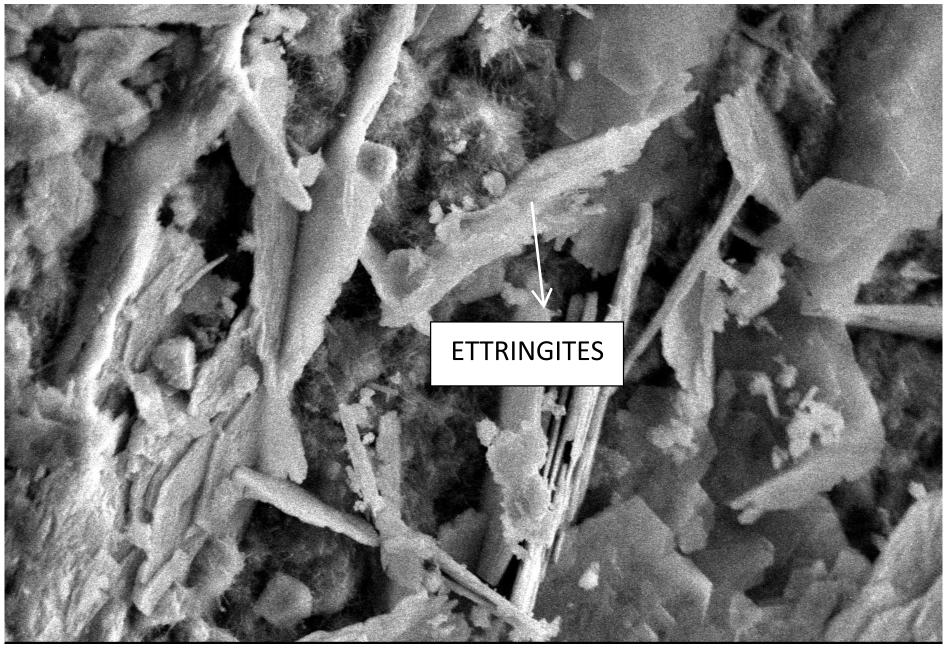


Figure 4.1(f): SEM micrograph of CNF 0.05% (28 days hydrated) showing ETTRINGITES

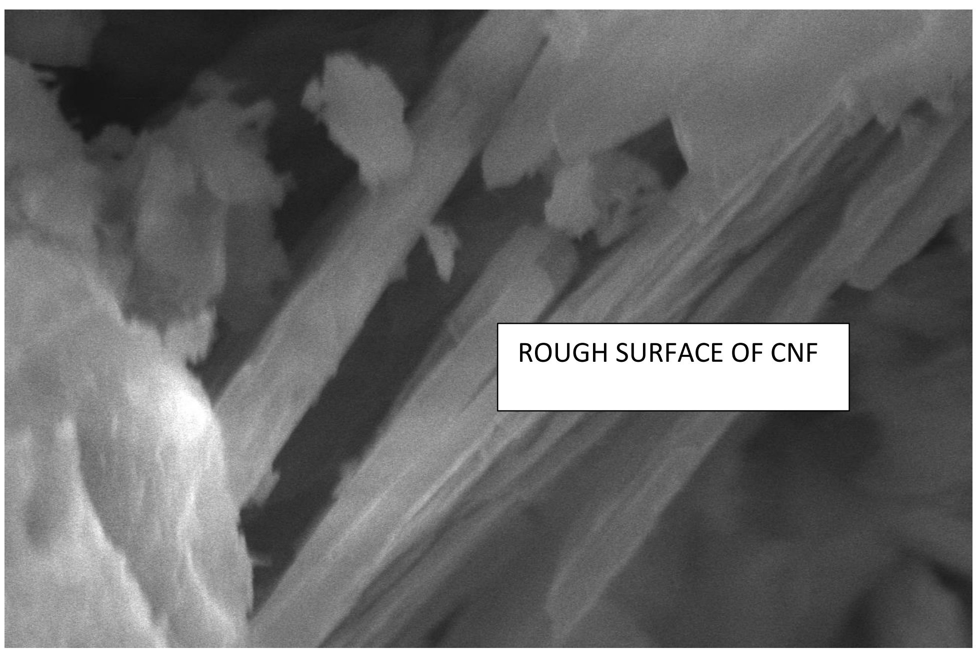


Figure 4.1(g): SEM micrograph of CNF 0.05% (28 days hydrated) showing Rough Surface of CNF

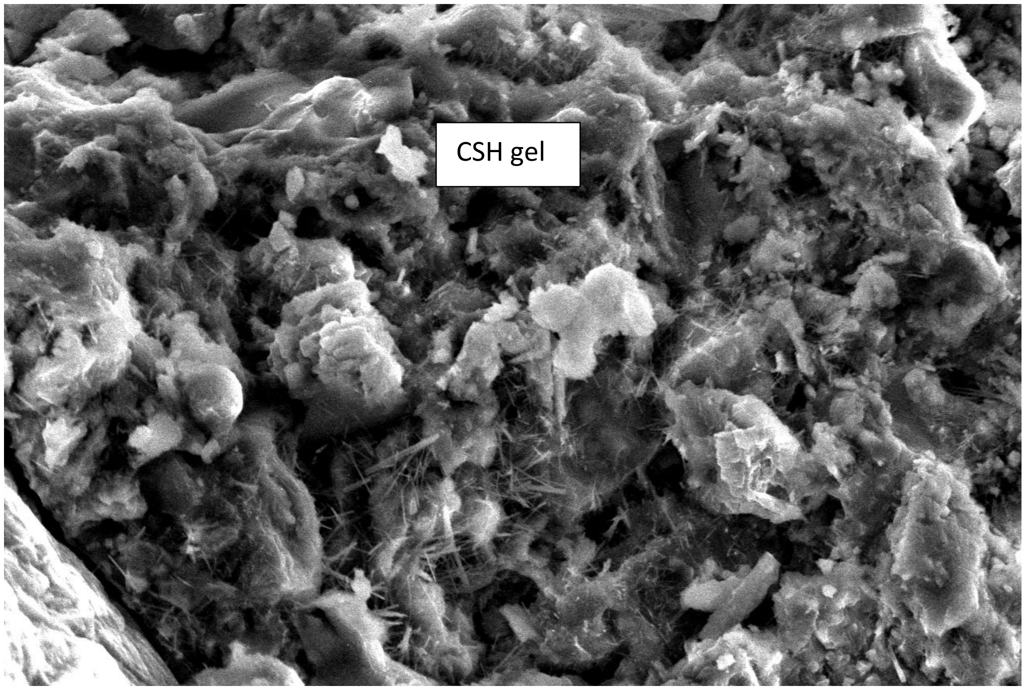


Figure 4.1(h): SEM micrograph of CNF 0.05% (28 days hydrated) showing CSH gel

DISCUSSION

The specimens used in SEM experiment are of control cement mortar and 0.050% CNF modified cement mortar . Fig 4.1 (a) shows clearly Ettringites formed in OPC and Fig 4.1 (b) shows ettringite at 7 days .Fig 4.1 (c) shows silica particle at 28 days. Fig 4.1(d) shows CNF at 3 days. Fig 4.1(e) shows calcium hydroxide at 7 days. Fig 4.1(f) shows Ettringites and Fig 4.1 (h) shows CSH gel at 28 days. From the comparison of SEM images of control mix with 0.050% modified cement mortar with CNF indicated dense microstructure formation of cement mortars in CNF modified specimens as compaired to control mix hence CNF improves the micro-structure and strength of the cement paste.

4.2.1.2 SEM of Nano Clay

SEM micrographs of Cloisite 30B NC have been carried out at the age of 28 days. The test samples of the micro-structure have been obtained from the central part of the specimens.

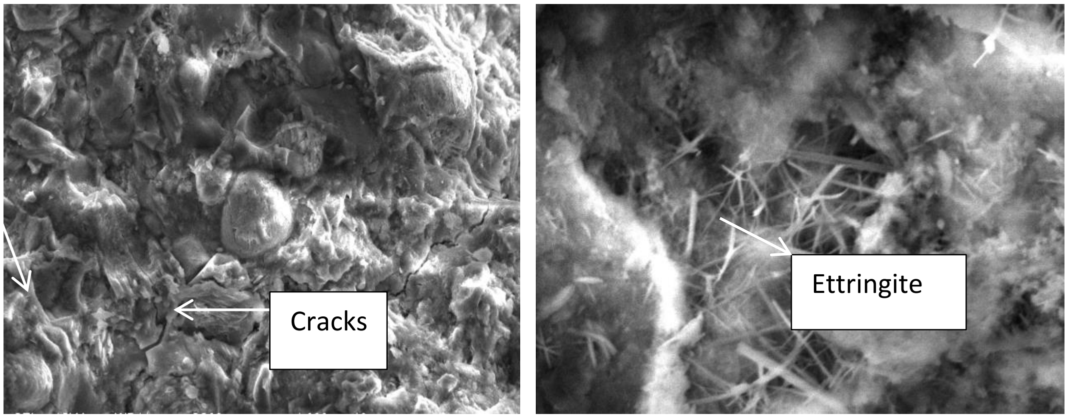


Fig 4.2 (a) Contol Mix hydrated for 28 days.

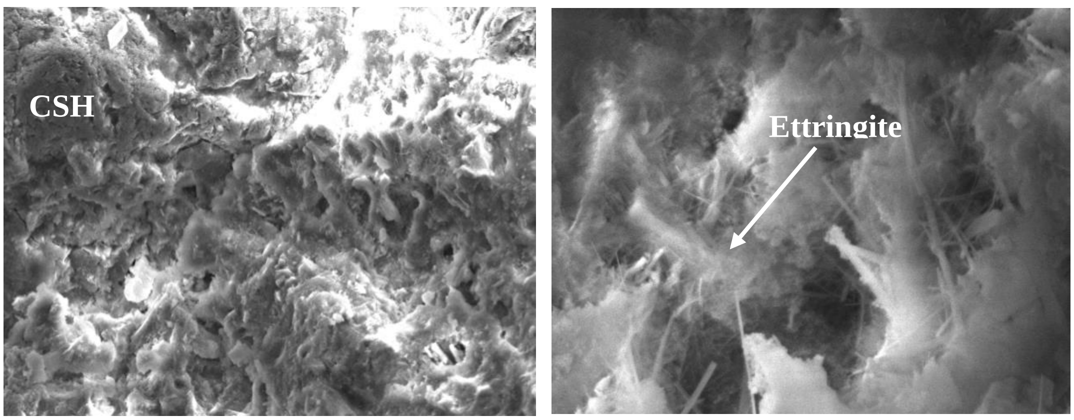


Fig4.2 (b) N1 addition in cement mortar hydrated for 28 days**.**

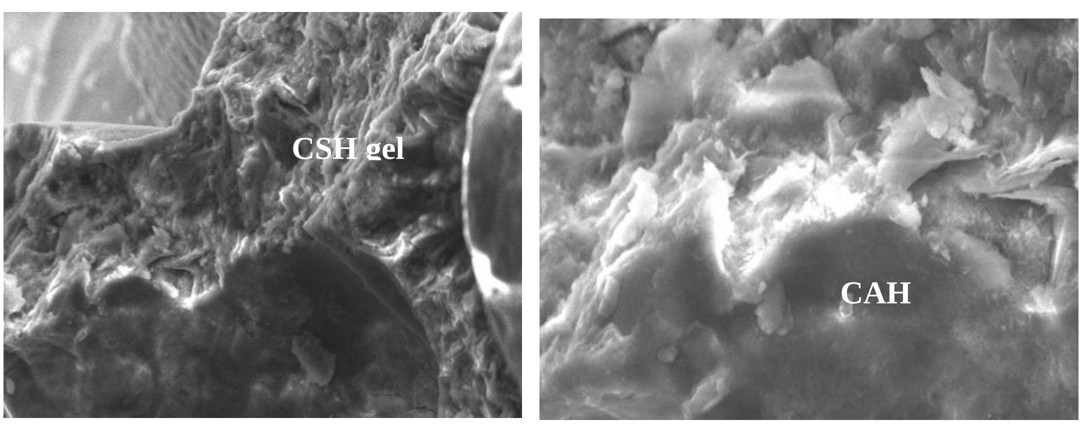
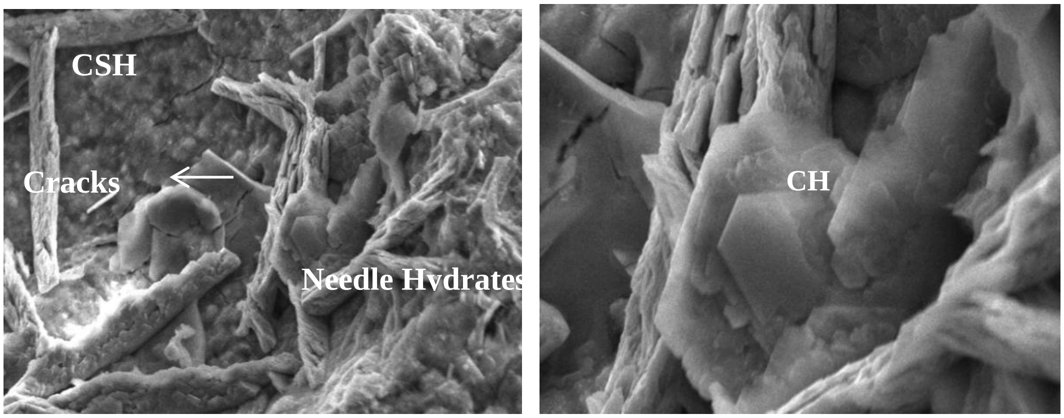


Fig 4.2 (c) N3 addition in cement mortar hydrated for 28 days**.**



Fg 4.2 (d) N4 addition in cement mortar hydrated for 28 days.

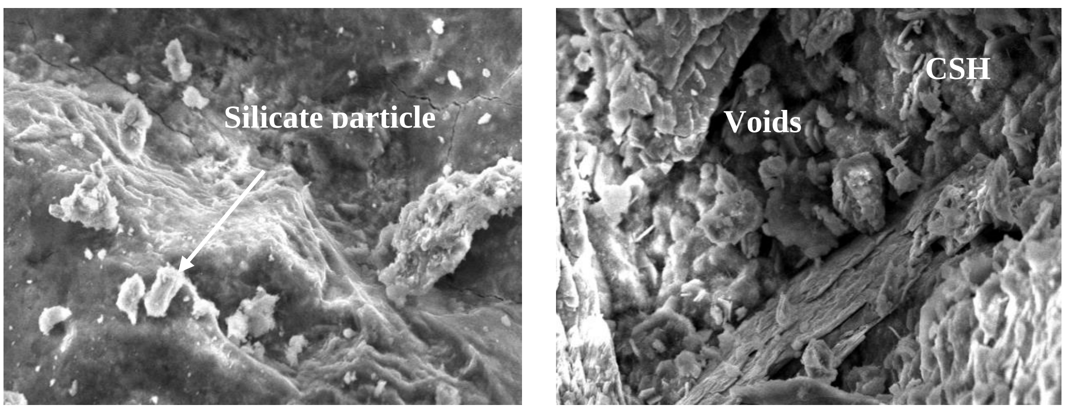


Fig 4.2 (e) N5 addition in cement mortar hydrated for 28 days**.**

DISCUSSION

SEM have been conducted on different samples of NC modified samples as well on control mix. Fig 4.2(a) shows cracks and ettringite for control mix. Fig4.2(b) shows CSH gel and ettringite for sample N1 at 28 days. Fig4.2(c) shows CSH gel and CAH for sample N2 at 28 days. Fig4.2(d) shows CSH gel ,cracks and CH for sample N4 at 28 days. Fig4.2(e) shows Silica Particle Voids and CSH gel for sample N5 at 28 days.It can be concluded that CSH gel exited in the form of gel.The Cloisite 30B NC improves the micro-structure and strength of the cement paste by a mechanism; when the nano-particles are uniformly dispersed in the cement paste the hydrated products of cement will deposit on nano-particles due to their more surface area during hydration. Cloisite 30B will participate in the hydration process to generate the CSH through reacting with CH therefore the strength increases with the addition of NC. Fig. 4.2 (e) represents the micro-structure containing 6% Cloisite 30B NC which causes decrease in the strength. The micro-structure represents the poor hydration and unhydrated cement grains. This results in decrease in mechanical properties of the sample

4.2.2 X-RAY DIFFRACTION (XRD)

4.4.2.1 Carbon Nano fibres

Figure 4.3 shows the variation of X-Ray diffraction (XRD) graph of plain and CNF modified cement mortar with 0.050% and controlled mortar paste at the age of 28 days

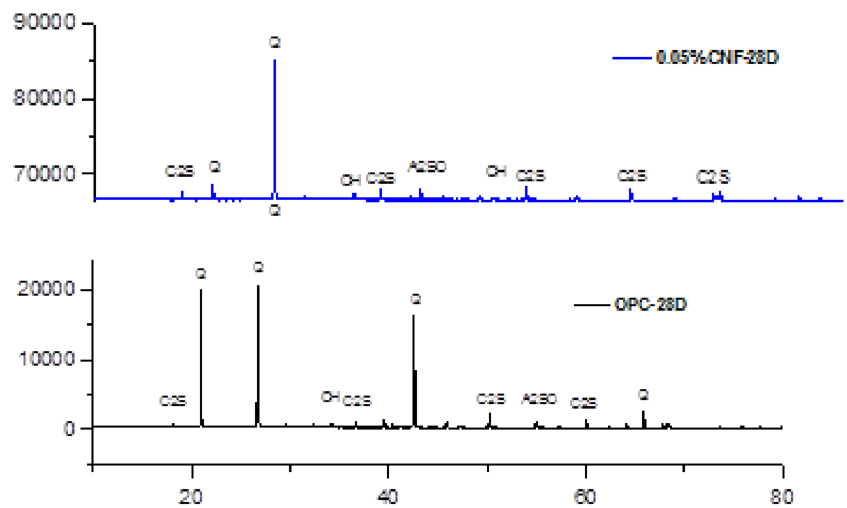


Fig 4.3 Variation of X-Ray diffraction (XRD) carbon nano fibres

Notations:

Q – Quartz

C_2S – Dicalcium silicate

CH – Calcium hydroxide

A_2SO – Dialuminium silicate oxide

XRD pattern for plain and CNF modified cement paste hydrated for 28 days (optimize addition 0.050%)

DISCUSSION

XRD has been performed on control cement mortars and 0.05% CNF modified cement mortar. The main compound deducted are calcium silicate hydrate (C-S-H) .It is clear from Fig 4.3 that CH and C_2S peak increase at 0.05% CNF, which are responsible for strength development and this is due to the pozzolonic reaction of CNF with the free line liberated during process of hydration.

4.2.2.2 Nano Clay

Fig. 4.4 shows the variations of X Ray Diffraction (XRD) graphs of plain and Cloisite 30B NC modified cement paste in which Cloisite 30B NC added in the proportion of 0.5%, 1%, 2%, 4% and 6% which are hydrated for 28 days.

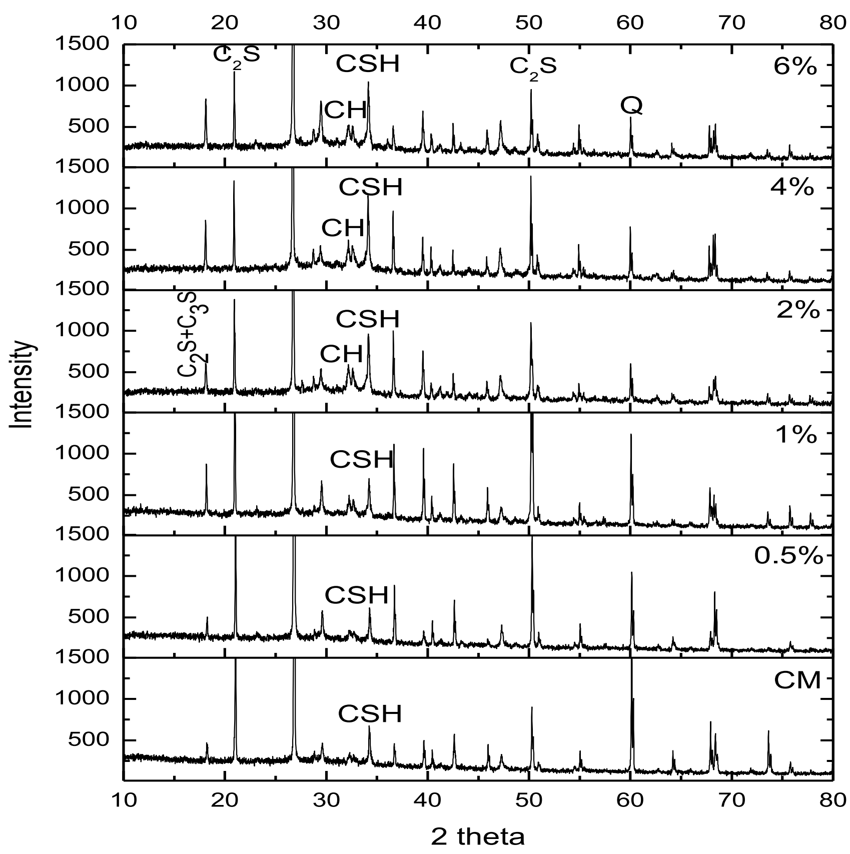


Fig. 4.4: XRD pattern for plain and Cloisite 30B NC modified cement pastes hydrated for 28days (at all additions)

DISCUSSION

The main compounds in XRD experiment are calcium silicate hydrate (CSH) and calcium hydroxide (CH). It is clear from the Fig. 4.4 that CH peaks decreases with increase in the quantity of Cloisite 30B NC whereas, CSH peaks goes on increasing with increase in the quantity of Cloisite 30B NC. The increase and decrease of CSH and CH intensity phases in Cloisite 30B NC cement paste hydrated for 28 days is mainly due to the pozzolanic reaction of Cloisite 30B NC with the free lime liberated during the process of hydration.

4.3 CARBON NANO FIBRES (CNF)

4.3.1 Mechanical Properties

4.3.1.1 Compressive Strength

All specimen (70.6 × 70.6 × 70.6mm) are cured in water and tested at age of 3 days, 7 days and 28 days. Following readings have been obtained during the test conducted at various stages.

Table–4.1 Compressive Strength of Cement Mortar in Control Mix & Cement Replacement with Carbon Nano Fiber at 3, 7 and 28days for Various Mixes

Sr. No.	Mix	Compressive Strength of Mortar (MPa)					
		3 -Days strength	% variation	7 -days strength	% variation	28 -days strength	% variation
1	**CM**	30.4	Control	36.42	Control	44.7	Control
2	**M1**	31.35	3.12	37.32	2.47	45.1	0.89
3	**M2**	32.73	7.66	39.78	7.17	46.34	3.66
4	**M3**	33.91	11.54	40.56	9.22	48.72	8.99
5	**M4**	32.29	6.21	38.79	6.52	46.35	3.69
6	**M5**	28.815	–5.21	35.21	–3.32	43.8	–2.01

Note: (+) indicates increase and (–) indicate decrease in compressive strength

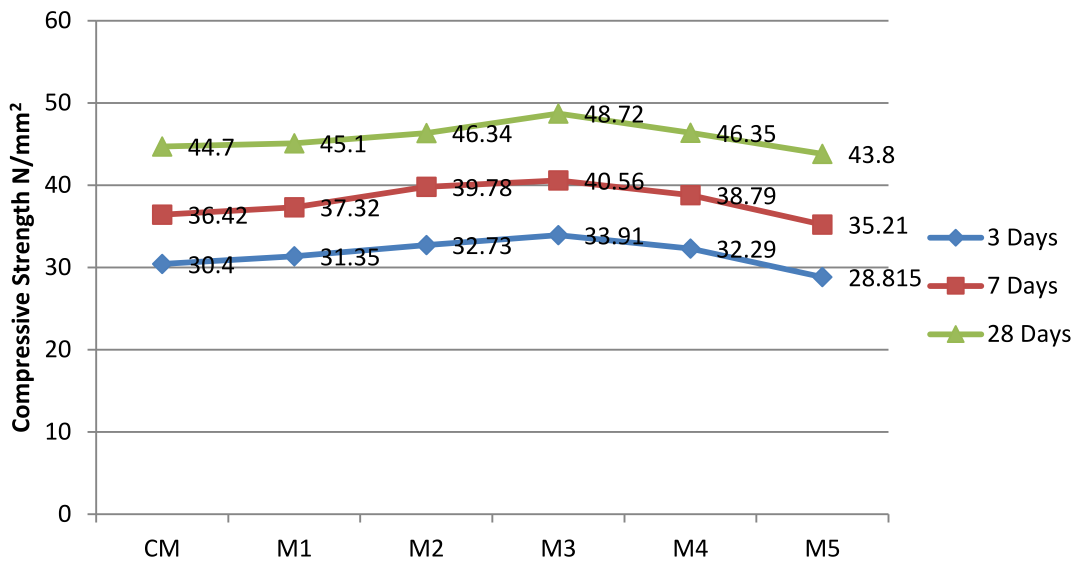


Fig4.5 Comparison of variation of compressive strength

ANALYSIS

Table 4.1 & Fig 4.5 indicated the percentage variation of the compressive strength for various mixes as compared to control mix. It is seen that 3 days strength, the percentage variation is maximum for mix M_3 with 11.54%, while for 7 days and 28 days of 8.99% and 9.22% respectively for carbon nano fibre It was evident that the compressive strength increased through increasing the amount of carbon nano fibers upto 0.050 % at low concentration and for higher concentrate 0.065% and 0.075%, the strength properties decreased. The trend of compressive strength result is shown in figure 4.5 shows that there is decrease in comparison strength for each mix after 0.050 of carbon nano fiber. This can be concluded that 0.050% replacement of CNF is the optimum level of replacement as after that strength starts decreasing.

The reason behind this high result is due to small particle size and low percentage of colloidal carbon nano fiber which promote the pozzolonic reaction and fill the pores resulting in high compressive strength.

DISCUSSION

Test results are shown in Tables 4.1 and Fig 4.5. In this case the homogenum dispersion of carbon nano fiber in the cement matrix must be accomplished .Good dispersion leads to reduction of the fiber free area in the material and improve the efficency of the CNFs/CMFs in the nation (S.P.Shah 2011).

It is evident that the compressive strength increased through increasing the amount of carbon nano fibers upto a certain amount (Metaxa et.al. 2011) and and for higher concentrate 0.065% and 0.075%, the strength decreases (Gdoutos et.al. 2009). The reason this strength improvement is the efficient mixing of colloided carbon macro fiber. For the contents higher than 0.050%, carbon nano fiber fiber could not easily disperses within the cement matrix and due to their higher surface energy, particular become afflomeceted. Consequently structure formed in such condition was not homogenance properly compacted as seen in the XRD and SEM test conducted on the broken samples of same specimens. The trend of compressive strength result is shown in figure 4.5 shows that there is decrease in comparison strength for each mix after 0.050 of carbon nano fiber.

4.3.1.2 Flexural Strength

All specimen (40 x 40 x 160 mm) are cured in water and tested at age of 7 days, 14days and 28 days. Following readings have been obtained during the test conducted at various stages.

Table – 4.2 Flexural Strength of Cement Mortar in Control Mix & Cement Replacement with Carbon Nano Fiber at 7, 14 and 28days for Various Mixes

Sr. No.	Mix	Flexural Strength of Mortar (MPa)					
		7 -Days strength	% variation	14 -days strength	% variation	28 -days strength	% variation
1	**CM**	6.02	Reference	10.88	Reference	12.46	Reference
2	**M1**	6.1	1.33	10.9	0.183824	13.1	5.136437
3	**M2**	6.29	4.49	11.67	7.261029	14.34	15.08828
4	**M3**	6.87	14.12	12.81	17.73897	14.98	20.22472
5	**M4**	6.38	5.98	12.21	12.22426	13.13	5.377207
6	**M5**	5.85	-2.82	10.75	-1.19485	11.69	-6.17978

Note: (+) indicates increase and (–) indicate decrease in flexural strength

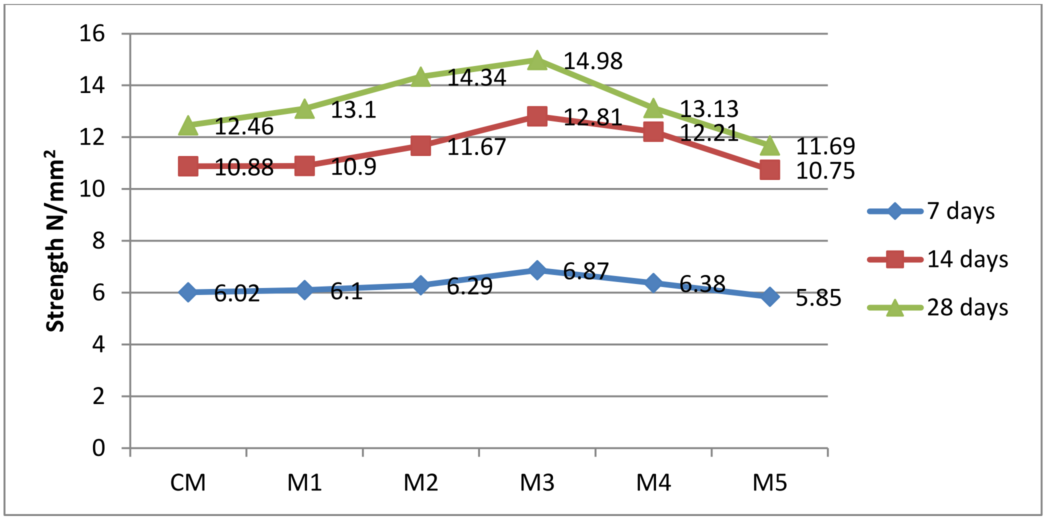


Fig 4.6 Comparison of Flexural strength

ANALYSIS

Flexural strength of control sample of mortar mix CNF have been carried out at the age of 7, 14 and 28 days. Test results are shown in Table 4.2 & Fig 4.6. As seen in quoted table, test result indicated the addition of CNF in cement mortar at different percentage. There is a increase of strength in CNF 0.05% at 7 days, 14 days and 28 days observed as 14.22%, 17.8% and 20.26% respectively, compare to strength at control mixes.. However, after 0.05% and 0.065% decrease of strength was noted as compare to control mix samples. There is a decrease of flexural strength is mainly at 0.065% and 0.75% by weight of cement CNF due to improper dispersion of carbon fibers and more vides in cement matrix or lack of formation CSH gel. This can be concluded that 0.050% replacement of CNF is the optimum level of replacement as after that strength starts decreasing.

DISCUSSION

Homogenum dispersion of carbon nano fiber in the cementation matrix must be accomplished Good dispersion leads to reduction of the fiber free area in the material and improve the efficency of the CNFs/CMFs (S.P.Shah 2011).

It is evident that the flexural strength increased through increasing the amount of carbon nano fibers upto 0.050% (Metaxa et.al. 2011) and for higher concentrate 0.065% and 0.075%, the strength properties decreased (Gdoutos et.al. 2009). The reason for this strength improvement is the efficient mixing of colloided carbon macro fiber in the cement matrix. For the contents higher than 0.050%, carbon nano fiber fiber could not easily disperses within the cement matrix and due to their higher surface energy, particular get separated. Consequently structure formed in such condition was not homogenance properly compacted as seen in the XRD and SEM test conducted on the broken samples of same specimens . The trend of compressive strength result is shown in figure 4.6 shows that there is decrease in flexural strength for each mix after 0.050% of carbon nano fiber.

4.3.2 DURABILITY PROPERTIES

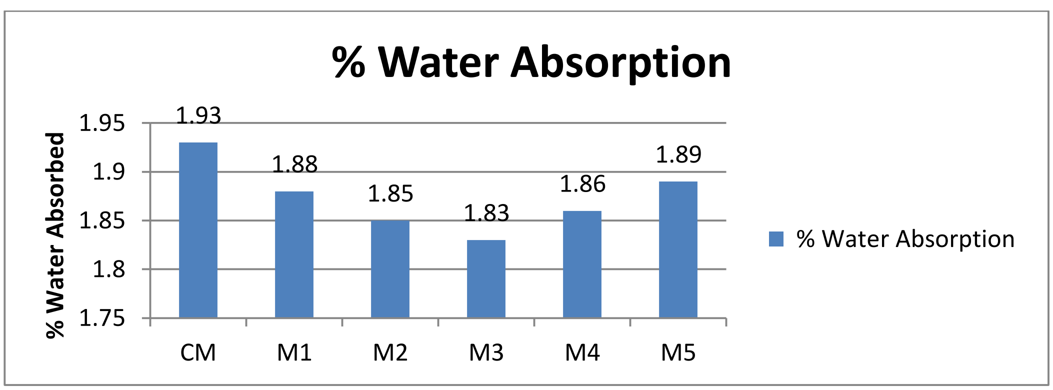
4.3.2.1 Water absorption Test

All specimen (70.6 × 70.6 × 70.6mm) are cured in water for 28 days. Water absorption test have been conducted after 28 days of curing and following readings have been obtained.

Table 4.3 Water Absorption of Cement Mortar in Control Mix & Cement Replacement with Carbon Nano Fiber at 28days for Various Mixes

Sr. No.	Mix	Water Absorption %
1	**CM**	1.93
2	**M1**	1.88
3	**M2**	1.85
3	**M3**	1.83
4	**M4**	1.86
5	**M5**	1.89

Table 4.4 Comparison of water absorbed by different mortar mixes of carbon nano fibres



DISCUSSION

From Table 4.4 it is observed that there is decrease in water absorption level from 1.93% to 1.83% till 0.050% replacement of CNF .Water absorption test have been conducted to access the durability property of the mortar mixes of carbon nano fibres . Water can penetrate in the form of liquid or paper within the capillary voids into the porous material. It can be seen with clarity that with increase in the percentage amount of carbon nano fibers decreases the water absorption of mortar specimen, this is due to the result of the enhancement impermeability mechanism of mortars due to super pozzolonic performance of carbon fiber particles as seen in the XRD and SEM test conducted. The fine particles block the channels connecting the capillary pores in the cement paste and more homogeneous distribution of C-S-H gel resulting in less porus structure and less permeable voids.

4.3.2.2 Acid Resistance Test

All specimen (70.6 × 70.6 × 70.6mm) are cured in water for 28 days. Acid resistance test have been conducted after 28 days of curing and at an regular intervals i.e 7 days, 14 days ,21 days, 28 days using sulphuric acid and nitric acid. Following readings have been obtained:

Table 4.5 % Mass Loss of Cement Mortars under the influence of Sulphuric Acid (.1M)

S. No	**Mix**	**7 days**	**14 day**	**21 days**	**28 days**
1	**CM**	3.01	4.81	5.83	6.53
2	**M1**	2.95	4.79	5.82	6.52
3	**M2**	2.93	4.78	5.82	6.52
4	**M3**	2.9	4.73	5.8	6.51
5	**M4**	2.96	4.81	5.84	6.52
6	**M5**	3.1	4.98	5.92	6.55

Table 4.6 % Mass Loss of Cement Mortars under the influence of Sulphuric Acid(.1M)

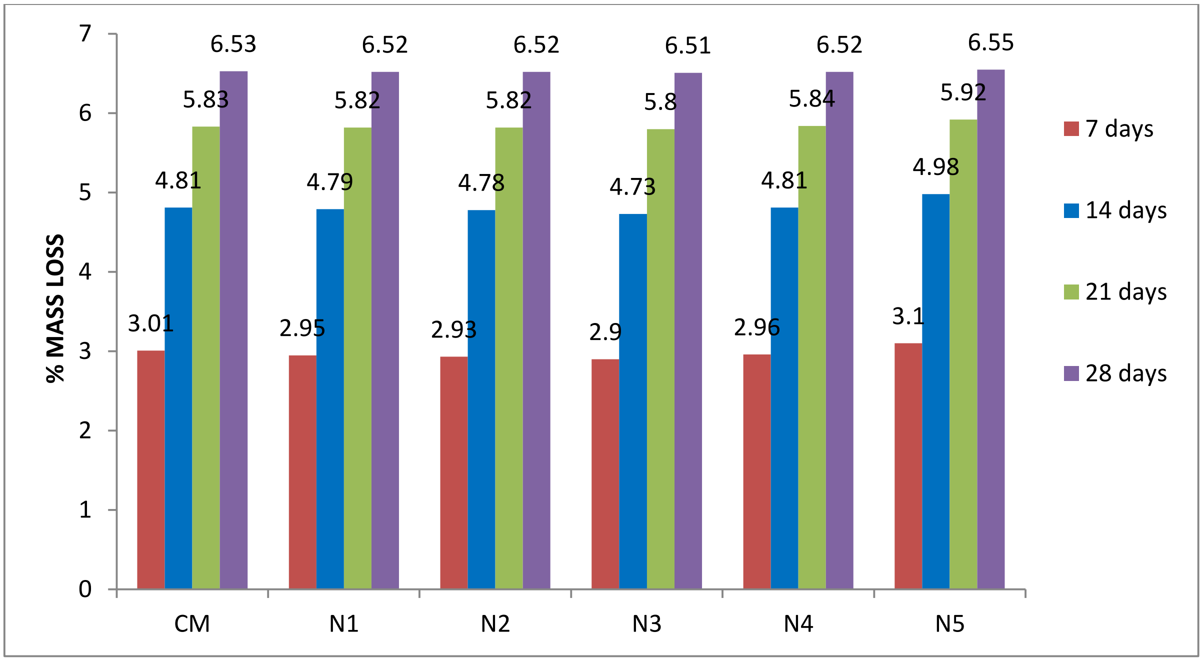
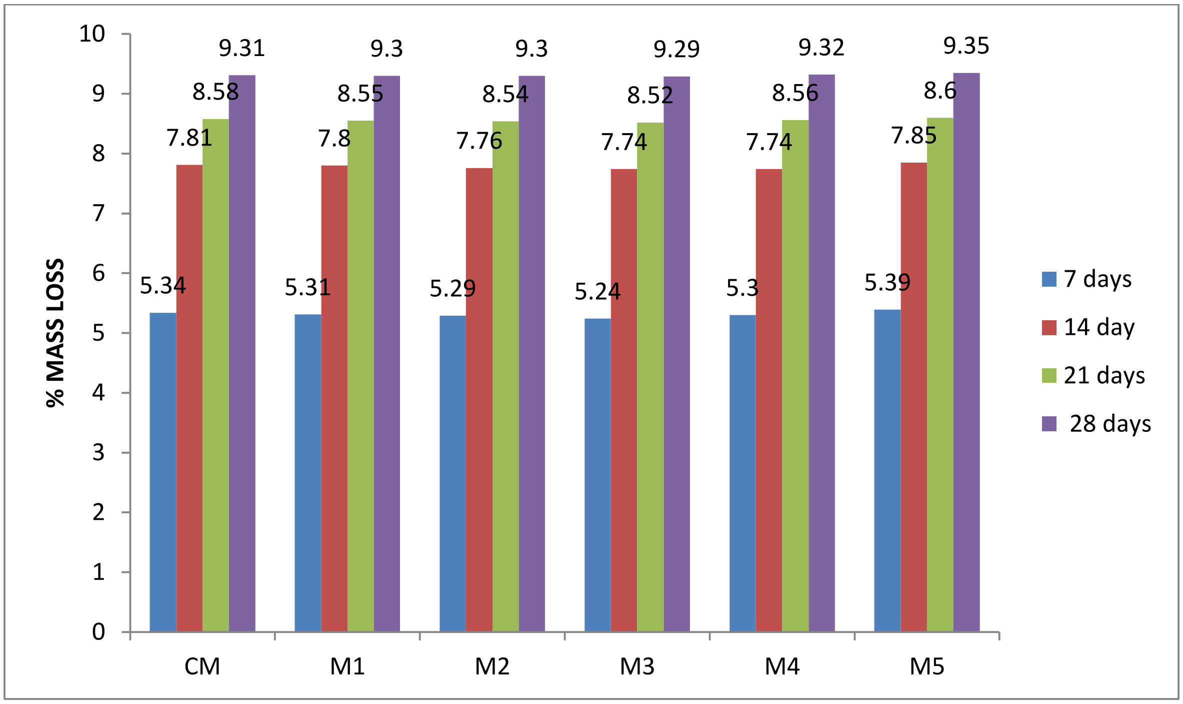


Table 4.7% Mass Loss of Cement Mortars under the influence of Nitric Acid (.1M)

S. No	Mix	7 days	14 day	21 days	28 days
1	**CM**	5.34	7.81	8.58	9.31
2	**M1**	5.31	7.8	8.55	9.3
3	**M2**	5.29	7.76	8.54	9.3
4	**M3**	5.24	7.74	8.52	9.29
5	**M4**	5.3	7.74	8.56	9.32
6	**M5**	5.39	7.85	8.6	9..35

Table 4.8% Mass Loss of Cement Mortars under the influence of Nitric Acid (.1M)



ANALYSIS

Table 4.5 and Table 4.6 shows results for sulphuric acid resistance test and it have been observed that there is decrease in mass loss for 7 day 14 day 21 day 28 day till 0.050% as compared with control mixes, but after that for higher percentages resistance against acid penetration decreased severely. Table 4.7 and Table 4.8 shows results for nitric acid resistance test and it have been observed that there is decrease in mass loss for 7 day 14 day 21 day 28 day till 0.050% replacement but after that for higher percentages resistance against acid penetration decreased severly. It has been observed that percentage mass loss was more in case of nitric acid as compared to sulpuric acid.

DISCUSSION

It can be clearly seen that that there is loss of mass when the mortars are immersed in acid solution this is due to the chemical reaction between cementitious componds and acids. (Turkel et al., 2007)

<u>Sulphuric acid</u>

$Ca(OH)_2+H_2SO_4 \rightarrow CaSO_4.2H_2O$

$CaSiO_2.2H_2O+H_2SO_4 \rightarrow CaSO_4+Si(OH)_4+H_2O$.

$3CaO.Al_2O_3.12H_2O+3(CaSO_4{:}2H_2O)+14H_2O \rightarrow 3CaO.Al_2O_3{:}3CaSO_4{:}32H_2O$ (ettringite)

Nitric acid

$Ca(OH)_2+2HNO_3 \rightarrow Ca(NO_3)_2+2H_2O$

The primary reaction product manifested on the concrete surface is gypsum induces tensile stresses in concrete which results in cracking. Further reaction of gypsum with calcium aluminate phases in the cementitious matrix can form ettringite, which has more volume increase (up to a factor of 7)(Turkel et al. 2007) than that of gypsum, thus leading to more micro- and macro-cracking. $Ca(NO_3)_2$ is a soluble salts that may easily be transported to the outer parts of mortars. In this situation, continuous reactions increase the porosity of cement paste and increased pore volume speed up the rate of reaction This loss is more in case of nitric acid solution because of formation of soluble salts in the nitric acid solution as in case of sulphuric acid gypsum is formed as a by product of the raction which is insoluble in water.

4.4 NANO CLAY

4.4.1 Mechanical Prpoperties

4.4.1.1 Compressive Strength

All specimen (70.6 × 70.6 × 70.6mm) are cured in water and tested at age of 3 days, 7 days and 28 days. Following readings have been obtained during the test conducted at various stages.

Table–4.9 Compressive Strength at 3, 7 and 28days for Various Mixes Nano Clay

Sr. No.	Mix	Compressive Strength of Mortar (MPa)					
		3 -Days strength	% variation	7 -days strength	% variation	28 -days strength	% variation
1	**CM**	30.9	Reference	36.42	Reference	44.7	Reference
2	**N1**	31.85	3.07	37	1.59	46.13	3.10
3	**N2**	32.35	4.69	38.72	6.32	48.41	8.30
4	**N3**	35.37	14.47	40.89	12.27	50.91	13.89
5	**N4**	37.18	20.32	43.825	20.33	52.94	18.43
6	**N5**	32.1	3.88	39.28	7.85	48.82	9.22

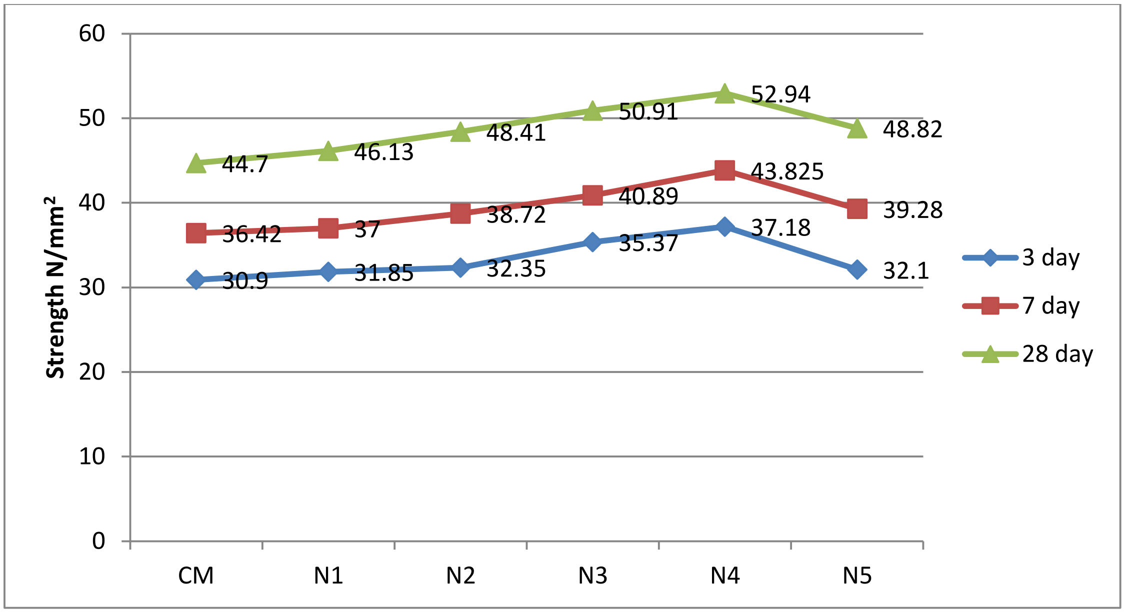


Table 4.10 Comparison of compression strength

DISCUSSION

It is observed that when NC is added by increasing proportion, the strength increases progressively up to 4%. In case of N2 for 3 days strength increases by 4.46% where as in case of N4 the strength increases by 12.34% as compared with the results of control mix samples where as for N6 there is only 3.4% increase in strength which is very less as compared to N2 and N4 results. For 7 days strength in case of N2 the strength increases by 1.45% where as in case of N4 there is 12.81% increase in strength as compared with results of control mix samples where as in NC6 there is 7.34% decrease in strength. For 28 days strength in case of N2 and N4 samples the strength increases by 3.78% and 13.58% where as for N6 strength decreases by 9.22% as compared to 28 days strength of control mix samples. This can be concluded that 4% replacement of NC is the optimum level of replacement as after that strength starts decreasing.

The test results indicated that by .5 to 4 percent by weight addition of Cloisite compressive strength increases progressively. When N6 was added to the weight of cement, strength starts decreasing. The Cloisite 30B NC belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of Cloisite 30B NC acts as a filler and fills the voids of the cement mortar and make the mixture denser as seen in the XRD and SEM test conducted and the mechanical property is improved due to pozzolanic reaction of Cloisite 30B NC with free lime which adds the bonding strength and solid volume which results into higher compressive strength

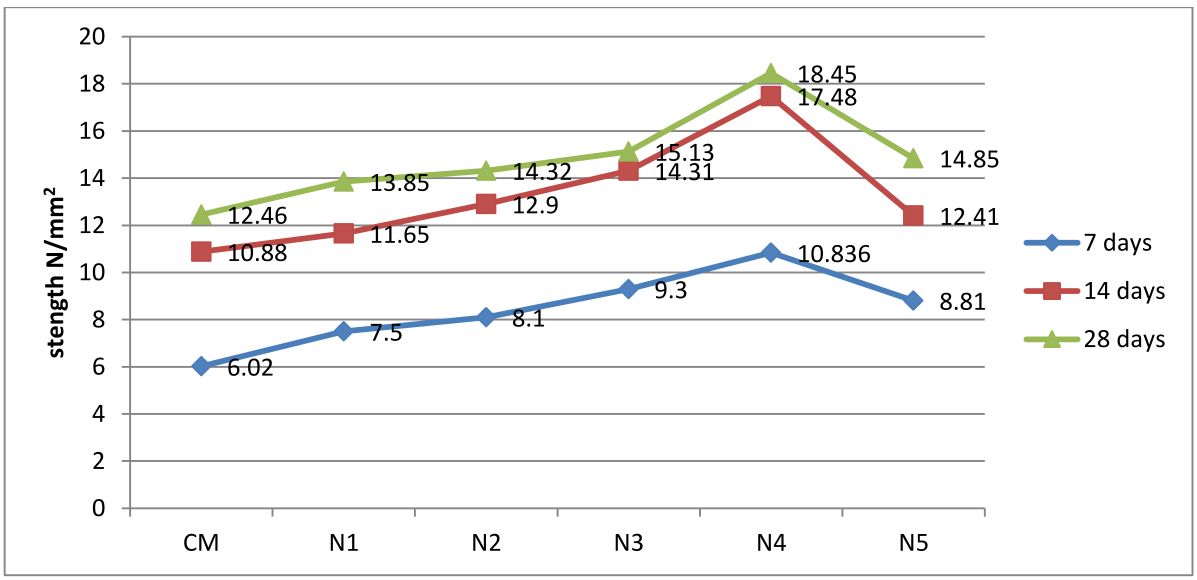
4.4.1.2 Flexural Strength

All specimen (40 x 40 x 160 mm) are cured in water and tested at age of 7 days, 14days and 28 days. Readings have been obtained during the test conducted at various stages.

Table 4.11 Flexural Strength of Cement Mortar in Control Mix & Cement Replacement withNano Clay at 7, 14 and 28days for Various Mixes

Sr. No.	Mix	Flexural Strength of Mortar (MPa)					
		7 -Days strength	% variation	14 -days strength	% variation	28 -days strength	% variation
1	CM	6.02	Reference	10.88	Reference	12.46	Reference
2	N1	7.5	24.58	11.65	7.08	13.85	11.16
3	N2	8.1	34.55	12.9	18.57	14.32	14.93
4	N3	9.3	54.49	14.31	31.53	15.13	21.43
5	N4	10.836	80.00	17.48	60.66	18.45	48.07
6	N5	8.81	46.35	12.41	14.06	14.85	19.18

Table 4.12 Comparison of Flexural strength



DISCUSSION

Table 4.12 indicated the variation of flexural strength after addition of Cloisite 30B NC at different percentages. There is increase of 21% and 48% strength with 2 to 4%addition of NC in the cement mortar respectively, when compared to control mix at age of 28 days. it is clear that with the addition of Cloisite 30B NC flexural strength goes on increasing. it is clear that for N1 for 7 days the strength increases by 24.17% where in case of N2 the strength increases by 34.35% as compared to control samples. For 14days in case of N1 the strength increases by 11.06% whereas in case of N2 the strength increases by 12.9% as compared to control mix. For 28 days in case of N1 and N2 there was increase in strength i.e. strength increases by 11.6% and 14.15% as compared to control samples.it is observed that when NC is added by increasing proportions from 2%, 4% and 6% it is observed that the strength increases progressively up to 4%. In case of N3 for 7days strength increases by 80.66% where as in case of N4 the strength increases by 48.74% as compared with the results of control mix samples where as for N5 here is 19.73% increase in strength For 14days strength increases by 19.32 % in case of N4 as compared with results of control mix samples where as in N5 there is 16.07% increase in strength. This can be concluded that 4% replacement of NC is the optimum level of replacement as after that strength starts decreasing.

The Cloisite 30B NC belongs to mineral admixture, which improves the macro-structural and mechanical properties of the blended cement. The ultra-fine particles of nanoclay fills the voids of the cement mortar and make the mixture denser and the mechanical property is improved due to pozzolanic reaction of Cloisite 30B NC with free lime as seen in the XRD and SEM test conducted. At 6% there is decrease of flexural strength is mainly due to improper filling effect of NC particles at the voids or pores in cement paste, and also due to the lack of formation of CSH which is actually formed by the reaction of alumino-silicate containing Cloisite 30B NC with calcium hydroxide which makes the cement paste denser.

4.5 CLOSING REMARKS

In this chapter, the test results have been discussed. It is clear from the result that nano carbon fiber and nano clay act as filler/reinforcement in mortar mix to increase the strength and durability. Well dispersed CNF/NC improve the strength durablity & stiffness of cement mortar, excess concentration have a negative impact of strength.

1. It can be clearly seen that cement replaced with 0.050% replacement has maximum strength both compressive as well as flexural and this value is 4% when we use nano clays.
2. Compressive and flexural strength of mortar cubes replaced with CNF increases first upto 0.050% replacement and decreased after further addition of carbon nano fibres.
3. Durability to mortar cubes replaced with carbon nano fibres increases upto 0.050% replacement.
4. Resistance of cement mortars with carbon nano fibres against sulphuric acid and nitric acid is maximum for 0.050% replacement, infact resistance against acid sharply decreased upon further addition of carbon nano fibres.
5. Compressive and flexural strength of mortar cubes replaced with nano clay increases first upto 4% replacement level and then decreased on further addition.
6. Formation of CSH gel, ettringites ,silica particles etc can be clearly seen in the microstructure analysis of cement mortar

CHAPTER – 5

CONCLUSIONS AND FUTURE SCOPE

5.1 GENERAL

High potential has been predicted for nano technology application in construction & even minor improvement in strength could bring large accumulated benefits. The role on application of the carbon nano fiber and nano clay with cement mortar have been reviewed and discussed in details. The present study aims to study the effect of varying proportion of carbon fiber and nano clay on the properties of cement mortar. The present experimental study have conceived following the general purpose of testing new sustainable building processes and modern production system aimed at saving natural raw materials and reducing energy consumption.

5.2 CONCLUSIONS AND MAJOR FINDINGS

Based on the scope, materials, techniques, procedure and other parameter associated with this work, the following major conclusion are derived from the present study.

5.2.1 Effect of CNF/NC on Compressive Strength

- Incorporating optimized CNFs/NCs to cement mortar mixtures generally enhance their mechanical properties.
- Cement mortar replaced with 0.050% CNF has maximum strength both compressive as well as flexural hence this content is said to be the optimized level of replacement.
- Cement mortar replaced with 4% NC has maximum strength both compressive as well as flexural hence this content is said to be the optimized level of replacement.
- Compressive strength of modified cement mortar by CNF at optimized level 0.05% shows increase in strength for 3, 7 and 28 days by 11.05%, 9.25% and 8.99% compared to control mixes.
- Similarly for NC addition shows progressive increase in strength for 3, 7 and 28 days by 18.90%, 20.98% and 20.23% respectively, as compare to control mixes sample.

- The reason behind this high increase in strength is due to the small particle size and low percentage of colloidal Carbon Nano Fibers and Nano Clay which promote the pozzolonic reaction and fill the pores resulting in high compressive strength.

5.2.2 Effect of CNF/NC on Flexural Strength

- Flexural strength shows progressive increase in strength with the addition of CNF and NC .The flexural strength in case of mortar with carbon nano fibres for 7 days increases by 14.12%, 14 days increase by 17.73% and 28 days increases by 20.26% as compare to control mix samples.
- Similarly in case of NC modified cement mortar flexural strength of 7 days increases by 80.49%, in case of 14 days, increases by 60.66% and in case of 28 days, increased by 48.07.

5.2.3 Effect of CNF on Water Absorption And Acid Resistance

- The increase in the amount of carbon nano fiber decreases the water absorption of Cement mortars upto 0.050% replacement. The fine particles of pozzolonic block the channels connecting the capillary pores in the cement paste and generate a more homogonous distribution of C-S-H gel resulting in less pore structure and permeable voids. For higher percentages increase in water absorption is due to non-homogeneous mixing which results in less porous structure.
- The increase in CNF increases acid resistance of cement mortar against acid penetration upto 0.050% replacement but after that there is decrease in acid resistance. The reason behind this increase is that the fine particles of pozzolonic block the channels connecting the capillary pores in the cement paste and generate a more homogonous distribution of C-S-H gel resulting in less pore structure and permeable voids. For higher percentages structure is non-homogeneous mixing which results in less porous structure.

5.2.4 Effect of Carbon Nano Fiber and Nano Clay on Microstructural Properties

- Reason for improvement in strength properties is seen in XRD, which represent the higher formation of CSH and more consumption of CH.

- The main compounds detected are calcium silicate hydrate (CSH) and calcium hydroxide (CH). CH peaks decreases with increase in the quantity of CNF/NC whereas, CSH peaks goes on increasing with increase in the quantity ofCNF/NC. The increase and decrease of CSH and CH intensity cement paste is mainly due to the pozzolanic reaction of CNF/NC with the free lime liberated during the process of hydration..
- SEM micrographic show that the addition of CNF/NC makes the microstructure quite dense.
- SEM micrograph shows C-S-H gel existed in the from of clusters, lapped & connected to together by little amount of needle hydrates

5.3 WORK LIMITATIONS

There are limitations in present study as the study of effect of CNF/NC in proportion of mortar is a vast subject of interest for research work.

- The limited quantity of CNF/NC due to its uncommon availability & high cost allowed only for limited scope of experiment to be conducted.
- The replacement of cement with NC was 0.5%, 1%, 2% 4% 6% the intervals can further be increased in future studies. .

5.4 FUTURE SCOPE OF RESEARCH WORK

- Considering all aspects, it is suggested to optimize the use of carbon nano fiber and nano clays from micro to nano scale to obtain more strengthened, long lasting concrete structure in the future.
- Codes of practice should be introduced for testing connection material with nano composite to determine how to choose the suitable percentages for each particle size of CNF to be added to concrete & appropriate water to cement ratio..
- It is proposed to further check for advanced durability test like chemical test rapid chloride permeability test.

REFERENCES

Barzegar.A, : Sadrmomtazi. (2010). "Assessment of the Effect of Nano-SiO_2 on Physical and Mechanical Properties of Self-compacting Concrete Containing Rice Husk Ash." Second International Conference on Sustainable Construction Materials and Technologies. June 28 – June 30, 2010.

Balaguru. : Chong.K (2006). "Nanotechnology and Concrete: Research Opportunities. ACI FALL 2006 Convention" Nanotechnology of Concrete Recent Developments and Future Perspectives.

Chung.D, (2000) "Cement Reinforced with Short Carbon Fibers: A Multifunctional Material. Composites" Construction and Building Materials.

Chung.D (2005). "Dispersion of Short Fibers in Cement." Journal of Materials in Civil Engineering.

Sanchez.F : Sobolev.K, (2010). "Nanotechnology in Concrete – A Review". Construction and Building Materials.

Gaitero.J : Campillo.I.: Mondal P.: Shah S.P. (2010). "Small Changes can make a Great Difference In Transportation Research Record" Journal of Transport Research Board. Washington DC: Transportation Research Board National Academy.

http://www.google.com
http://www.wikipedia.com
IS-650
IS456

Hakamy.A, : Shaikh.F, ; Low (2013). "Microstructures and Mechanical Properties of Hempo Fabric Reinforced Organoclay-cement Nanocomposites." Construction and Building Materials.

Harsh.S., : Arora.A. : Ali.M. : Vasudeva.M.(2010). “Investigatiosn on the Effect of Nanosilica on the Performance of Cement” National Council for Cement and Building Materials, New Delhi.

Hewayde.E : Nehdi.M : Nakhla.G.(2007) : “Using concrete admixture for sulphuric acid resistance” Constuction Material

Hosseini.P. : Mohamad.M. : Nekooie.M., : Teherkhani.R. : Booshehrian A (2011). “Toward Green Revolution in Concrete Industry: The Role of Nanotechnology” Australian Journal of Basic and Applied Sciences.

Indian Standard Code IS 4031 Part 2-7, 1988, Testing of Cement.

Kay.W ; Kenneth.J. : Loh (2010). “Nanoengineering Ultra-High-Performance Concrete with Multiwalled Carbon Nanotubes, Transport Research Record” Journal of the Transportation Research Board No. 2142, Washington, D.C. 2010.

Man.S.(2006). “Nanotechnology and Construction.” Nanoforum Report, Institute of Nanotechnology” Nanotechnology of Concrete Recent Developments and Future Perspectives.

Metaxa : Maria.S : Konsta.G: Gdoutos; Zoi.S. : Surendra.P : Shah (2009). “Multi-scale Mechanical and Fracture characteristics and Early-age Strain Capacity of High Performance Carbon Nanotube/Cement Nanocomposites.” Cement & Concrete Composites.

Metaxa, : M.S. Konsta ; Gdoutos : S.P. Shah (2011). “Mechanical Properties and Nanostructure of Cement-based Materials Reinforced with Carbon Nanofibers and Polyvinyl Alcohol (PVA) Microfibers.”

Mo.Y : Rachel.H (2013). “Carbon Nanofiber Concrete for Damage Detection of Infrastructure.” This is a Paper Distributed under the Terms of the Creative Commons Attribution Licence (Chapter 5).

Ozyildirim.C. : Zegetosky.C. (2010). “Exploratory Investigation of Nanomaterials to Improve Strength and Permeability of Concrete”. Construction and Building Materials

Pigeon.M : Pleau.R.,: Azzabi.M. : Banthia.N. (1996). “Durability of Microfiber-Reinforced Mortars.” Cement and Concrete Research.

Porro.A. : Dolado J. (2005). “Overview of Concrete Modeling. In: Proceedings of the International Conference on Applications of Nanotechnology in Concrete Design.”

Qing.U. : Zenan.Z. : Deyu.K., : Rongshen C. (2007). “Influence of Nano-SiO_2 Addition on Properties of Hardened Cement Paste as Compared with Silica Fume”. Construction and Building Materials.

Sanchez.F : Sobolev.K, (2010). “Nanotechnology in Concrete – A Review”. Construction and Building Materials.

Shiho.K, : Pengkun H : David.C : Surendra P. Shah (2013). “Modification of Cement-based Materials with Nanoparticles.” Cement & Concrete Composites 2013

Tyson.M, : Rashid, : Abu Al-Rub, : M. ASCE (2011). “Carbon Nanotubes and Carbon Nano Fibers for Enhancing the Mechanical Properties of Nanocomposite Cementitious Materials.” Journal of Materials in Civil Engineering .

Turkel,: Felekoglu.B : Dulluc.S, (2007): “Influence of various acids on the physico-mechanical properties of pozzolanic cement mortars” Materials and structures

Wao.Z,. : Bartos.j : A. Porro (2004). “Application of Nanotechnology in Construction.” Materials and Structures.

Zhi, : Zhili. : G (2008). “Applications of Nanotechnology and Nanomaterials in Construction.” Advancing and Integrating Construction Education, Research & Practice. August 2008, Karachi, Pakistan

Zhu.W., : Bartos.P. : Porro.A. (2004). “Application of Nanotechnology in Construction Summary of a state-of-the-art Report.” Materials and Structures, November.2004.