STUDY OF CARBON NANO-FIBER AGGREGATES WITH AC MEASUREMENTS

A Thesis

Presented to

the Faculty of the Department of Civil & Environmental Engineering

University of Houston

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

in Civil Engineering

by

Avinash Gautam

May 2019

STUDY OF CARBON NANO-FIBER AGGREGATES WITH AC MEASUREMENTS

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ABSTRACT

Past studies have demonstrated the use of self-consolidating carbon nanofiber concrete (SCCNFC) as a structural sensor which led to the development of carbon nanofiber aggregates (CNFAs). Many researchers have adopted the four probe technique to measure DC electrical resistance variation of concrete composites like CNFAs to study the effect of stimuli on structures. In this research, four probe CNFAs were modified into two-probe, and its response in circuits with DC and AC (20Hz to 300kHz) inputs for loaded and non-loaded states were compared. The study was further extended with the optimization of AC frequency and carbon nanofiber (CNF) content to achieve a maximum and reliable response from CNFAs in response to various stimuli. The optimized CNFAs were then tested to develop waterproof CNFAs with the outer coating. The study finally gave the optimized waterproof CNFA to be used in an AC circuit of optimized frequency that can be implemented in reliable and consistent real-time structural health monitoring.

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CHAPTER 1. INTRODUCTION

1.1 Overview of Research

Today, concrete is the second most used building material across the globe. It is a mixture of cement gel matrix with granular coarse-fine aggregates and water with the necessary amount of additive and mineral materials in the proper ratio. The researchers in this field of study have been working to improve the technical functions and performance of concrete by using a different proportion of its ingredients and different types of additives. Hydrated cement as a major constituent of concrete in itself is a brittle material, and the tensile strength is typically only one-tenth of its compressive strength. To compensate for this weakness, a reinforcement of rebars and fibers are added to concrete.

The fiber reinforcement of brittle construction materials is not a new concept. Anciently, straw and horse-hair were used in a mortar to improve the brittle behavior of construction materials. Asbestos fibers were used in construction concrete in the 1900s, but the health risk associated with asbestos were discovered. Thus, there was a need to find the replacement for this substance in concrete and other building materials. In the 1950s, the concept of composite material and fiber reinforcement came as the topic of interest. It was the 1960s when the fiber research and industrialization began with the addition of steel fibers to reinforced concrete structures. The research progressed in the 1970s, 80s, and 90s, with the addition of polymeric fibers, glass fibers, and carbon fibers respectively (Li 2002).

Various previous research show that fibers check the brittle constituents', such as concrete, properties by arresting cracks improving the tensile strength, ductility, toughness, and conductivity (Shah and Naaman 1976; Chen and Chung 1993a; Li et al., 2004; Li, Zhang, et al., 2007; Gao et al., 2009). Fibers in concrete are also employed to check the cracking due to plastic shrinkage and to drying shrinkage. Also, fibers also reduce the permeability of concrete, thus reducing the bleeding of water. Nano-imaging of the fracture surfaces of cement nanocomposites has shown that fiber reinforces cement paste by bridging nano-cracks and pores, indicating that the addition of fibers can enable the control of the matrix cracks at the nanoscale level (Konsta-Gdoutos et al., 2008).

Increasing the strength of concrete has been one of the key fields of investigation. On the other hand, enhancing the sensing ability of concrete is another vast field of concrete research. The sensing ability of concrete that responds its environment and the changes in strain, temperature, moisture, pH, and electric or magnetic fields is an area of interest for a big fraction of scientists and researchers in the concrete study. These sensing abilities make the concrete smart enough to be used to monitor its health regarding stress-strain, temperature, pH, moisture, electrical/magnetic responses. The concrete can even obtain an awareness of damage on itself and its surroundings. This property is utilized in Structural Health Monitoring (SHM). The technology of structural health monitoring helps in providing the capability of non-destructive flaw detection allowing concrete to be repaired before it is too late (Chen and Chung, 1993). This evaluation of safety and the durability of a structure is essential during its lifetime.

This study has used the carbon nanofibers (CNFs) for the fiber research in concrete construction with strain sensing abilities. Previous research at the University of Houston has demonstrated that self-consolidating CNF concrete (SCCNFC) can be used as a strain sensor with implementation (Gao et al., 2009; Howser et al., 2011). Construction of the entire structure with these CNFs would have been ideal as the entire structure itself would have the self-sensing ability. But, because of the availability and high cost of CNFs, an aggregate of mortar with CNFs as the admixture is developed (Howser et al., 2013).

The CNFA is 2.54 cm.×2.54 cm.×2.54 cm. so that it is roughly the same size as a normal aggregate found in the concrete. The development of a CNFA is significant in that it is possible to use the strain-sensing capabilities of SCCNFC with a greatly reduced cost because only the CNFAs placed in the structure would contain CNFs. A CNF aggregate (CNFA) embedded inside the structures was able to detect the strain, temperature hydration, and damage in reinforced or prestressed concrete structures (Howser 2013) using a 4-probe AC circuit.

The response of the CNFAs in DC and AC circuits to measure electrical resistance has not been studied previously. To better understand the behavior of CNFAs in AC circuit and to develop and optimize CNFs and AC frequency to be used in the study of 2-probe CNFAs, different CNFAs with varying CNF content were studied in various AC frequencies.

1.2 Objectives of Research

The objectives of this research can be shortened as follows:

1) Develop CNFAs and investigate its' behavior in DC vs. AC Circuit

2) To optimize the CNFs content and AC frequency for CNFAs implementation

3) Investigate the waterproofing of CNFAs

1.3 Outline of The Thesis

This thesis is divided into six chapters. Chapter 1 introduces an overview and the objectives of the research in addition to an outline of this thesis. Chapter 2 presents a literature review of the past relevant works in CNFs in concrete or mortar and CNFAs. Chapter 3 describes the development of CNFAs with the investigation of CNFAs in DC and AC circuits. Chapter 4 describes the optimization of CNFs content and AC frequency for implementation of 2-probe CNFAs in AC circuit. Chapter 5 describes the effect of water on CNFAs with different waterproofing materials. Chapter 6 presents the conclusion of the study and suggests possible future works in CNFAs.

CHAPTER 2. LITERATURE REVIEW

2.1 Introduction

The field of fiber reinforced concrete research has been much enthusiasm for the development of the self-sensing structural system with major implementation as a structural sensor. Short electrically conducting fiber pull-out that aids the slight and reversible crack opening which enables the short fiber composites to behave as a strain sensor. Mortar or concrete reinforced with well-dispersed fibers of a diameter smaller than crack width and conductance higher than that of the matrix have strain sensing ability independent of their orientation and contact with one another (Chung 1995; Chen and Chung 1996). The electrical conductivity of the added fibers enables the magnitude of direct current in the composite to change in response to strain variation, allowing sensing (Chung 1995; Bontea et al., 2000; Li et al., 2004).

2.2 Fiber Reinforced Concrete

Hydrated cement that holds fine and coarse aggregates in concrete is a brittle material which is stronger in compression than in tension. To compensate for this tensile weakness, a reinforcement consisting typically of rebar or fibers is added to the concrete. Horsehair and straw were added as fibers to mud bricks, adobe, mortar, and plaster since ancient times followed by steel fibers, polymers, glass, and carbon fibers in the 1960s, 70, 80s, and 90s respectively (V. Li 2002).

Material properties of concrete like tensile strength, toughness, ductility and conductivity is enhanced by use of fibers (Shah and Naaman 1976; Naaman 1985; Iijima

1991; Chen and Chung 1993b; Li et al., 2004, 2006; Li, Zhang, et al., 2007; Gao et al., 2009; Konsta-Gdoutos et al., 2010a). Two different practice of fiber use can be seen in concrete research and industry. Randomly dispersed short fibers mixed in concrete and other is the use of fibers as a thin sheet inside the concrete. This thesis adopts the use of randomly dispersed short fibers as a concrete admixture arresting the cracks while loading. These cracks that are initiated with the onset of cracks in nano-level of concrete which are arrested by the fibers by bridging action. Increasing stress will further stretch these cracks. However, fibers will reduce this impact by forming bridges between the cracks. The same bridging action and fiber pull out causes a phenomenon that improves the tensile strength, ductility, and toughness in concrete.

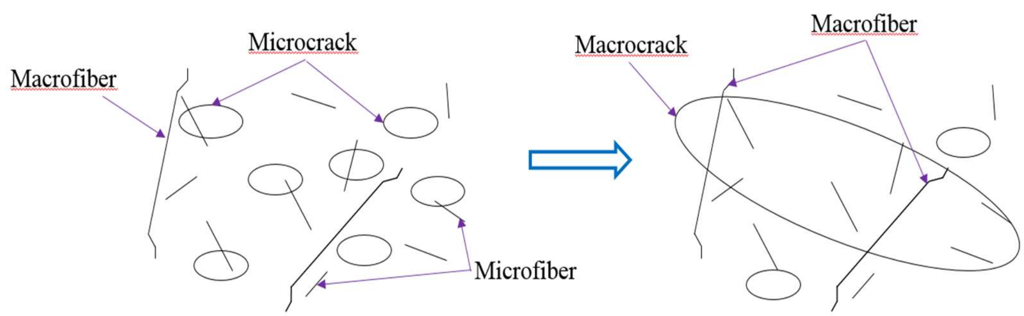


Figure 2.1 Bridging Action of Fibers across Micro and Macro-cracks

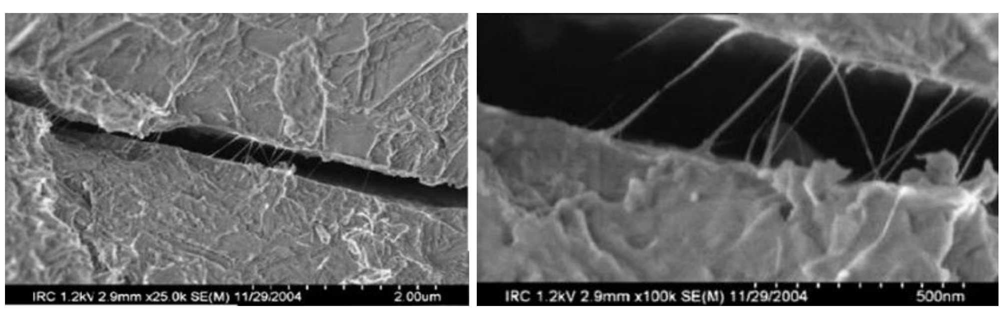


Figure 2.2 Crack Bridging in Cement-CNT Composites (Makar et al., 2005)

Figure 2.1 and Figure 2.2 show the bridging action of fibers in concrete and carbon nanotubes (CNTs) bridging a crack in an electronic scanning microscope (SEM) image respectively. In return, concrete becomes a strain sensor. For different stimulus, these bridging fibers elongate and contract showing the response to its environment. These sensing abilities make the concrete smart enough to be used to monitor its health regarding stress-strain, temperature, pH, moisture, electrical/magnetic responses. The concrete can even obtain an awareness of damage on itself and its surroundings. This property is utilized in Structural Health Monitoring (SHM).

2.3 Nanotechnology and Nano-reinforcement in Cement-Based Materials

National Science Foundation and National Nanotechnology Initiative, defines nanotechnology to have three elements: a) size of material around 100 nanometers, b) should have the ability to measure and transform at the level of nanoscale, and c) properties specific to the nanoscale (Roco 2007). Today nanotechnology has found its application from medical to construction fields. However, the progress is uneven and is in the early stage of its practical exploitation. There have been substantial advances in understanding the fundamentals of nanoscale phenomena in cement including structural and mechanical properties of cement hydration, interfaces in concrete, hydrate phases, the origin of cement cohesion, and mechanism of degradation (Mondal et al., 2007; Sanchez and Sobolev 2010). One of the most innovative applications of nanotechnology in infrastructure construction is by the inclusion of nano-sized admixtures and reinforcements in cement-based materials like carbon nanotubes and nanofibers.

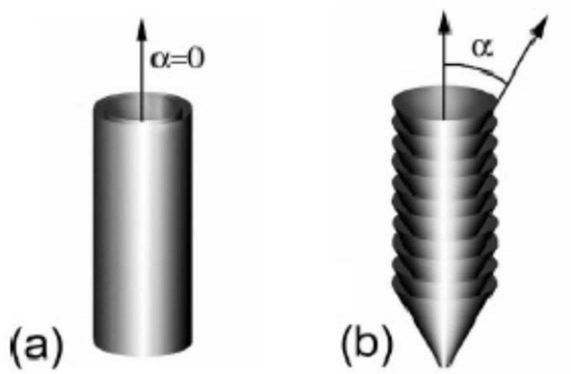


Figure 2.3 Structure of a) CNT and b) CNF (Dume 2007)

Implementation CNTs and CNFs in cement-based materials with its discovery in 1991 (Iijima 1991) because of their unique mechanical, thermal, and electronic properties. They have a very high aspect ratio with a modulus of elasticity and tensile strength in the range of terra-pascals and gigapascal respectively (Salvetat et al., 1999; Makar and Beaudoin 2004; Li et al., 2005; Li, Wang, et al., 2007; Sanchez and Sobolev 2010). CNTs are graphene sheets wrapped around a hollow core whereas, CNFs are graphene sheets arranged as stacked cones, cups, or plates. Figure 2.3 shows the structural difference between CNT and CNF. The stacked structure of CNFs shows exposed edges which increases the surface area with a better bond. Also, CNFs are more accessible to produce and cost less than CNTs. These properties of CNFs have advantageous for the application in cement-based materials. Figure 2.4 shows the CNFs' SEM image.

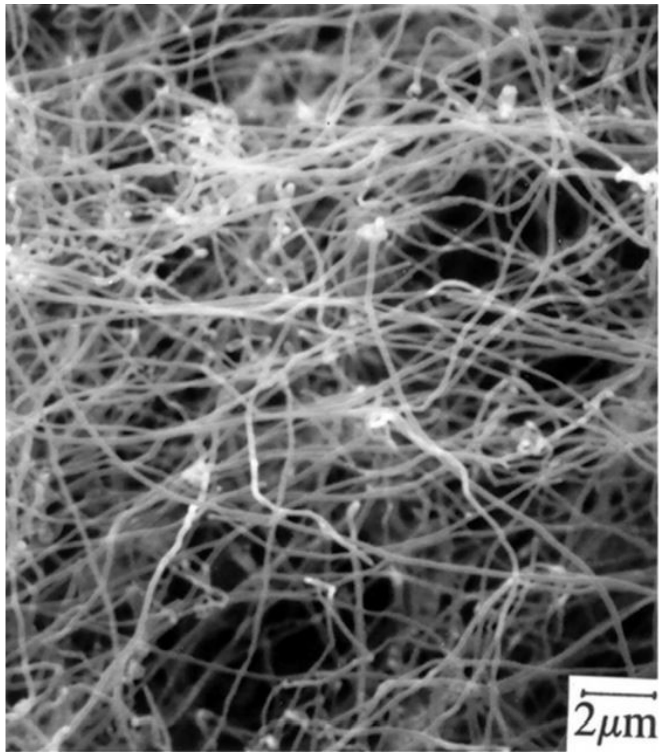


Figure 2.4 Scanning Electron Microscopic (SEM) photograph of the carbon nanofibers (Hong et al., 2017)

Chung (Chung 2005) explained that the well-dispersed CNFs in uniform calcium-silicate-hydrate (CSH) improves the structural and electrical properties of the concrete. But, the well-dispersed CNTs and CNFs is difficult to be observed in cement-based composites as these are inherently hydrophobic and are attracted to one another due to Van der Waals forces. These forces cause the fibers to agglomerate, hindering their dispersion (Baughman et al., 1999, 2002; Hilding et al., 2003; Makar and Beaudoin 2004; Tzeng et al., 2004).

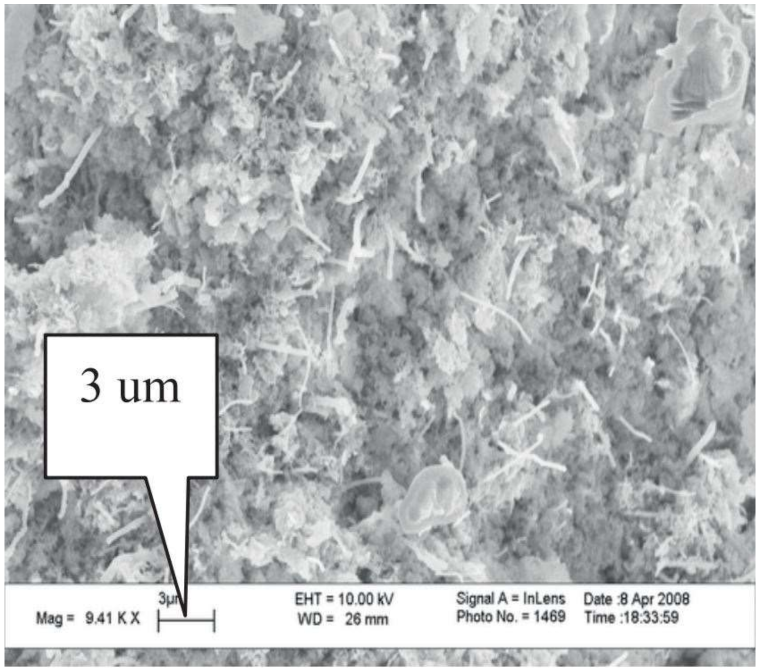


Figure 2.5 Scanning Electron Microscopic Image of Well-Dispersed CNFs in a Uniform Self-Consolidating Cement (9410X Magnification)

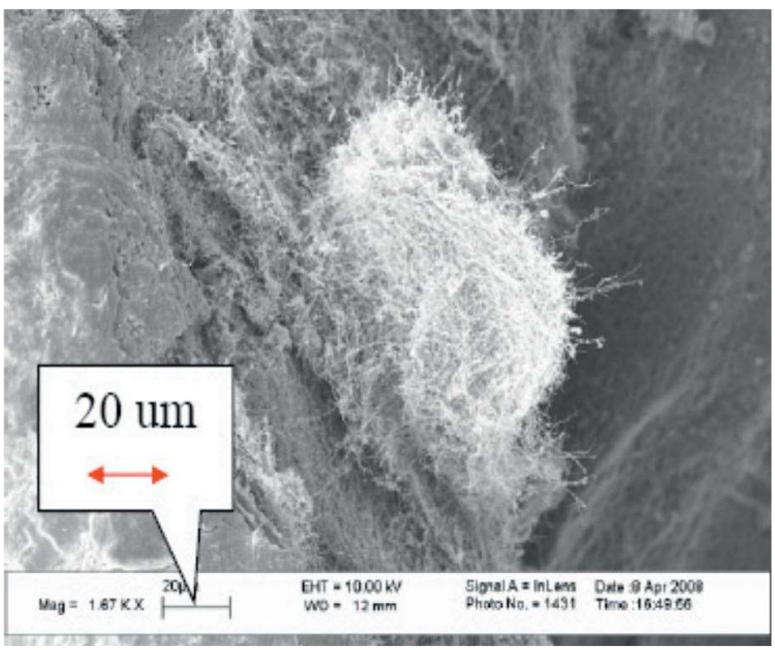


Figure 2.6 Scanning Electron Microscopic Image of CNFs Clump in Normal Cement (1670X Magnification)

Various methods for dispersion of CNTs and CNFs in cement-based composites have been studied in the past with not much success. Chen et al., (Chen and Chung 1993b; Chen et al., 1997) suggested studying mechanical and electrical properties of cement paste as both features are negatively affected by poor dispersion. On this basis, Chen et al., (Chen and Chung 1993b; Chen et al., 1997) showed that the addition of methylcellulose and silica fume dispersion of the carbon microfibers. Gao et al., (Gao et al., 2009) proposed the use of highly workable and self-consolidating concrete (SCC) with a high-range water reducer (HRWR) with well-dispersed CNTs and CNFs compared to significant CNF clumping in specimens made of the normal CNF concrete as shown in Figure. 2.5 and Figure 2.6 respectively.

2.4 Strain Sensing Ability of CNT/CNF Cement-Based Materials and Application

Increasing the strength of concrete has been one of the critical fields of investigation. On the other hand, enhancing the sensing ability of cement based composites is another vast field of research. The sensing ability of these cement-based composites that respond to its environment and the changes in strain, temperature, moisture, pH, and electric or magnetic fields is an area of interest for a significant fraction of scientists and researchers in the concrete study.

CNTs and CNFs cement-based composites qualify as smart materials due to its response to strain and temperature (Yang and Chung 1992; Chung 1995, 2000; Li et al., 2004; Wang et al., 2007; Gao et al., 2009; Howser 2011, 2013, Avinash et al., 2019). The strain sensing ability may be reversible or irreversible. The reversible strain sensing allows dynamic load monitoring and real-time detection of loads on structures. Whereas, irreversible sensing allows structural health monitoring and damage detection. As reversible strain magnitude is smaller than irreversible strain and should be performed in real time, its tracking is challenging (Chen and Chung 1996). CNTs/CNFs cement composites are a better sensor option for reversible strain monitoring as conventional strain sensors are expensive with poor durability.

In 1992, Yang et al., (Yang and Chung 1992) showed a significant decrease in electrical resistivity of mortar containing carbon microfibers. Later Chen et al., (Chen and Chung 1993a) proposed smart concrete with carbon microfibers. These researchers concluded that the electrical resistivity of the concrete increased upon the compressive loading up to approximately one-third the compressive strength of the mortar. Later Chen et al., (Chen and Chung 1996) conducted series of cyclic load test in carbon microfiber mortar as shown in Figure 2.7 concluding that the irreversible permanent damage due to fiber-matrix interface weakening attributed the reversible crack opening and closing with fiber movement.

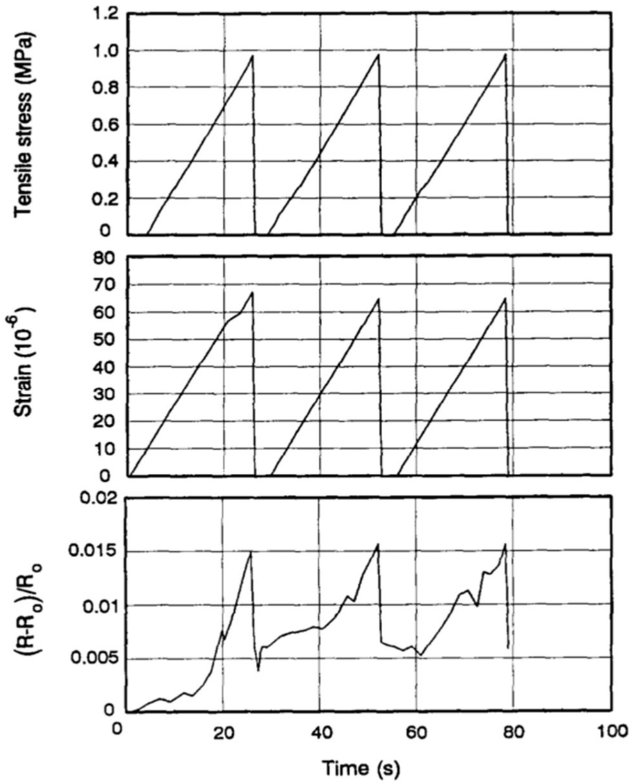


Figure 2.7 Stress, Strain, and Electrical Resistance Variation of a Carbon Microfiber Mortar Composite (Chen and Chung 1996)

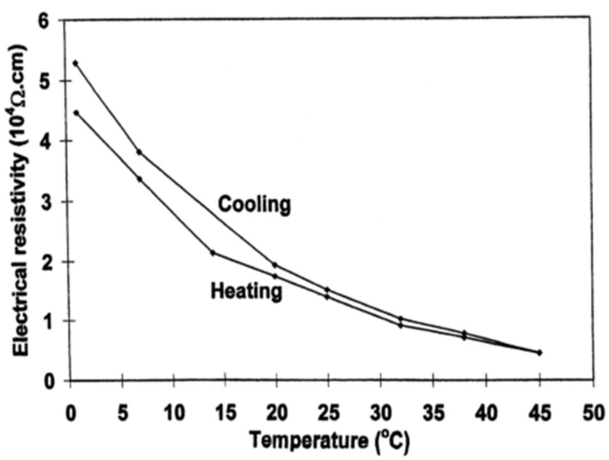


Figure 2.8 Electrical Behavior during the Heating and Cooling of a Carbon Microfiber Silica Fume Cement Paste (Chung 2000)

In addition to strain sensing, carbon fiber composites have been used to monitor temperature as shown in Figure 2.8 (Chung 2000) and create self-healing composites

(Chang et al., 2009; Chung 2004). Chen et al., 2004, studied the effects of hydration and relative humidity on carbon fiber reinforced cement-based composites with inconclusive results. Again in 2010, Han et al., (Han et al., 2010) examined the change in Electric Resistance Variation (ERV) of cement-based materials containing carbon fibers and carbon black during the hydration process. Chen et al., (Chung 1995, 1998, 2000) explained that the short-fiber composites acted as a strain sensor based on the concept of short electrically-conducting fiber pull-out that aids the slight and reversible crack opening. For CNT/CNF fibers of a diameter smaller than the composite crack width, and more conducting than the matrix, have the strain sensing ability independent of their orientation and contact.

Gao et al., (Gao et al., 2009) later studied cylinders with concrete containing CNFs under monotonic loading and observed electrical resistance variation (ERV) up to 80%. Later, Howser et al., (Howser et al., 2011) conducted reversed cyclic loading tests on full-scale columns made up of self-consolidating concrete containing CNFs (SCCNFC) proving concrete containing CNFs can be used as a structural sensor. The electrical resistance showed a significant correlation between peaks in the applied horizontal force, strain and resistance plots for the SCCNFC columns but the little relationship between resistance plots and stress-strain plots for self-consolidating reinforced concrete (SCRC) and self-consolidating steel fiber concrete (SCSFC).

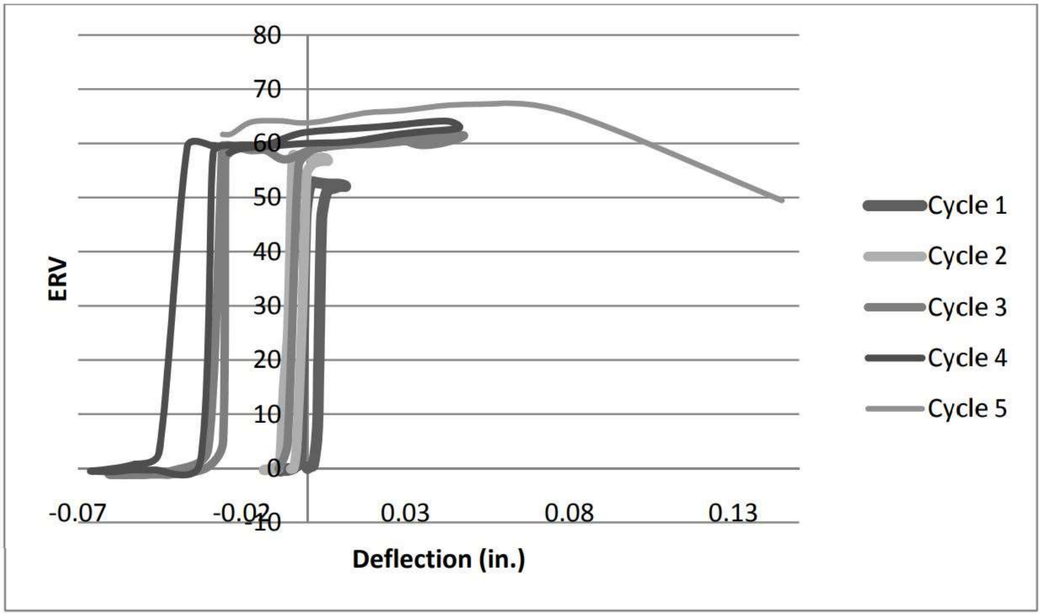


Figure 2.9 SCCNFC Column ERV versus Horizontal Deflection (Howser et al., 2011)

Because of this strong correlation in SCCNFC columns, electrical resistance variations (ERV) were calculated. These ERVs were compared to the deflection at the top of the column. ERV is the electrical resistance minus the initial electrical resistance quantity divided by the initial electrical resistance. Figure 2.9 displays the ERV and deflection at the top of the column match for the first five cycles of the test proving that the SCCNFC can be used as a self-structural health monitoring system when an appropriate dosage of CNFs is mixed into SCC.

2.5 Electrical Response Measurement of Carbon Nanofiber Aggregates

Carbon fibers are electronic conductors with electrons and holes as charge carriers. The electrical response of concrete with carbon fibers in the applied electric field has been studied and utilized in structural health monitoring by numerous scientists. The electrical flow in CNF reinforced cement is due to electrons and ions. Wen and Chung (Wen and Chung 2006) explained that the ionic conductivity in dominant in the water-saturated state whereas, electronic conductivity is dominant in the dry state. Most cement scientists assume that ionic conduction is dominant over electronic conduction in carbon fiber reinforced cement composites because of the cement matrix. Further, a decrease in the free water content (for example, by drying) increases the electrical resistivity of cement composites irrespective of the presence of CFs.

There are two theories that are employed to interpret the electrical conductivity of carbon fibers (CF) reinforced cement composites: percolation theory and tunneling effect theory. In percolation theory, adjacent CFs physically contact and form geometrically connected network conducting the electrons and ions when fiber content is greater than the percolation threshold. When the CF content is less than the percolation threshold, the CFs cannot form a geometrically connected network; the electrical response is dominated by the tunneling effect (Wen and Chen 2001).

Two different techniques, namely AC and DC measurements are used to determine the electrical response of concrete. In both of these techniques surface and embedded probes are used, and measurements can be done both with two and four probe methods.

The four-terminal technique for the DC electrical resistance measurement of concrete for electrical sensing is implemented since long (Chen and Chung 1993; Bontea et al., 2000, Chen et al., 2004; Chung 2001). The four-probe method is preferred over the two-probe method for measuring small resistances, as there is little or no potential drop at voltage contacts that are distinct from the current contacts. However, for measuring high resistance like in case of dry CF cement composites, the two-probe method is quite commonly used, particularly in AC impedance measurement (Dotelli and Mari 2001). Also, in DC measurements, the resistance obtained includes contact resistance which also changes with applied load/stresses. To eliminate the contact resistance, i.e., to study the actual sensing ability of CNFs reinforced cement composites, AC measurements of high frequency is used.

In the DC circuit, the ions gather around at one end of the specimen causing electric polarization. The polarization results in a voltage associated with the resulting electric dipole within the specimen. This voltage affects the flow of charges, hence causing the measured resistance/resistivity to increase (Cao and Chung 2004; Wes and Chung 2001). Under AC condition, the ions move back and forth as the voltage polarity repeatedly changes, thereby avoiding polarization. However, Concrete is a heterogeneous mixture of several different phases and interfaces between those phases making the overall electrical response frequency dependent (F. Reza et al., 2004).

In extended work of Gao et al., Howser et al., (Howser et al., 2011) tested full scale reinforced concrete columns containing CNFs in four terminal configurations of the DC circuit. Due to the success of Gao et al., (Gao et al., 2009) and Howser et al., (Howser et al., 2011) demonstrating that the self-consolidating carbon nanofiber concrete (SCCNFC) can be used as a strain sensor, carbon nanofiber aggregate (CNFA) was developed. Howser et al., (Howser et al., 2013) used four probe method to utilize the self-sensing capability of CNFAs. In CNFA, four probe resistance measurement technique was accomplished by supplying the current to a pair of outer terminals current lead (1 and 4) measured across a known resistor for a voltage source, and the voltage drop was measured across the inner terminals (2 and 3) as shown in Figure 2.10.

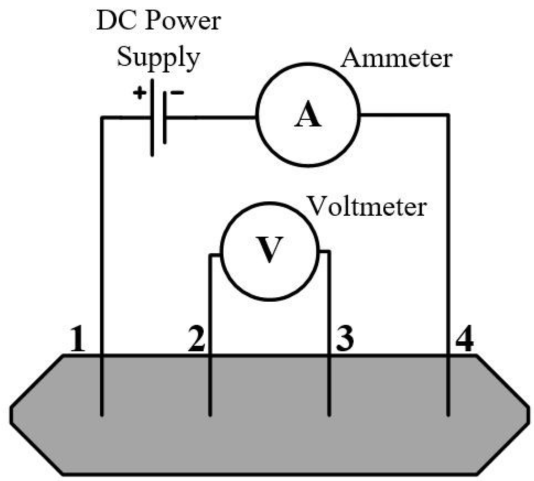


Figure 2.10 Schematic for Four Point Probe DC Resistance Measurement

The electrical resistance variation (ERV) was calculated as the percentage change in resistance under stimuli using equations as:

$$V = IR \quad \text{and} \qquad \text{Equation 2.1}$$

$$ERV = \frac{R_i - R_0}{R_0}, \qquad \text{Equation 2.2}$$

where,

V = Voltage (in Volts),

I = Current (in Amperes),

R = Resistance (in Ohms),

ERV = Electrical Resistance Variation,

R_i= Resistance at step I, and

R_0= Initial Resistance.

CNFAs developed by Howser (Howser 2013) had four steel meshes embedded inside the carbon nanofiber mortar as shown in Figure 2.11 The meshes had prongs that were soldered to the electrical wires which were then connected to the data acquisition. For optimization, the CNFA is sized as 1.00 in. (25.4mm) by 1.00 in. (25.4 mm) by 1.00 (25.4mm) cube (Howser 2013).

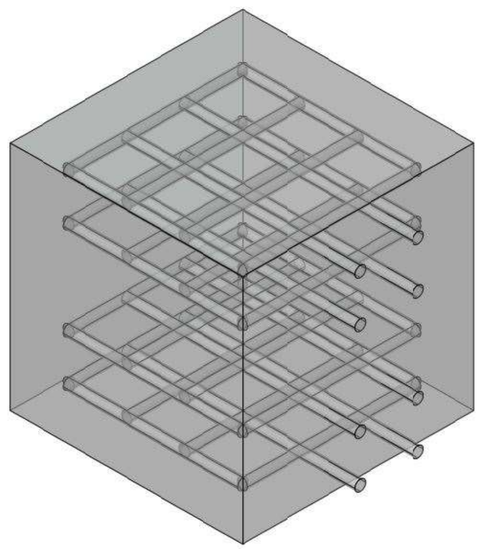


Figure 2.11 Schematic of Carbon Nanofiber Aggregate (CNFA) with Four-Mesh

2.6 Summary

Well-dispersed carbon nanofibers (CNFs) in concrete improves the strength of concrete while the excess concentration of CNF leading to poorly dispersed CNF clumps has a negative impact in composite's strength. CNFs in concrete not only increase the strength but also aids to ductility, stiffness and electrical conductivity by bridging action of nanofibers between the cracks at the micro level. Literature review shows that the highly workable self-consolidating concrete (SCC) can yield well dispersed CNF concrete composite.

Gao et al., (Gao et al., 2009) were successful in demonstrating self-consolidating carbon nanofiber concrete (SCCNFC) has an ability for stress-strain monitoring and measuring the damage in structure thus can be implemented as a reversible strain sensor. Later Howser et al., (Howser et al., 2011) also disclosed SCCNFC's could be used as structural sensors with full-scale structural testing at the University of Houston. Howser et al.'s test showed that the electrical resistance readings of the SCCNFC applied force and the strain peaks in the concrete whereas the electrical resistance readings of the self-consolidating reinforced concrete (SCRC) and self-consolidating steel fiber concrete (SCSFC) specimens showed that these could not be used as a reversible strain sensor. This showed that the appropriate dosage of CNFs in SCC could be implemented in structural health monitoring (SHM).

With this success, Howser (Howser 2013) developed 1.00 in. (25.4mm) by 1.00 in. (25.4 mm) by 1.00 (25.4mm) cube made up of SCCNFC called as carbon nanofiber aggregate (CNFA). Howser et al.'s tests showed that CNFA using a four-probe DC resistance technique could be used to monitor localized damage and stress-strain strain in structure economically.

CHAPTER 3. CARBON NANOFIBER AGGREGATE IN DC AND AC CIRCUITS

3.1 Introduction

The University of Houston successfully implemented self-consolidating carbon nanofiber concrete (SCCNFC) as strain sensor (Gao et al., 2009; Howser et al., 2011) leading to the development of carbon nanofiber aggregate (CNFA) for localized strain monitoring in concrete structures (Howser et al., 2013). This development of CNFA led to the economical strain monitoring of structures as constructing the entire structure with SCCNFC would cost 20 times more than normal concrete.

The CNFA is a cubic structure (25.4 mm. x 25.4 mm. x 25.4 mm.) made up of carbon nanofiber (CNF) mortar which can sense localized stress/strain where it is embedded in the structure. This chapter describes the elaborative and comparative study of two and four-probe CNFAs in DC and AC circuits. Figure 3.1 shows the schematic CNFA with two and four meshes.

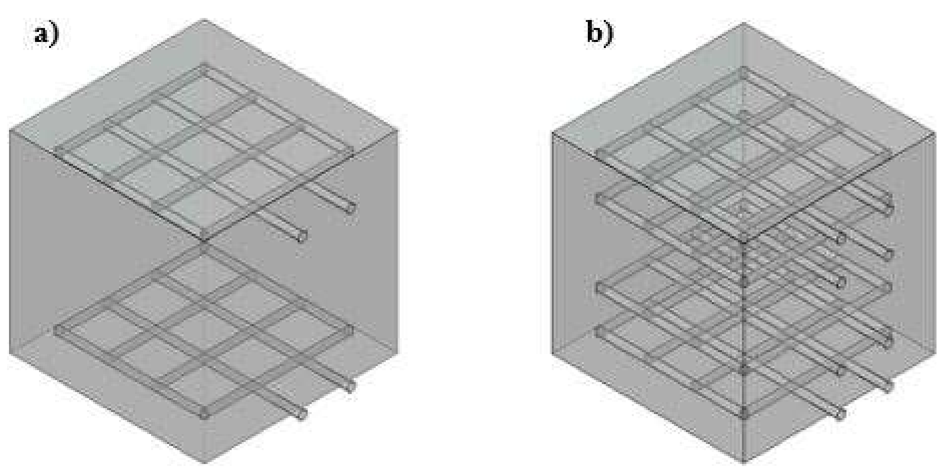


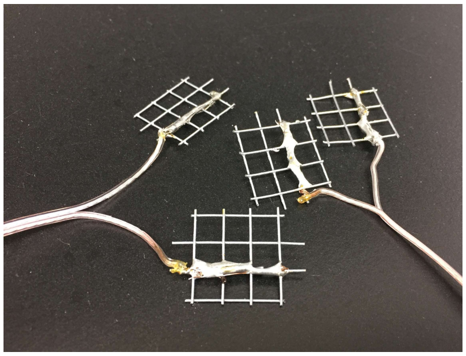
Figure 3.1 Schematic of CNFAs a) Two Mesh and b) Four Mesh

3.2 Development of Carbon Nanofiber Aggregate (CNFA)

The self-sensing response of CNFAs can be measured by the change in electrical resistance or impedance of two and four wire arrangements in DC and AC circuits as discussed in the literature review. The probes are made of steel meshes embedded in CNFA at a predefined distance. These meshes have extended prongs that are soldered to the electrical wire which is connected to the external circuit and data acquisition.

CNFA were size optimized with size limitation on coarse aggregates defined by the American Concrete Institute (ACI) (ACI 318 2008) as they had to be embedded into large concrete structures without any casting problems to minimize honeycombing and ensuring proper encasement of reinforcement. Also, CNFAs had to be large enough to easily place steel meshes within aggregate without touching each other. The optimal CNFA size was chosen to be 25.4 mm. x 25.4 mm. x 25.4 mm. (1.0 in. x 1.0 in. x 1.0 in.) satisfying all mentioned requirement (Howser et al., 2013).

The mesh embedded in CNFAs were 23 gauge 6.35 mm. x 6.35 mm. (0.25 in.x 0.25in.) welded galvanized steel hardware cloth. Then the cloth was cut into 19 mm. x 19 mm. (0.75 in. x 0.75 in.) square with four extending prongs as shown in Figure 3.2. 24-gauge copper wire was soldered to one of the prongs of each mesh. The adopted spacing between the meshes is shown in Figure 3.3.



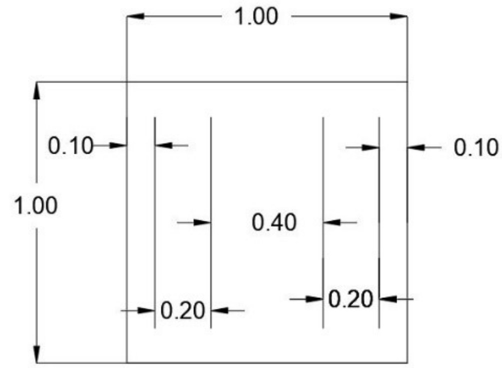


Figure 3.2 Four Meshes with Soldered Wire Figure 3.3 Mesh Spacing (Units: in.)

Another end of soldered prongs is inserted into the holes at the bottom of the metallic framework to hold the meshes in place as shown in Figure 3.4. The sides of the formwork were then assembled into place as shown in Figure 3.5. The prongs on the top of vertical mesh were slid into grooved cut into top formwork ensuring the correct spacing between meshes during and after casting of CNF mortar.

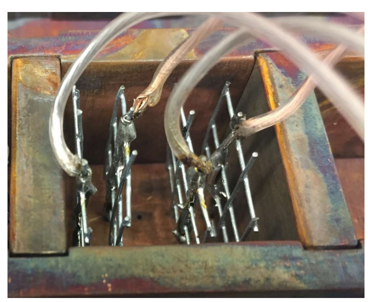


Figure 3.4 Meshes Inserted Vertically into Formwork for 4-Probe Response Measurement

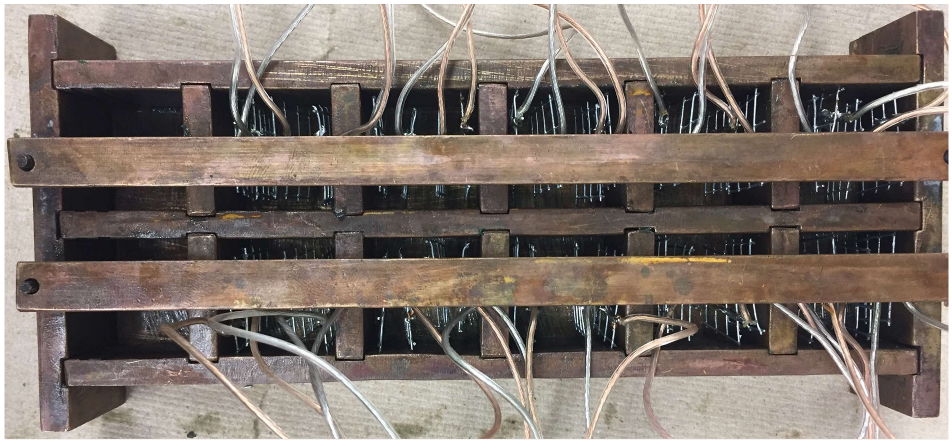


Figure 3.5 Meshes into Complete Formwork for 4-Probe Response Measurement

CNFA mortar is the typical mortar with different admixtures. The first and primary admixture is carbon nanofiber (CNF) which allows the mortar to have the ability of strain sensing under stimulus (Chen and Chung 1996). The second admixture is superplasticizer otherwise known as high-range water reducer (HRWR) that is capable of creating self-consolidating concrete (SCC) which also aids in the dispersion of fiber as shown by Gao et al., (2009). This would let the mortar to flow under its weight flowing around the mesh without voids with no mechanical vibration. The third admixture is silica fume as these can enhance CNF dispersion in cement-based material (Chen and Chung 1993b; Chen et al., 1997). The fourth admixture is Krystol Internal Membrane (KIM) which is a hydrophilic crystalline admixture used to create permanently waterproof concrete. The material properties used in the mix are as follows:

a) Fine Aggregate: Quikrete ® premium play sand ® which is a specially graded, washed, dried, and screened was used as fine aggregate.
b) Cement: Martin Marietta's ASTM Type III Portland cement was chosen for high early setting strength and speedy production of CNFAs.

c) Carbon Nanofibers: PR-19-XT-LHT-OX by Pyrograf ®-III Product Inc. were used in this study. PR-19 has a diameter on average of about 150 nanometers and has a chemical vapor deposited (CVD) carbon layer on the surface of the fiber over a graphitic tubular core fiber (catalytic layer). These were processed with an improved de-bulking method (labeled as XT in the product code) that creates loose structures of the carbon nanofiber bundle. The LHT grade implied that the production of these fibers by heat-treating at 1500°C. This treatment converted any chemical vapor deposited carbon present on the surface of the fiber to a short-range ordered structure. The inherent conductivity of the fiber is thus increased. The OX designation is shown that the produced is oxidized making it easy to mix and disperse with water due to ionic and hydrogen bonds between CNFs and water molecules. The specific gravity, diameter, and length of the fibers are 0.0742, 149 nm (5.87e-6 in.), and 19 μm (7.48e-4 in.) respectively. This CNF has an aspect ratio of 128. Gao et al., (Gao et al., 2009) completed an extensive study on various CNFs and found PR-19-XT-LHT-OX fibers to have the best self-sensing behavior in concrete.

d) High Range Water Reducer (HRWR): Master-Glenium 3400 is a poly-carboxylate admixture from BASF Chemicals Co was used as HRWR in the mix. SCC produced with this admixture achieves significant higher early compressive strength compared to plain concrete.

e) Silica Fume: Master-Life SF 100 was used as a silica fume in the mix. It is a dry, densified silica fume admixture which aids in the dispersion of CNFs and production of strong and durable concrete.

f) Waterproofing Admixture: Krystol internal membrane (KIM®) was used in a mix to lower the permeability of concrete, and is used in place of the surface applied waterproofing membrane. When added to concrete, it reacts with water and un-hydrated cement particles to form insoluble needle-shaped crystal that fills the capillary pores and micro-cracks in the concrete and block the pathways for water penetration.

The mortar mixing is unique and is a hybrid of the mixing procedure proposed by Liao et al., (Liao et al., 2006) for a high-performance self-consolidating steel-fiber reinforced concrete mix and mixing procedure proposed by Gao et al., (Gao et al., 2009) for a self-consolidating CNF concrete. Liao et al. proposed to premix water and the chemical admixtures and then add to the cement, fly ash and fine aggregate in several steps producing homogenous slurry before adding fibers and coarse aggregates. However, Gao et al., suggested the premixing of water, chemical admixtures and CNFs followed by addition to the cement, fly ash, fine and coarse aggregate in one step. Howser (Howser 2013) recommended the hybrid mixing procedure. The similar mixing procedure with simple modification is suggested as follows.

a) Pour CNFs, HRWR, and three-fourths of weighted water into a blender in sequence and blend for 30 seconds. The water is added at last to make sure all weighted CNFs and HRWR is utilized in mixing.
b) Remove the liquid mix into a separate container.
c) Pour approximately one half of the sand, all the cement, the silica fume, the KIM, and the remaining half of sand in the same sequence into a blender and dry mix for about a minute.

d) Use a hand or tool to scrap the sides and bottom and hand mix homogeneously.

e) Pour about one half of the liquid mixture of CNF, HRWR, and three-fourths water and mix for about 45 seconds until mixture looks like wet granulated sugar.

f) Pour another half of liquid into the mortar mix and blend for 30 seconds. Hand or tool can be used to scrap sides and bottom and mix homogeneously.

g) Pour remaining one-fourth of water into a container that had a liquid mix. Cleaning that container with that water, pour the liquid into the mix again and blend for the next 30 seconds. This will ensure all weighted HRWR and CNFs is utilized in the mix. The mix now will look like a semi-fluid mixture. Additional water should be avoided as it makes fibers float on the surface, making the non-homogenous distribution of CNFs in the mix.

h) Pour the mortar into the greased (with grease or WD-40) assembled formwork with all the meshes inserted into the place as soon as possible. Self-consolidating mortar flows by its weight with no mechanical vibration. The external vibration may misalign the meshes.

i) Remove the aggregates from the formwork after 72 hours and cure in water for 14 days. Figure 3.6 shows the different stages of CNF mortar mix and developed CNFAs.

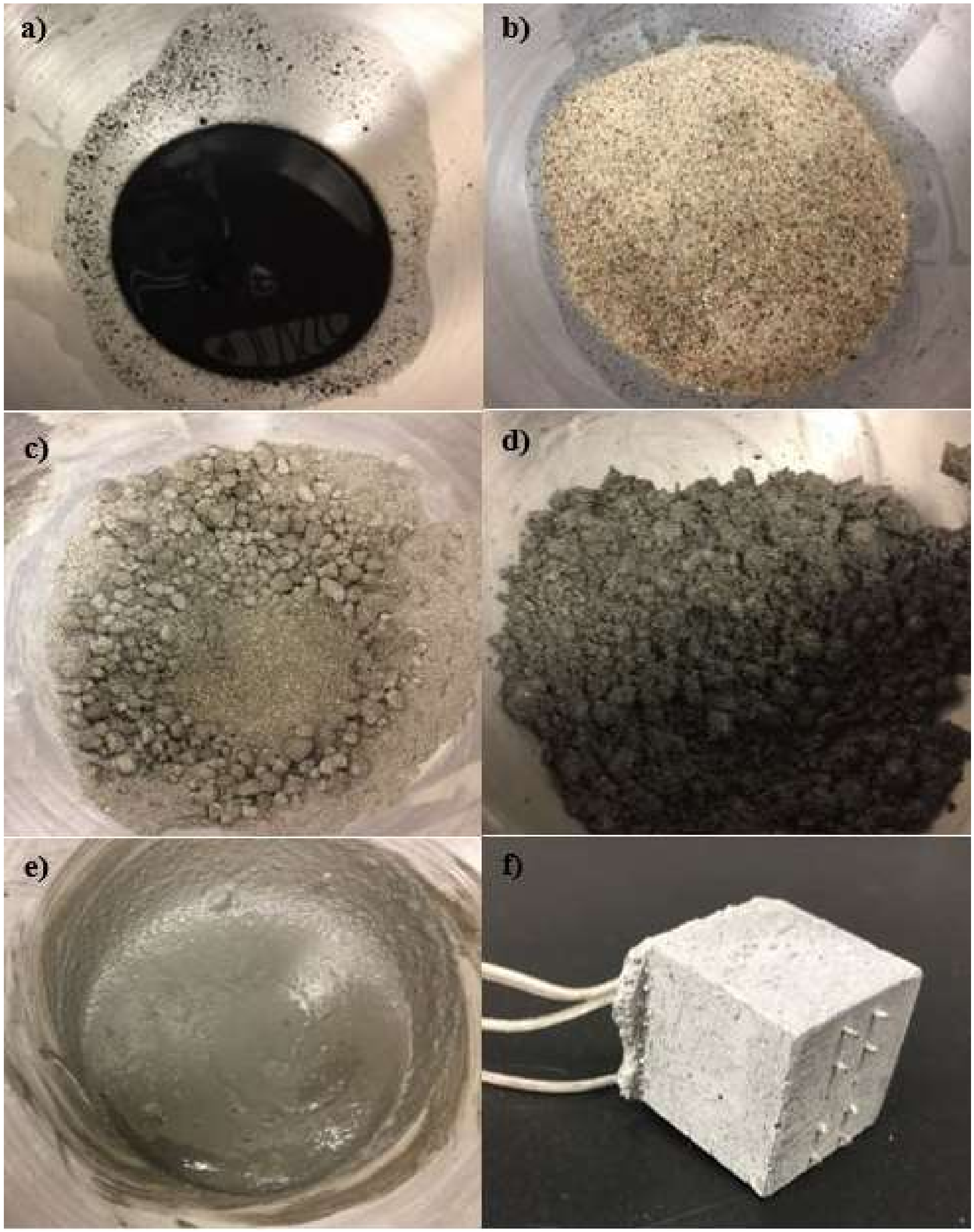


Figure 3.6 Mortar Mixing Procedure a) Wet Mix of CNFs, HRWR, & Water; b) Dry Mix of Sand, Cement, Silica Fume, & KIM; c) & d) Mixing of Dry and Wet Mix in different steps; e) CNFA Mortar Mix; f) 4-Probe CNFA after 14 Days

3.3 Circuit Optimization for CNFA Study

The electrical properties of CNFAs depend on many factors: type and quantity of CNFs, quality of CNF dispersion, the water content in the mix, and circuit type/setup to measure response. This topic is mainly focused on finding the circuit configuration that gives accurate and reliable response measurement for CNFAs with and without the stimulus.

Howser et al., (2011), through the series of over 100 CNFAs tests under compression, demonstrated the use of four probe resistance measurement technique in DC circuit to measure the change in ERV as shown in Figure 3.7. A similar circuit was used by various researchers utilizing DC circuits (Chen and Chung 1993; Bontea et al., 2000, Chen et al., 2007; Chung 2001; Gao et al., 2009). Howser et al., (Howser et al., 2011) used Keithley Source Meter SMU Instruments used for the DC resistance and electrical resistance variation (ERV) measurements as shown in Figure 3.8.

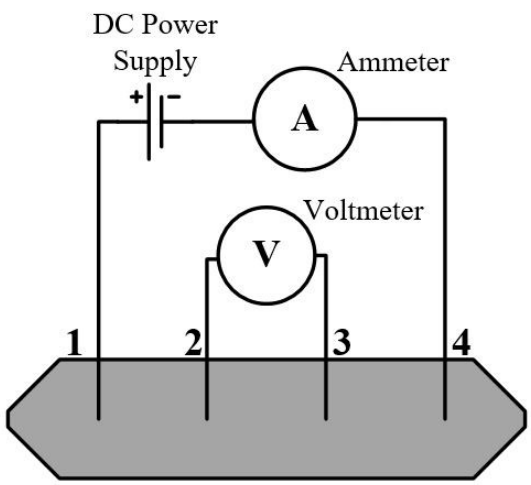


Figure 3.7 Four Probe DC Resistance Measurement

Figure 3.8 4-Probe DC Resistance Measurement Circuit in Keithley Source-meter

To study the behavior of CNFAs using the four-probe DC resistance measurement technique as shown in Figure 3.7 and Figure 3.8, the resistance of CNFAs were observed without a loading. It was expected that the change in resistance would not have a significant change with no stimuli; unexpectedly, that was not the case. The results indicated that the electrical DC resistance of CNFAs changed with time without any stimuli as shown in Figure 3.9. Within a time of 20 minutes, the 4-probe DC resistance of the same specimen changed by almost 5 M-Ohms (7.5 M-Ohm to 12.5 M-Ohm), i.e., ERV~ 66% without any stress and stimuli independent to the dosage of CNFs. The change in resistance was observed to be faster initially which slowed down with increasing time, and this change was not stable even after half an hour of no-load observation. This showed that the ERV measurements for a CNFA specimen using 4-probe DC technique under any stimuli or stress would not be reliable as it changes on its own with time even without any load. This might be because of the electrical polarization effect discussed in the literature review.

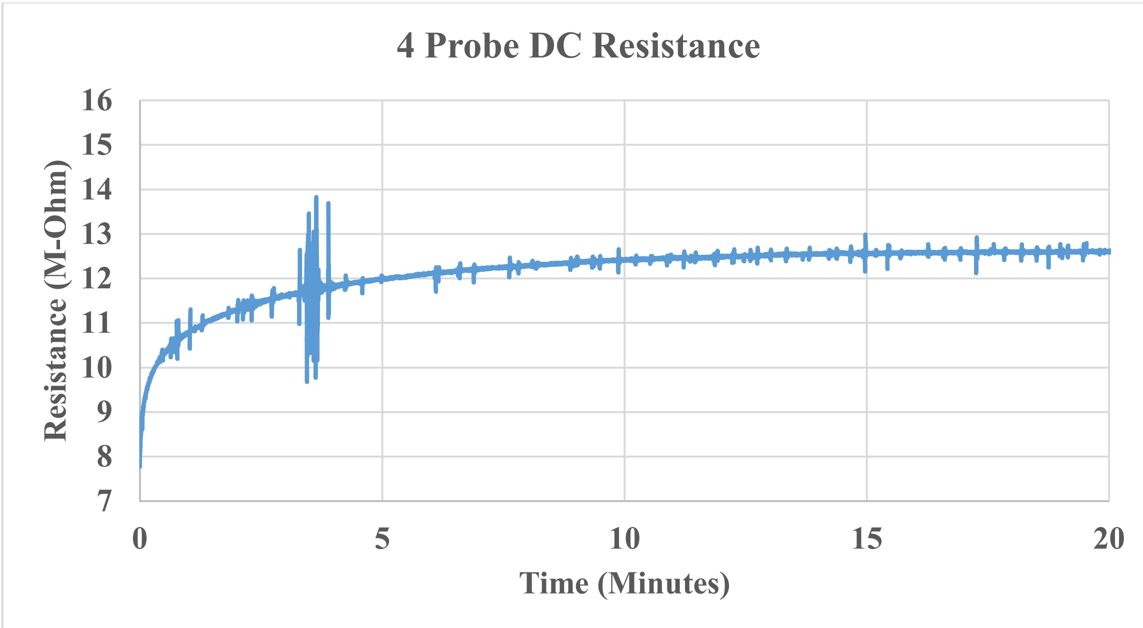


Figure 3.9 Variation of 4-Probe DC Resistance of CNFA with Time in No-Loading

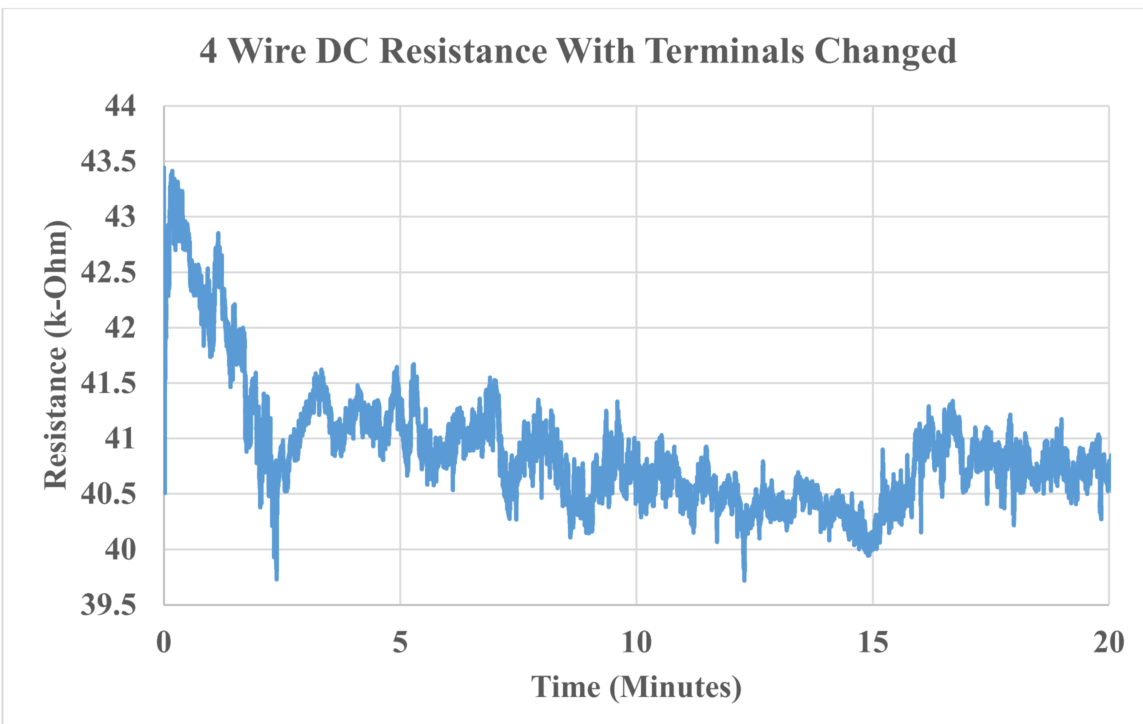


Figure 3.10 Variation of 4-Probe DC Resistance of CNFA with Time in No-Loading when Terminals Changed

To check the terminal sensitivity of 4-wire DC measurement, the current probe of CNFA was changed (Force High to Force Low and vice versa) followed by the change in voltage probe (Sense High to Sense Low and vice versa) i.e., maintaining Figure 3.8 configuration by changing terminals of resistor (CNFA in our case). Figure 3.10 shows the 4-probe DC resistance measurement after the terminal change. After changing the terminals, the resistance of the same CNFA specimen was in the range of k-Ohms (M-Ohms previously), and this was still changing with time without any stimuli or load (now decreasing). The total range of resistance variation in the 4-probe system is thus from around 40 k-Ohm to 13M-Ohms for different terminal configuration for same CNFA without external stimulus.

Figure 3.11 2-Probe DC Resistance Measurement Circuit in Keithley Source-meter

The CNFAs were then studied in 2-probe DC resistance measurement technique without any loads with Figure 3.11 configuration. The DC resistance is changing from 1.4 k-Ohm to 7.8 k-Ohm within 20 minutes without any stress and stimuli independent to the dosage of CNFs. The change in resistance was observed to be faster initially which slowed down with increasing time, and this change was not stable even after half an hour of no-load observation. This again showed that the ERV measurements for a CNFA specimen using 2-probe DC technique under any stimuli or stress would not be reliable as it changes on its own with time even without any load. This might again be because of the electrical polarization effect discussed in the literature review.

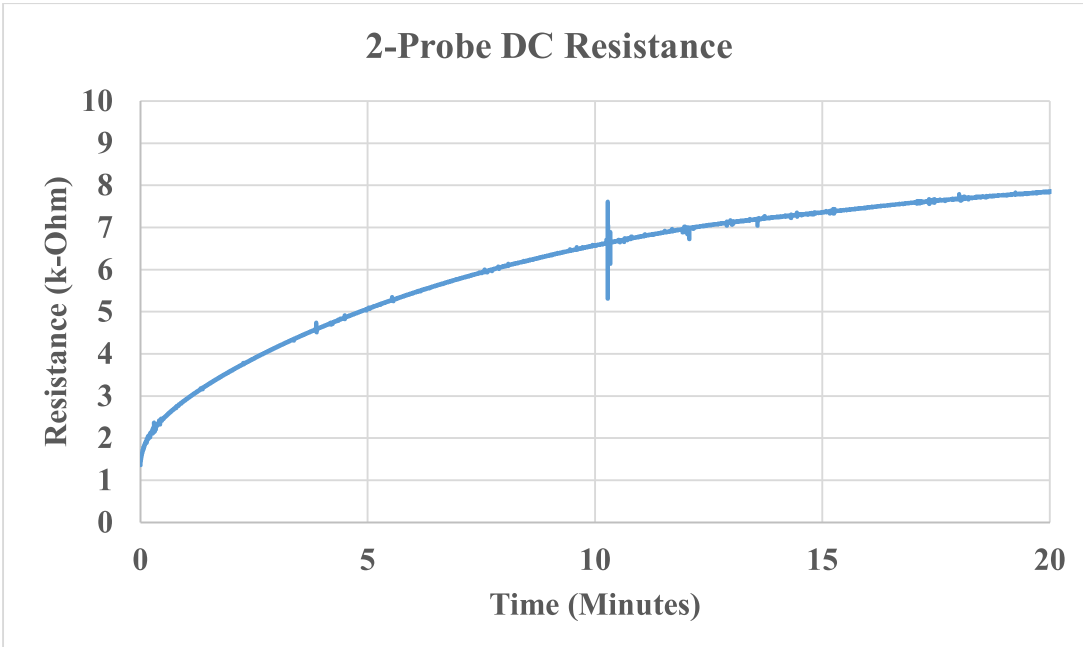


Figure 3.12 Variation of 2-Probe DC Resistance of CNFA with Time in No-Loading

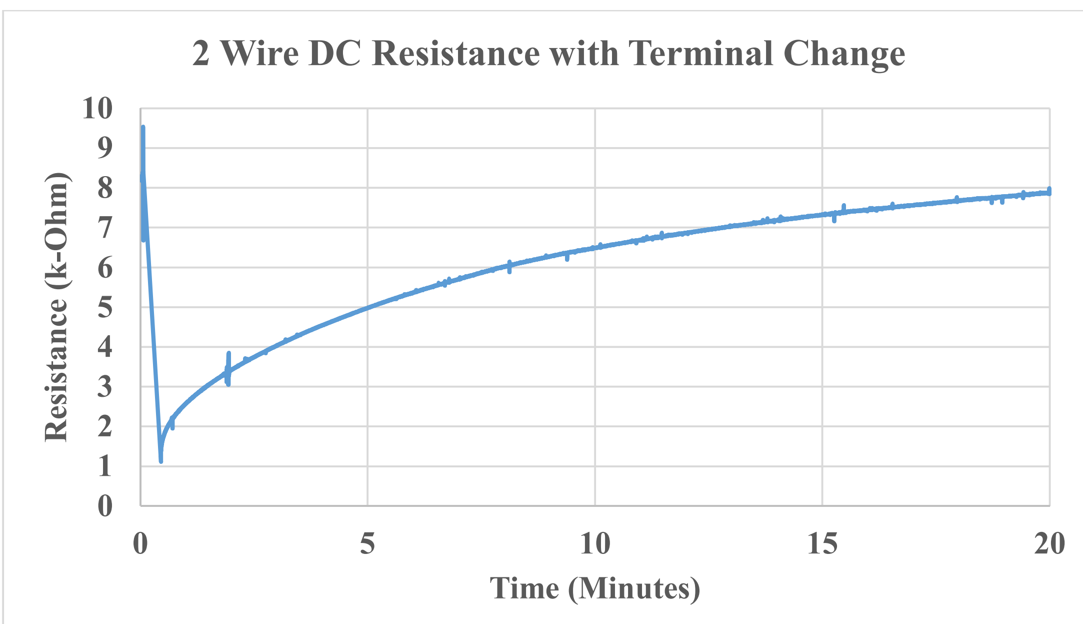


Figure 3.13 Variation of 4-Probe DC Resistance of CNFA with Time in No-Loading when Terminals Changed

Again to check the terminal sensitivity of 2-wire DC measurement, the current probe of CNFA was changed (Force High to Force Low and vice versa), i.e., maintaining Figure 3.11 configuration by changing terminals of the resistor (CNFA in our case). Figure 3.13 shows the 2-probe DC resistance measurement after the terminal change. After changing the terminals, the resistance of same CNFA specimen dropped and increased again in the range of k-Ohms (k-Ohms before terminal switch also), and this was still changing with time without any stimuli or load (now decreasing). The total range of resistance variation in the 2-probe system is thus from around 1 k-Ohm to 9 k-Ohms for different terminal configuration for same CNFA without external stimulus.

All the above study aids to the concept of electric polarization. The charge accumulated in the first terminal configuration is discharged when the terminal is changed, decreasing the resistance with time till next polarization starts in the opposite direction increasing the resistance again. For reliable and accurate stress sensing, it should be noted that, without the stable steady-state response, i.e., a unique ERV for unique strain for a CNFA, the study of ERV with varying stress cannot be correctly estimated. Thus, it was necessary to look for alternatives, as the study of ERV in DC circuit would not lead to correct stress-strain monitoring of CNFA embedded structures in both 4-probe and 2-probe configuration.

This led to the study CNFAs in AC circuit as an alternative to find a stable, steady state for each unique load/strain. The AC circuit was introduced for CNFA to observe the steady-state response. Figure 3.14 shows the time-dependent study of CNFA's impedance under the no-loading stage for various frequency from 1Hz to 500KHz of AC. Two probe CNFAs were selected for impedance measurement with varying frequencies on unloaded conditions. CH Instruments Model 600E Series electrochemical analyzer/workstation with a unit AC amplitude of 0.5V was used as an input for the measurements.

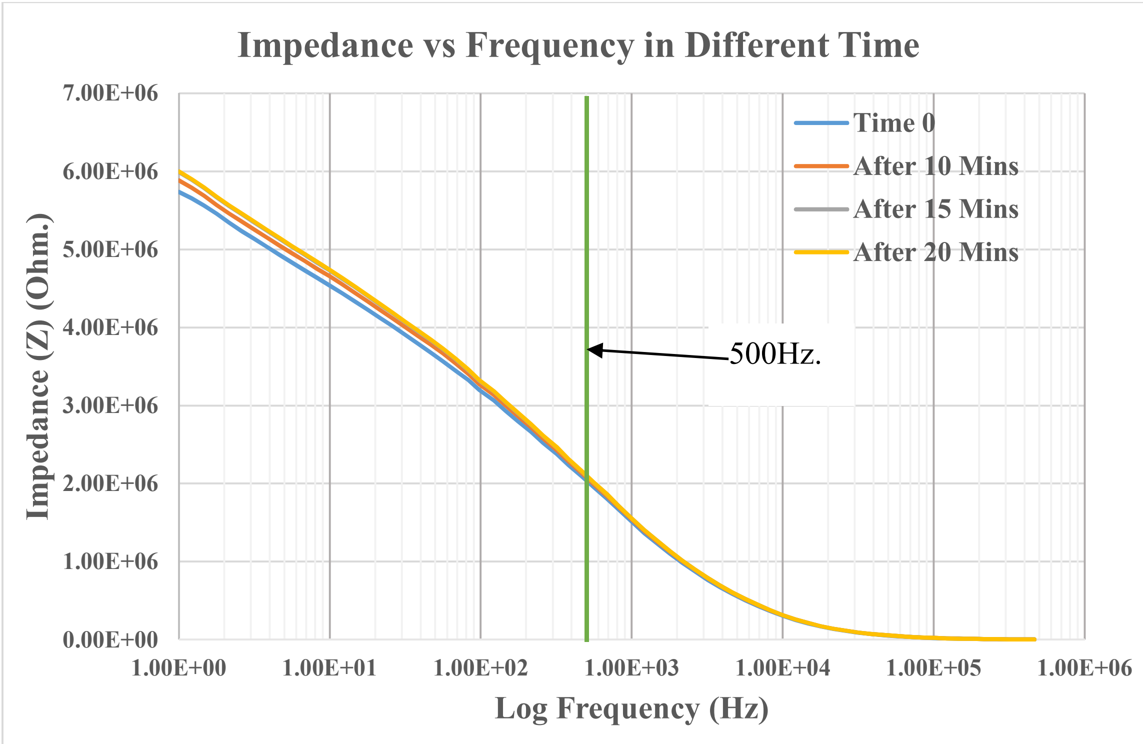


Figure 3.14 Variation of 2-Probe AC Impedance of CNFA with Time in No-Loading for Different Time Intervals

The results indicated that the electrical impedance of CNFAs did not change significantly with time in the absence of any stimuli as shown in Figure 3.14. Within a time of 20 minutes, the 2-probe impedance of the same specimen changed only within few K-Ohms for lower AC frequency while the change was negligible for higher frequencies of AC. This showed that the electrical impedance variation (EZV) measurements for a CNFA specimen using 2-probe AC technique under any stimuli or stress would be reliable for higher frequencies (>500 Hz.) of AC as it does not change significantly on its own with time. This might be because, under AC condition, the ions move back and forth as the voltage polarity repeatedly changes, thereby avoiding polarization.

Again to check the terminal sensitivity of 2-wire AC measurement, the positive and negative terminals of the same CNFA was switched. Figure 3.15 shows the 2-probe AC impedance measurement after the terminal change. After changing the terminals, the impedance of the same CNFA did not change significantly with time without any stimuli or load. Impedance for lower frequencies changed in small magnitude, but for higher AC frequency (>500 Hz.) there was no change in electrical impedance before and after terminal switching.

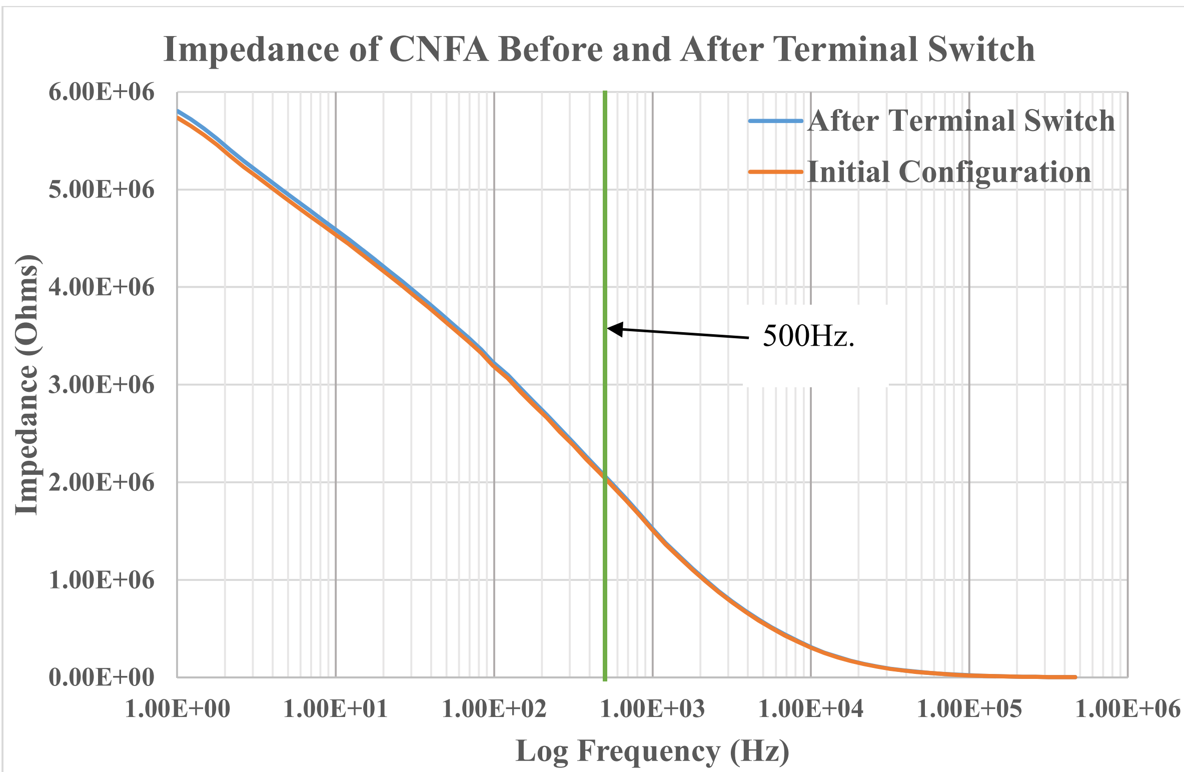


Figure 3.15 Variation of 2-Probe AC Impedance of CNFA in No-Loading with Terminal Change

In the AC circuit, the impedance of CNFA is frequency dependent. This is because concrete is a mixture of several different phases and interfaces between those phases making the overall electrical response frequency dependent (F. Reza et al., 2004). Finding the optimum frequency for the AC circuit that gives maximum response for stimuli is necessary. Chapter 4 explains the detailed study for AC frequency optimization and optimum CNF content for maximum CNFA response in the 2-probe AC impedance measurement technique.

3.4 Summary

A carbon nanofiber aggregate (CNFA) with two and four probes (wire meshes) was developed. The CNFA is a cubic structure (25.4 mm. x 25.4 mm. x 25.4 mm.) made up of carbon nanofiber (CNF) mortar. The behavior of CNFA in AC and DC circuits were studied. The response of CNFA was measured in terms of electrical resistance and impedance. The CNFA were studied in no-loading study-state and terminal switching. It was observed that due to the electrical polarization effect, in DC resistance measurement was not stable and continuously was increasing with time. When the terminals were switched/changed the resistance of CNFAs decreased and increased later for both 4-probe and 2-probe CNFAs. For AC configuration, the 2-probe CNFAs were studied under no-load steady state and terminal switching. In the AC circuit, the electrical impedance of CNFAs did not change with time when no stimuli were subjected. There was very little change in lower AC frequencies which later became very insignificant for higher frequencies, i.e., greater than 500 Hz. The effect of the terminal change was also very small for lower frequencies which again became insignificant for higher AC frequencies, i.e., 500 Hz. This also showed the frequency dependent electrical response of CNFAs, higher AC frequencies (greater than 500 Hz.) are more reliable for response study of CNFAs under stimuli.

CHAPTER 4. OPTIMIZATION OF CARBON NANOFIBER AGGREGATE

4.1 Introduction

The carbon nanofiber aggregates (CNFAs) are 25.4 mm cubes (1.00 in) whose main target for development in 2013 was for strain sensing (Howser et al., 2013). The CNFAs could monitor localized damage and stress-strain in the embedded reinforced or prestressed concrete structures. The high cost associated with making the entire self-sensing with CNFs led to the development of CNFAs. Howser and Mo (Howser and Mo, 2013) utilized the self-sensing capability of CNF mortar by measuring the change of DC electrical resistance under stimuli using four-probe configuration. As discussed in the previous chapter, AC impedance variation using two-probe configuration is more stable and reliable to be implemented in real time structural health monitoring of structures. This chapter studies for the selection of an optimum frequency to be used in the AC circuit for measurement of impedance variation under stimuli and finding the optimum CNF content that gives the maximum response under stimuli.

4.2 Frequency Optimization

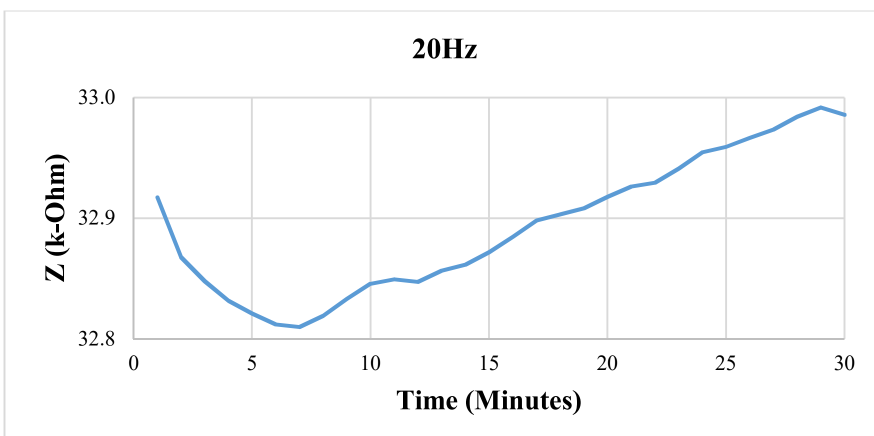
A study on the AC frequency for impedance change was carried out to discover the optimum frequency to be used in CNFAs response study. As the impedance of CNFAs is frequency dependent which will simultaneously lead for electrical impedance variation to be frequency dependent. As explained in chapter 3, the steady-state response of AC impedance was stable than DC resistance for same CNFAs, over 75 CNFAs were tested with varying frequencies of AC circuit in no loading stage to find the most stable steady-state response of CNFAs.

For the frequency optimization, all CNFAs studied contained CNF being 0.7% of the weight of cement. This CNFAs was selected because Howser (Howser and Mo, 2013) showed that CNFA having CNF concentration 0.7% of the weight of cement had maximum DC electrical response on loading. After casting, each of the specimens was cured for 14 days. After 14 days, the specimens were air dried for 24 hours. To remove all access moisture, they were oven dried for 24 hours at 100°C (212°F) again followed by air drying for the next 24 hours to bring all CNFAs to room temperature. This was also done because CNF mortar is found to be temperature sensitive.

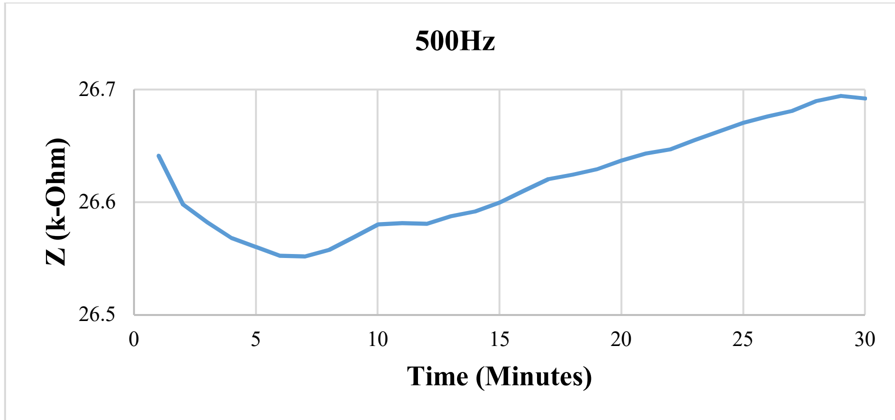
It was observed that the electrical impedance of CNFA was low in magnitude for all frequencies during curing. This electrical impedance magnitude increased with first air drying and further increased for CNFA specimens (at room temperature) that were oven dried specimens followed by air drying. This is because the electrical impedance of CNFAs is dependent on the moisture content of CNFAs. During the curing process, all the air voids are completely saturated, and the electric current could easily pass across, decreasing the electrical resistance of CNFAs. During air drying and oven drying followed by air drying, CNFAs' resistance increased due to vacant voids in concrete created due to escaping of moisture during the process. Further, it was also noted that during the drying process, the imaginary part of impedance (i.e., reactance (X)) increased significantly which increased the overall impedance of CNFAs.

The AC circuit was introduced for CNFA to observe the steady-state response with no loading. Two probe CNFAs were selected for impedance measurement with varying frequencies on unloaded conditions. Keysight E4980AL Precision LCR Meter with unit AC voltage as an input was used for the measurements. This LCR meter could measure impedances from 20 Hz to 300 kHz.

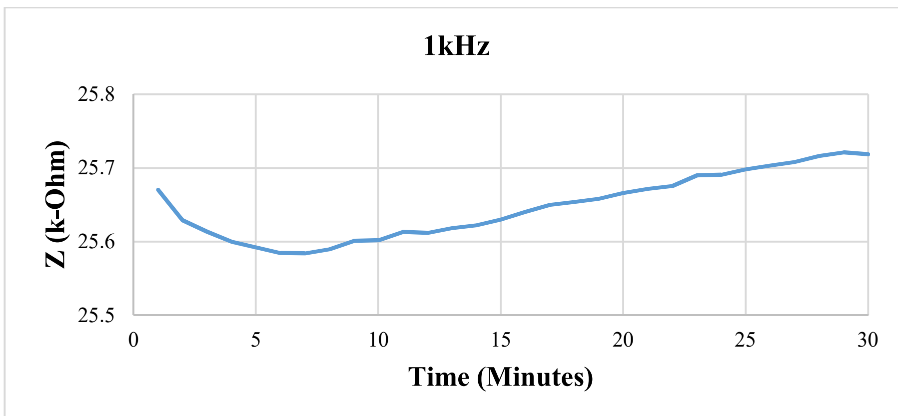
Figure 4.1 shows the impedance (Z) of 2-Probe CNFAs with different frequencies in a no loading stage. CNFAs had CNF content of 0.7% to the weight of cement. It is observed that the magnitude of the impedance is still changing, but the magnitude of variation is a lot lower than that of steady state electrical response in DC configuration. The change in impedance was observed over 30 minutes with no load. The variation in electrical impedance was less than 1% between maximum and minimum impedances. These impedance variations were significantly less than the DC resistance variation. Further, with the increase in AC frequency, the change in impedance (Z) with time is decreasing, i.e., giving a more reliable and stable steady-state response.



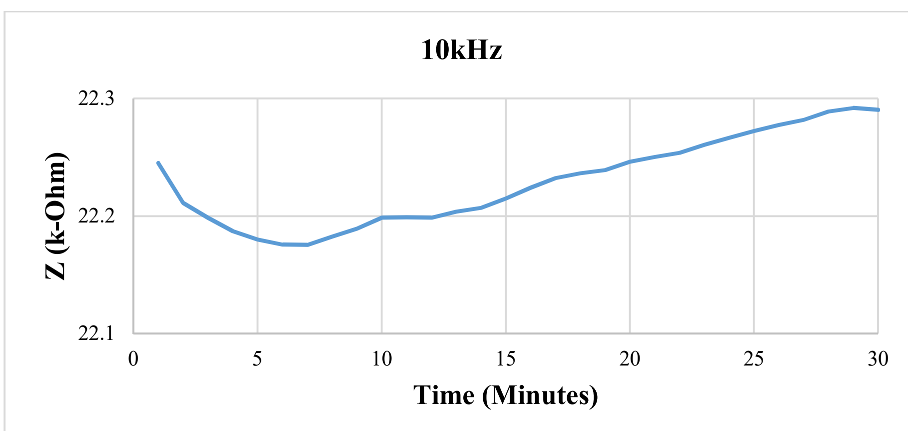
(a)


500Hz
26.7
26.6
26.5
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

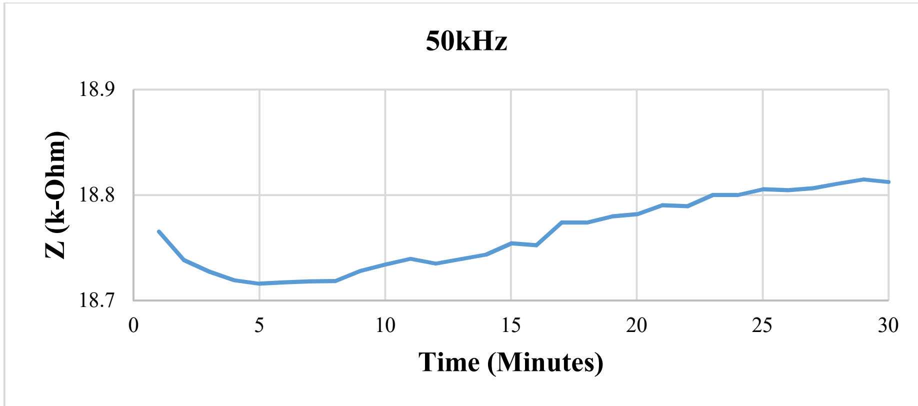
(b)


1kHz
25.8
25.7
25.6
25.5
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

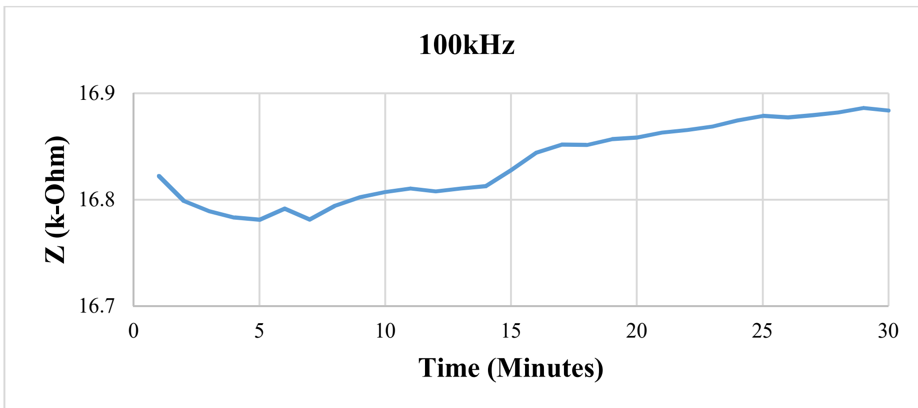
(c)


10kHz
22.3
22.2
22.1
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

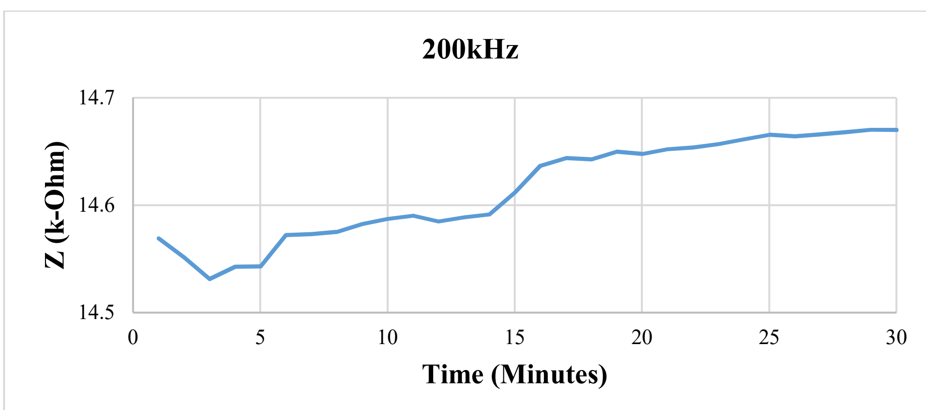
(d)


50kHz
18.9
18.8
18.7
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

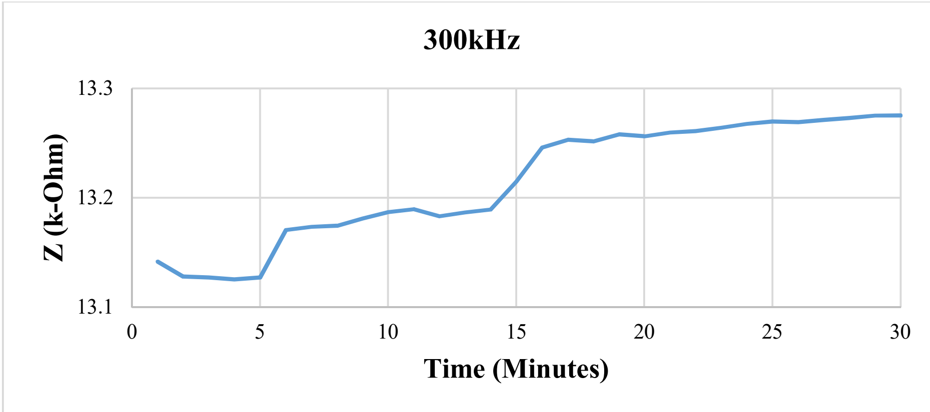
(e)


100kHz
16.9
16.8
16.7
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

(f)


200kHz
14.7
14.6
14.5
Z (k-Ohm)
0
5
10
15
20
25
30
Time (Minutes)

(g)



(h)

Figure 4.1 Variation of AC Impedance (Z) of 2-Probe CNFA with time in No-Loading Stage in Different Frequencies (a) 20 Hz.; (b) 500 Hz.; (c) 1 kHz.; (d) 10 kHz.; (e) 50 kHz.; (f) 100 kHz.; (g) 200 kHz.; and (h) 300 kHz.

The reason for the minimum variation of impedance with time can be further justified by studying the characteristics of CNFA for resistance (R) and reactance (X) independently. Figure 4.2 and Figure 4.3 show the resistance (R) and reactance (X) of CNFAs with different frequencies respectively. The magnitude of resistance and reactance plotted in Figure 4.2, and Figure 4.3 is an average of 30-minute observation from a set of data of Figure 4.1. The reactance value was always observed to be negative, dictating that CNFAs possessed the internal capacitance.

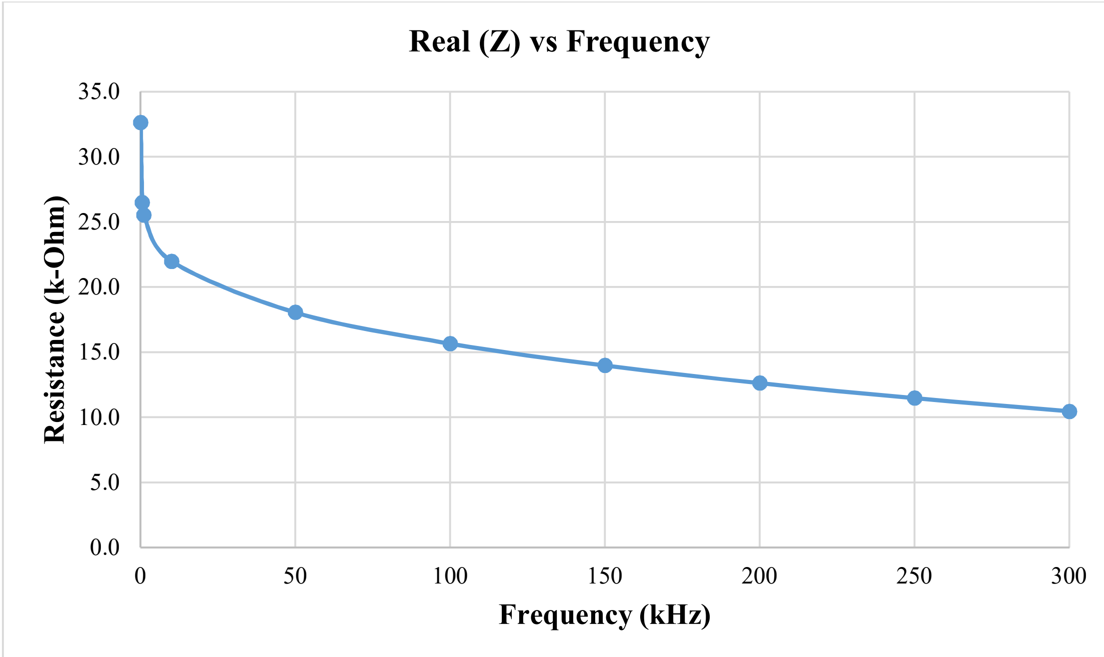


Figure 4.2 Real Part of Electrical Impedance (R) of 2-Probe CNFA in AC Circuit as a Function of Frequency

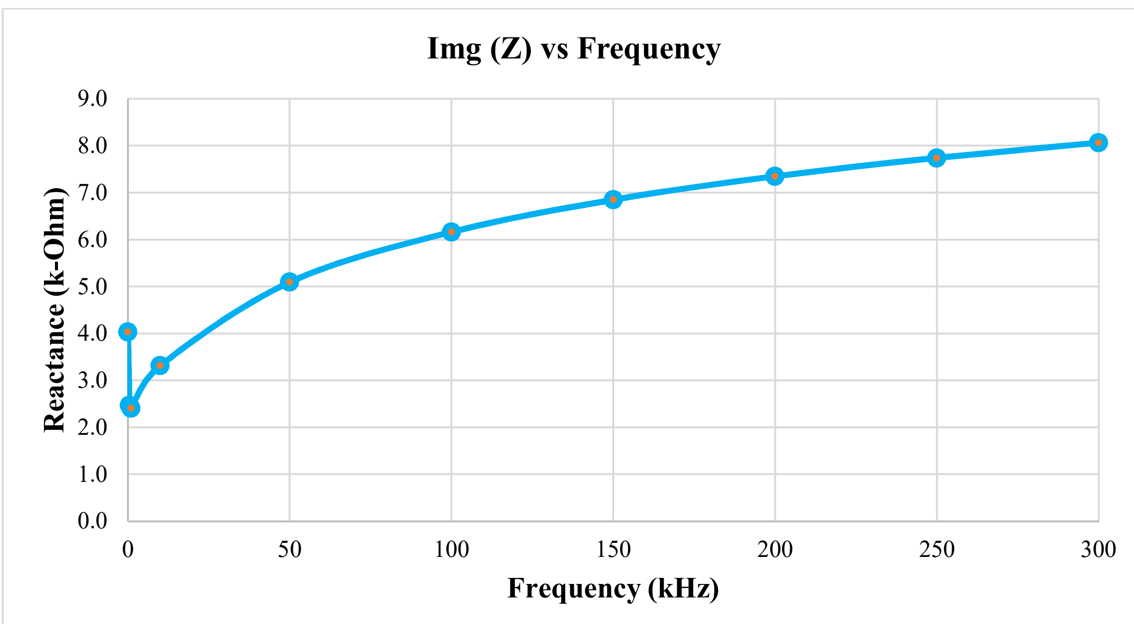


Figure 4.3 Imaginary Part of Electrical Impedance (X) of 2-Probe CNFA in AC Circuit as a Function of Frequency

It is seen from Figure 4.2 that the real part of electrical impedance (R) of CNFA decreases with an increase in AC frequency and Figure 4.3 shows that the magnitude of the imaginary part of electrical impedance, i.e., the reactance (X) of CNFA increases with an increase in AC frequency. Here, the decrease in resistance is less than the increase in reactance of CNFA. As impedance is the square root of the summation of squares (SRSS) of R and X, the decrease of resistance and increase of reactance, with time, limits the significant change in impedance. These comparatively stable results allow the use of the AC circuit for 2-probe CNFAs study. Figure 4.4 shows the variation of impedance 2-probe CNFA with frequency.

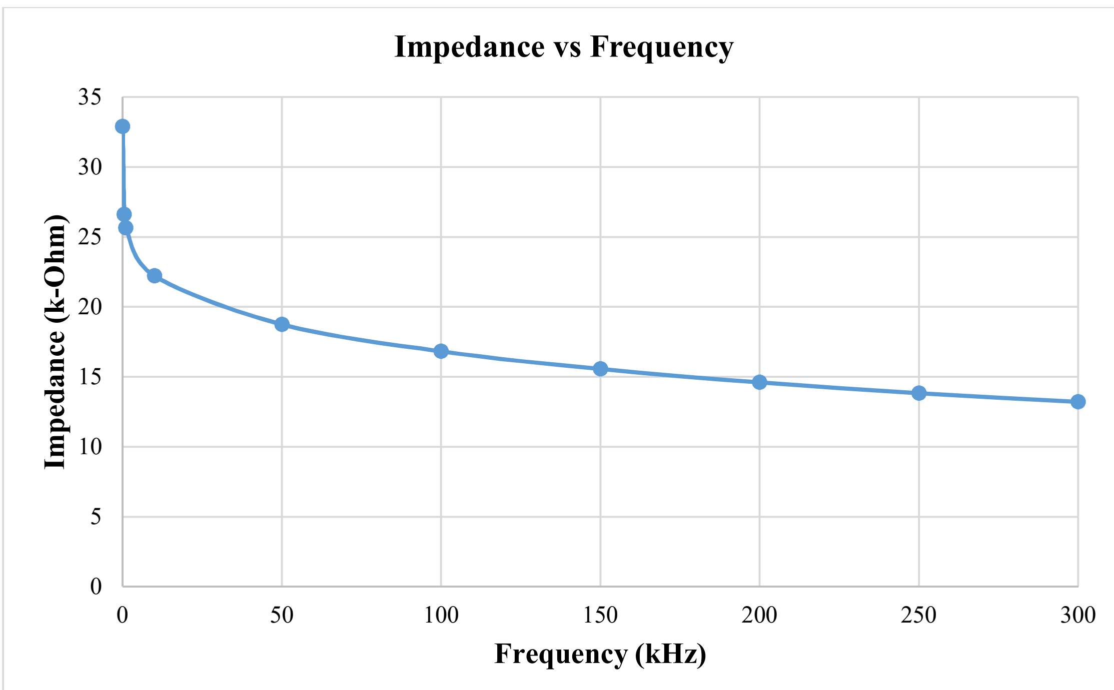
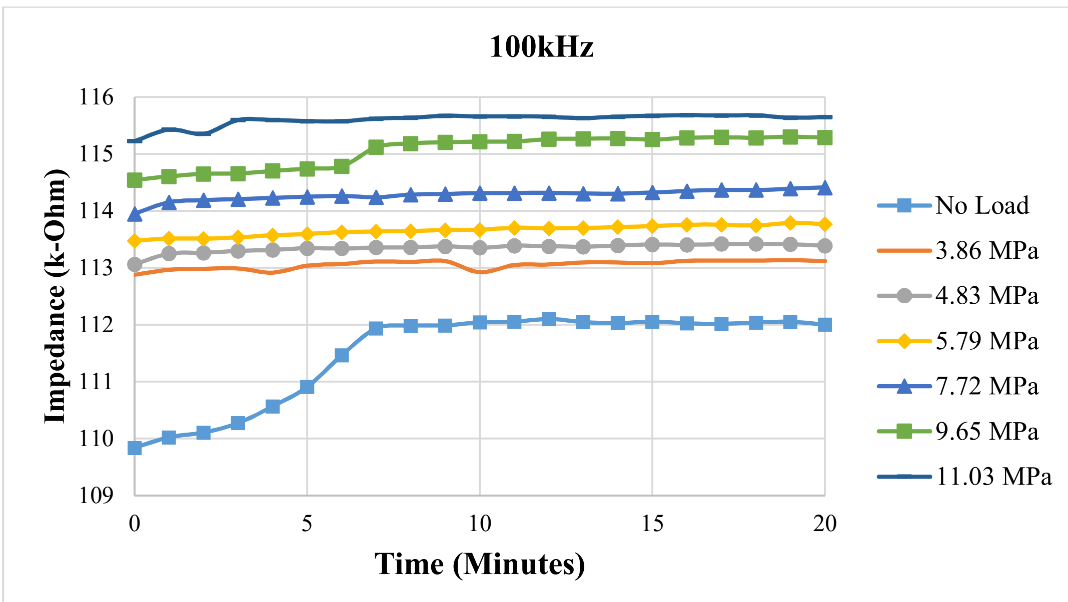


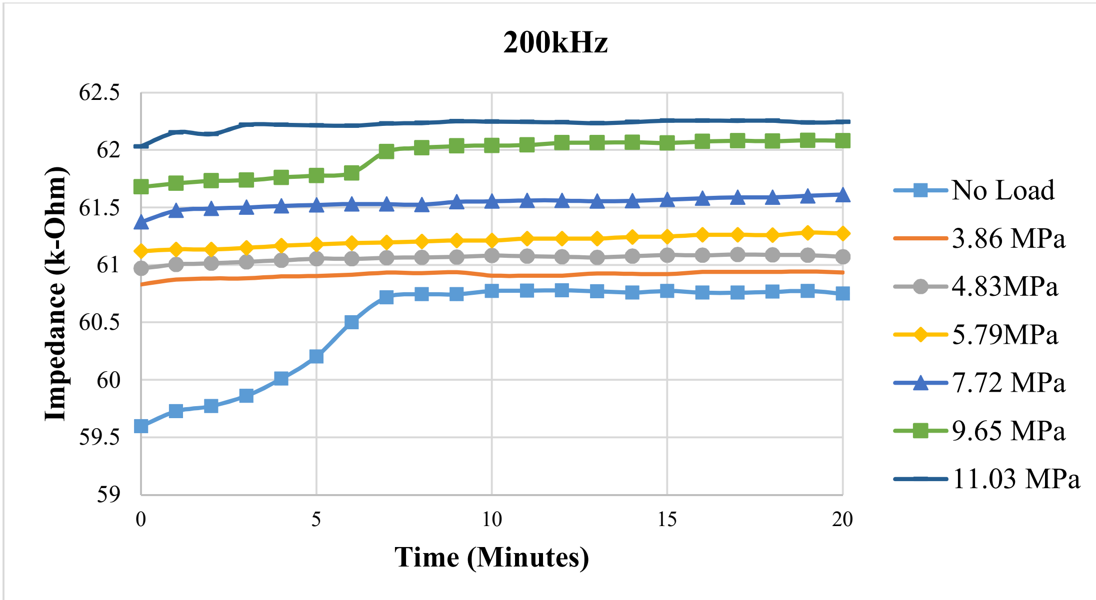
Figure 4.4 Electrical Impedance (Z) of 2-Probe CNFA in AC Circuit as a function of Frequency

Due to instrumental limitation, AC frequencies higher than 300 kHz were not able to be observed, but above a frequency of 100 kHz, the impedance response is already getting stable even with the increase in frequency. At lower frequencies, the change in impedance is significant considering a small change in AC frequency, but at frequencies higher than 100 kHz, the magnitude of impedance becomes independent of applied frequency. Thus, for further studies, this chapter has considered the frequency higher than 100 kHz.

The concept of steady-state response was also checked for the various load/stress stages. This is an important step as this observation assures that the CNFAs can be used to monitor long term loads. The specimens were subjected to different loading stages and were held at each load step for some time interval where the observation for impedance was made as seen in Figure 4.5.



(a)



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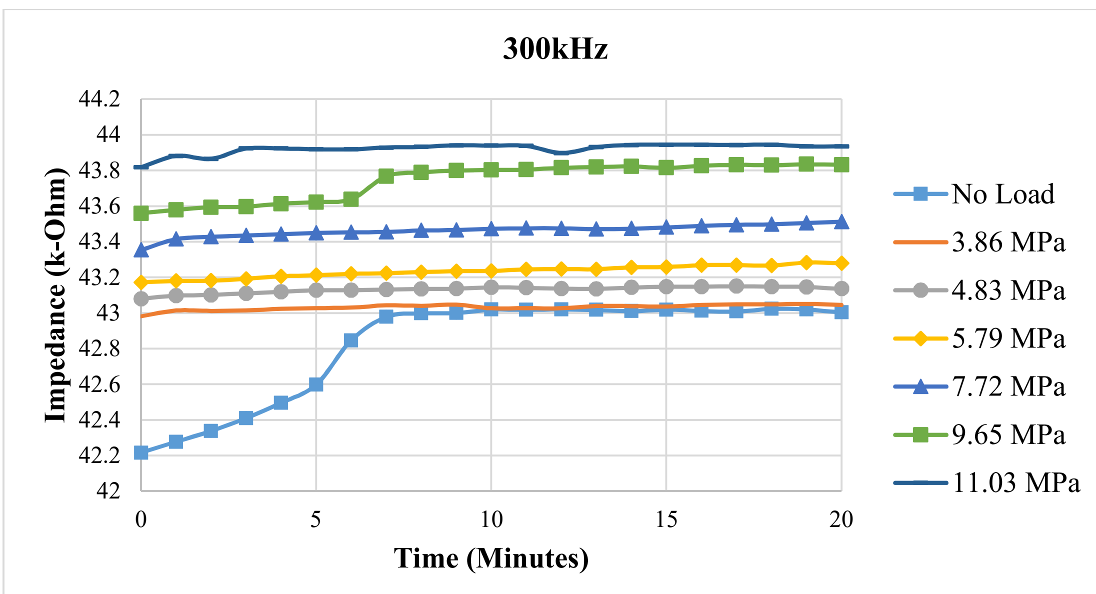

(c)

Figure 4.5 Static Stress Impedance Analysis for Different Frequencies: a) 100 kHz; b) 200 kHz; c) 300 kHz

The CNFAs have stable impedance within a few minutes of connection to the circuit. The linear trend of the impedance explains the reliability of CNFAs to monitor static loads/stresses. The distinct lines for impedance at each load stage ensures the unique response to a unique loading stage. The overlapping lines will not be accurate to determine the stress level. Figure 4.5 shows that the frequency of 300 kHz has overlap between stress levels. Thus this frequency for monitoring is not recommended. The impedance response between 100 kHz and 200 kHz frequency is more reliable. Thus 100 kHz and 200 kHz of AC frequency can be selected as the optimum frequency to evaluate the response of 2-probe CNFAs with CNF content of 0.7% of the weight of cement in the AC circuit.

4.3 Carbon Nano-Fiber Content Optimization

The impedance of CNFA is much higher than that of the wires; two probe impedance measurement is quite accurate to determine the electrical impedance variation of the CNFAs under loads/stresses. The calculation of variation is quite simple, and the electrical impedance variation (EZV) can be determined as shown in Equation 4.1,

$$EZV = {}^{(Z_i - Z_0)}/_{Z_0}, \qquad \text{Equation 4.1}$$

where,

EZV: Electrical Impedance Variation,

Z_0: Initial Impedance, and

Z_i: Impedance at Step i.

Several researchers have been studying to find the optimized content of CNF in concrete and mortar. Chen and Chung (Chen and Chung 1993a) studied carbon microfiber's electrical and mechanical properties. They observed that in 0.5% by weight of cement, the electrical resistivity decreased by 83%. This study later (Chen and Chung 1969) elaborated the study of microfibers with varying concentration. They studied properties of mortar and concrete with 0 to 4% and 0.5-3% by weight of cement, respectively, which showed that these as reversible damage sensors by measuring ERV. They observed that increasing fiber content increased the ERV in concrete; however, increasing fiber content did not appreciably increase ERV in the mortar. Gao et al., (Gao et al., 2009) showed that 0.7% of cement of CNF in concrete was optimal and higher than that caused fiber clumping in concrete.

Several 2-probe CNFAs with varying CNFs contents were tested under compression, and electrical impedance variation was determined to find the optimal CNFs percentage in the AC circuit. Each CNFAs were cast as explained above. After casting, each CNFAs were cured for 14 days and then air dried for the next 24 hours. To remove all excess water including pore water in CNFAs, they were oven dried at 100°C (212°F) followed by air drying for the next 24 hours to bring them to room temperature. Figure 4.6 shows the series of oven dried CNFAs with varying CNF content (0.00%, 0.20%, 0.50%, 0.70%, 0.80%, 0.90% & 1.00% of CNF by the weight of cement). It is seen that the higher the CNF concentration, the darker is the CNFA.

Figure 4.6 CNFA with Different Dosage of CNFs (0.0%, 0.00%, 0.20%, 0.50%, 0.70%, 0.80%, 0.90% & 1.00% the Weight of Cement)

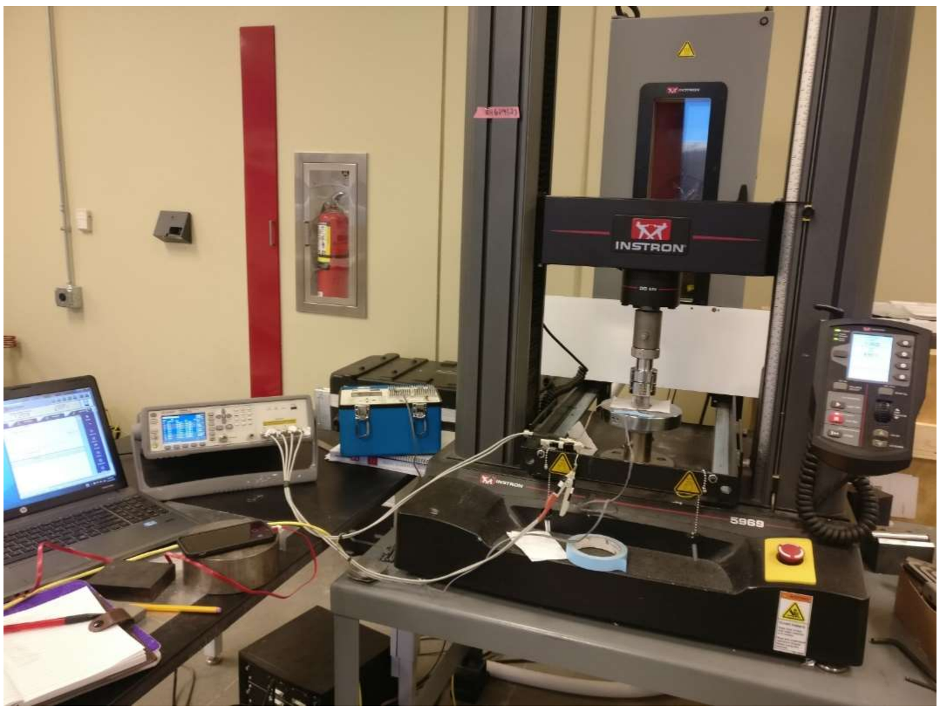

Figure 4.7 Test Setup for CNFA's CNF Optimization

Figure 4.7 shows the test setup for the compression test. Each CNFA was loaded in Instron 5960 Series Universal Testing Systems up to 50 kN (11,250 lbf.) force capacity. The CNFA's top and bottom surface were smoothened with grit to ensure even contact surface during loading. Two strain gauges were pasted to the surface of CNFAs to measure average strain from the Model P3 Strain Indicator and Recorder during the test. The CNFAs were tested in compression at a constant displacement rate of 0.254mm/min (0.01 in/min) until the load dropped to 40% of the peak load. The electrical impedance was measured using a two-probe technique with varying frequencies from Keysight E4980AL Precision LCR Meter. Figure 4.8 shows the peeling of strain gauge from the surface of CNFA under loading.

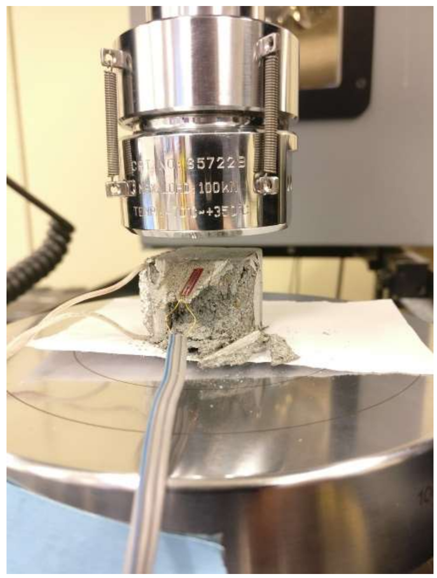

Figure 4.8 Peeling of Strain Gauge from CNFA Surface under Compression

The compression test showed a promising trend between the concentration of CNF and maximum EZV recorded. Since from Chapter 3, it was concluded that the AC frequency should be greater than 500Hz, the maximum EZV at each percentage of CNF to the weight of cement is the average response of CNFAs at peak load for different AC frequencies (500Hz, 1kHz, 100kHz, 200kHz, and 300kHz.). Figure 4.9 shows the average EZV response of each CNFA at peak load to different AC frequency. It clearly shows that the for all frequencies, 0.8% of CNF by weight of cement is maximum responsive at peak load.

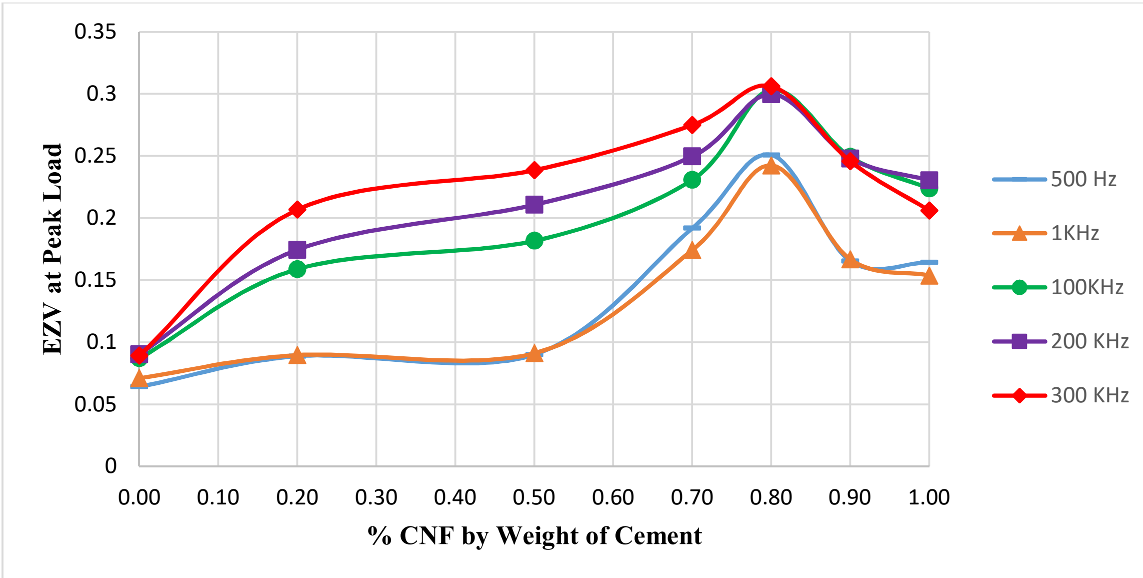

Figure 4.9 Impedance Analysis for Dosage of CNF in CNFA for Different Frequencies

Further, it should be noted that with an increase in AC frequency, the EZV at peak load is also high. Also, from Figure 4.5 it was noted that the frequency of 300 kHz has overlap between load levels and the impedance response between 100 Hz and 200 kHz frequency is more reliable. Thus the selection of 100 kHz and 200 kHz of AC frequency as the optimum frequency to evaluate the response of 2-probe CNFAs in AC circuit is further justified.

The maximum EZV at each percentage of CNF to the weight of cement is the average response of CNFAs at peak load for different AC frequencies. The standard deviation was then calculated. Figure 4.10 and Figure 4.11 show the averaged ERV with one standard deviation on each side of average for 100kHz and 200kHz of AC frequency.

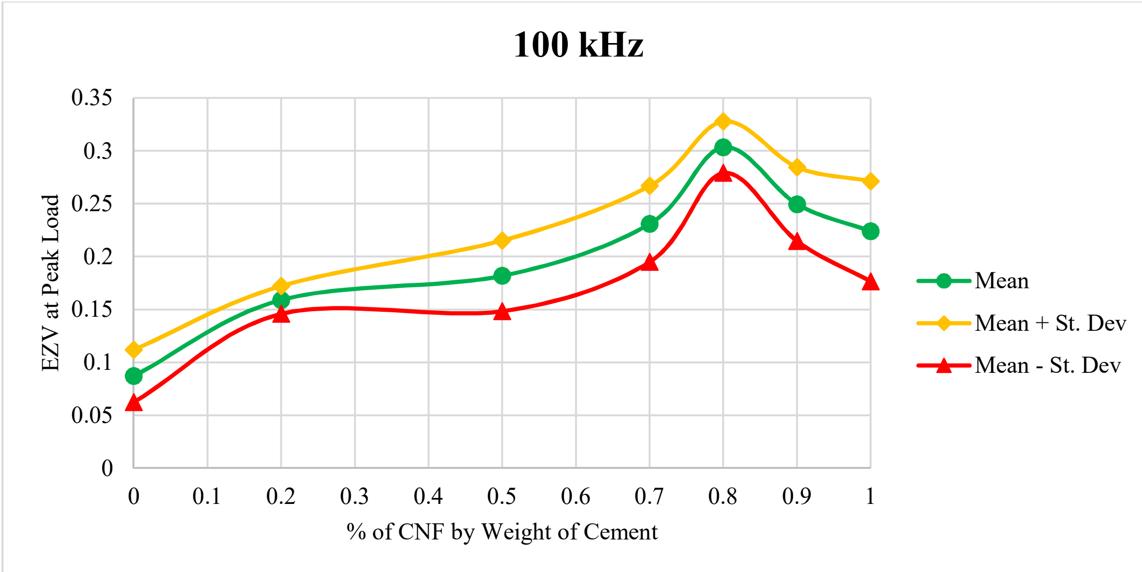

Figure 4.10 CNF Optimization of 2-Probe CNFA for 100 kHz AC Frequency

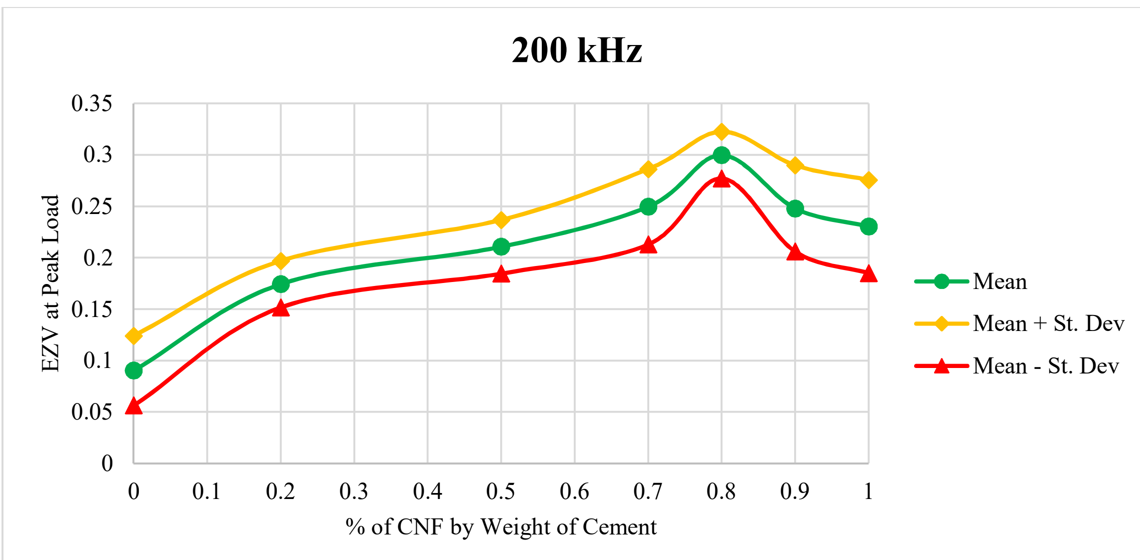

Figure 4.11 CNF Optimization of 2-Probe CNFA for 200 kHz AC Frequency

Figure 4.10 and Figure 4.11 demonstrates that for 100 kHz and 200 kHz of AC frequency respectively, the CNFA concentration with respect to the weight of cement of 0.8% exhibited the most distinct change in EZV, which is slightly higher than the results found by Howser et. al., (Howser et. al., 2011) for four-probe CNFAs in DC Circuit. This may be due to factors like changing 4-probe measurement technique to 2-probe, use of AC circuit, and the addition of new admixture Kim Krystol with the target of waterproofing. The variance in the above figure might be due to factors like temperature and remaining water in CNFA micro-pores even after drying.

By the above tests, the optimum CNF content for 2-probe CNFAs in AC was found to be 0.8% to the weight of cement, i.e., 0.3% of total mortar weight. Table 1. Below shows the final optimized 2-probe CNFA mix design.

Table 4.1 Optimized 2-probe CNFA Mix Design

Materials	Percentage of Total Mortar Weight
Fine Aggregate	52.3%
Cement	28.4%
Water	12.1%
Silica Fume	4.2%
HRWR	2.0%
CNFs	0.3%
Kim Krystol (waterproofing)	0.6%

4.4 Summary

The study of carbon nanofiber aggregate (CNFA) in DC circuit tests showed the unstable resistance variation resulting in unreliable data acquisition for stress/strain monitoring. This led to the development of two probes CNFA in AC circuit which is capable of sensing load/stresses with stable impedance measurements. The developed CNFA was 2.54 cm x 2.54 cm x 2.54 cm (1.00 in. x 1.00 in. x 1.00 in) cube with two steel wire meshes. The CNFAs were tested in different load stages to check the variation of impedance with time. The 30-minutes observation showed that the change in impedance was within 1% ensuring the reliability of stress-impedance data obtained from tests. The optimized AC frequency for response measurement was found to be between 100 kHz and 200 kHz while the optimum carbon nanofiber (CNF) content was found to be 0.8% of the weight of cement and based on this study, the optimized CNFA mix design was developed.

CHAPTER 5. WATERPROOFING OF CARBON NANOFIBER AGGREGATE

5.1 Introduction

Carbon nanofiber aggregates (CNFAs) are smart aggregates able to detect the stress-strain change in structural components. These structures and aggregates often come in contact with water. The resistance of carbon nanofiber concrete also changes with water content; more the water lesser will be the resistance of CNFAs as the water molecules will help the current to pass between the meshes in CNFAs. Researches in CNF concrete composite to study the hydration process is very inconclusive. Chen et al., (Chen et al., 2004) and Han et al., (Han et al., 2010) studied the hydration effect and change in ERV of carbon nanofiber cement composites.

Howser and Mo (Howser and Mo 2011) also did the hydration study of CNFAs. She tested how the electrical resistance of the CNFAs change with time to observe how the CNFAs can be used to monitor concrete hydration, and if a waterproof coating works when submerged in water. All three waterproofing coat she used failed during test just after coming in contact with water, and further, she observed that the bond behavior between coated CNFAs and embedded concrete. Thus those coated CNFAs were not able to be used in strain monitoring. An experiment was then set up at the structural laboratory at the University of Houston to observe the behavior more waterproof coats and admixtures. These waterproof coats were selected such that they have a similar property to concrete so that even embedded CNFAs will have good bonding. The waterproof coating is also necessary because of the changing electrical resistivity of CNFAs with ambiance moisture content.

5.2 Experimental Setup

The experiment studied the two parameters:

- Coating: Half of CNFAs were coated with a waterproofing coat while half were left uncoated with Kim Krystol as an admixture
- Environment: Half of the CNFAs were submerged in water while half were left in room temperature

To study the above mentioned parameters, four test groups were formed as shown in test matric in Table 5.1.

Table 5.1 Waterproofing Test Matrix

Group	Uncoated	Coated	In Air	In Water
A	X		X	
B		X	X	
C	X			X
D		X		X

The purpose of the above, different test groups are as follows:

- Groups A and B: Group A and B were the control groups. Hypothetically, their resistance should not change during the experiment. The experiment tested the stability of the impedance in the CNFAs.
- Groups C and D: Group C and G are the extreme environmental groups. The experiment tested the waterproof coating in the worst-case environment. This test is to check the implementation of CNFAs in water level monitoring where CNFAs are subjected to direct water head.

5.3 Waterproof Coating and CNFA Preparation

Four waterproof coatings were considered during the study of which three is cement based coating. The first waterproof coating was MasterSeal 581 (MS-581). MS-581 is a Portland cement based coating for concrete that resists both positive and negative hydrostatic pressure. Polymer modified with MasterEmaco A 660 (ME A-660), MS-581 creates a low maintenance and highly durable waterproof barrier. The second coating examined was MasterSeal 500 (MS-500). MS-500 is an acrylic-modified Portland cement based crystalline capillary waterproofing coating for concrete. It is designed for coating applications both above and below grade. The third was Xypex Concentrate. Xypex is the most chemically active product which is said to prevent the penetration of water from any course by causing a catalytic reaction. The reaction produces a non-soluble crystalline formation within the pores and capillary tracts of concrete and cement-based materials. The fourth coating was commonly available quick setting professional epoxy. These are general purpose adhesive prepared by mixing hardener and resin at a ratio of 1:1. The commercially available JB ClearWeld epoxy was used in the experiment.

For the experiment, the CNFAs were water cured for 14 days and then air dried for 24 hours. The excess moisture was removed by oven drying at 212^{o}F (100^{o}C) for 24 hours followed by air drying for the next 24 hours to bring the specimens to room temperature as CNFAs are also heat sensitive. The coats of waterproofing material were uniformly applied in instructed consistency and cured as guided. Three of the four waterproofing coats studied were cement based. All CNFAs had surface prepared to remove any dirt or foreign matter. If the surface was too smooth, the CNFAs were etched with grit. As per instruction of three cement based coats, all CNFAs were made in the state of saturate substrate with a dry surface (SSD condition).

The MS-581was well mixed with diluted ME A-660 till we had lump-free consistency of smooth, heavy batter as per instructions. The mix was set to rest for 10 minutes to fully wet out powder and mixed thoroughly again. The final blend was brush applied to CNFAs' surface evenly. Brush strokes were apparent in coating leaving some areas with a thin coat. To compensate uneven coating, the layers were employed in a perpendicular direction. After allowing the first coat to cure for 24 hours, the second coat was applied. In the end, it was ensured that CNFAs were evenly coated all around. After 24 hours of the second coat, the coated CNFAs were set to cure for seven days by spraying water whenever dry after 24. The second tested for CNFAs waterproofing was MS-500. MS-500 powder (Part B) was slowly added to Part A (liquid) in instructed consistency for 5 minutes. The SSD surface of CNFAs was brush-applied with mix with vertical strokes till uniformly applied. The bubbles left wile coating was also checked to ensure uniform coat application.

Second coat of MS-500 was applied only after 24 hours and cured for the next 14 days. The third type of surface-coat studied was Xypex. Xypex was mixed with clean water in the ratio 3:1 till creamy consistency was achieved. It was made sure that mixture was applied within 20 minutes to SSD surface of CNFAs. The mix was applied using a semi-stiff brush in perpendicular strokes. The second coat was applied after 24 hours similarly. The curing of coated specimens was done by misting the coat with water three times a day for three days and allowed to set for 15 days. The fourth coating studied was epoxy. The hardener and resin were mixed thoroughly in the ratio of 1:1 into a disposable surface. The mix was smoothly applied to CNFAs surface with flat stick covering all surface including corners, edges and protruded mesh points from the bottom of CNFAs. The coated specimens were set to cure for 24 hours.

Before testing all the coated specimens were oven dried for 24 hours at 212ºF followed by 24-hour air drying.

5.4 Experimental Results

Electrical impedance variation (EZV) is a measure adopted for this study. EZV is defined as the change in impedance divided by the initial impedance. The means of group C and group D was monitored until the coating failed. Group Groups C and D consisted of uncoated and coated specimens respectively, that were submerged in water. The electrical impedance was measured using two probe method and a Keysight E4980AL Precision LCR Meter with a capacity of 20Hz to 300KHz capability. The test was aborted when waterproofing coating failure was evident. It was expected that Group C would not have a significant drop in ERV immediately upon immersion in water as it contained Kim Krystol (expected waterproofing admixture) as one of its constituents which was supposed to resist water penetration to some extent. And together with the outer coat of Group D, it was assumed that there would be no change in EZV.

The first experiment studied the MS-581 as a waterproof coat for CNFAs. Both groups C and D behaved quite similarly when plunged into the water. Figure 5.1 and Figure 5.2 shows the mean EZV for 100KHz and 200KHz of AC frequencies of group C dropped to -70% while that of means of D fell by -50% in the first minute of plunging into the water. Even though group D was coated in an expectedly waterproof cement-based material, the mean EZV of group C and D dropped to -98% and -80% respectively within 4 hours of plunging and stayed there for 10 hours of observation. The drop in mean EZV is comparatively less in D group than in the C group because MS-581 waterproofed to some extent but not completely.

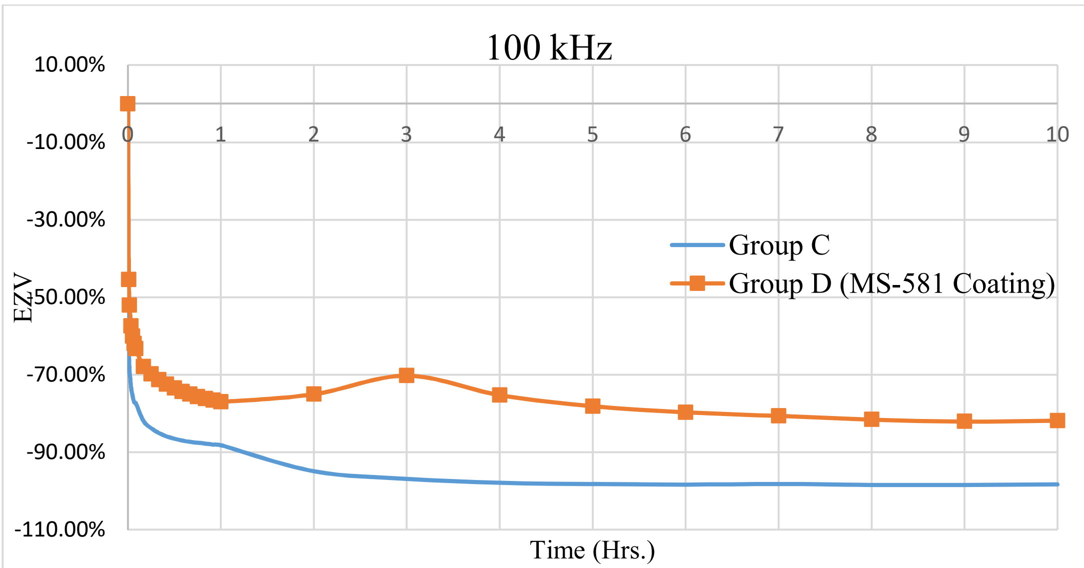

Figure 5.1 EZV for 100kHz vs. Time for Groups C and D with MS-581 Coat

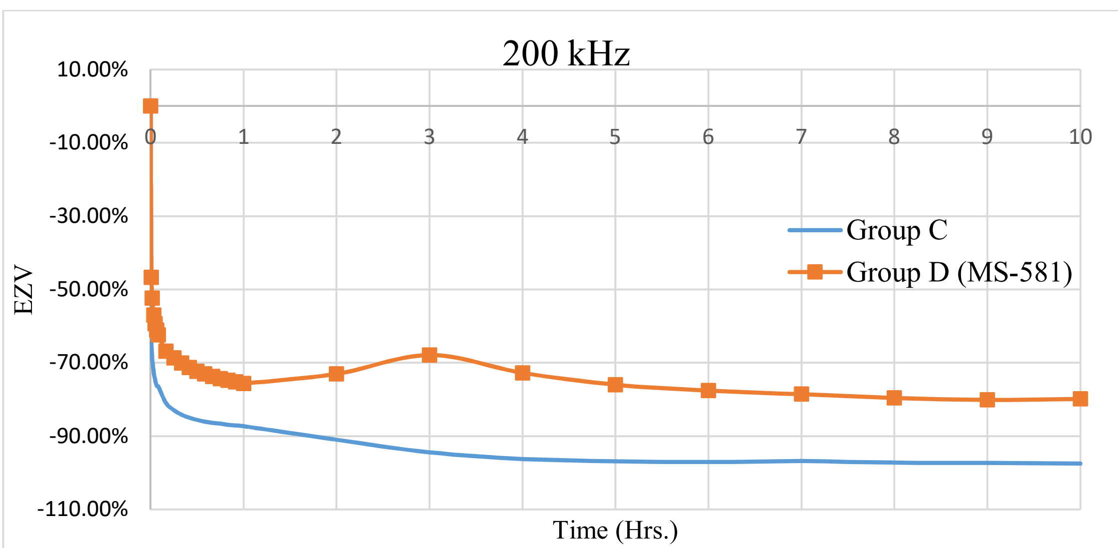

Figure 5.2 EZV for 200kHz vs. Time for Groups C and D with MS-581 Coat

The experiment was then repeated using MS-500 as expected waterproof coat. Unexpectedly this coating also failed. When group D was exposed to water, the EZV immediately dropped to -60% within a minute and further reduced to -93% within 6 hours and continued to stay till the same for 10 hours. Again MS-500 checked the entry of water into CNFAs to some extent than uncoated samples but did not prevent water completely. Figure 5.3 and Figure 5.4 shows the mean EZV of group C and D for AC frequencies of 100kHz and 200kHz respectively.

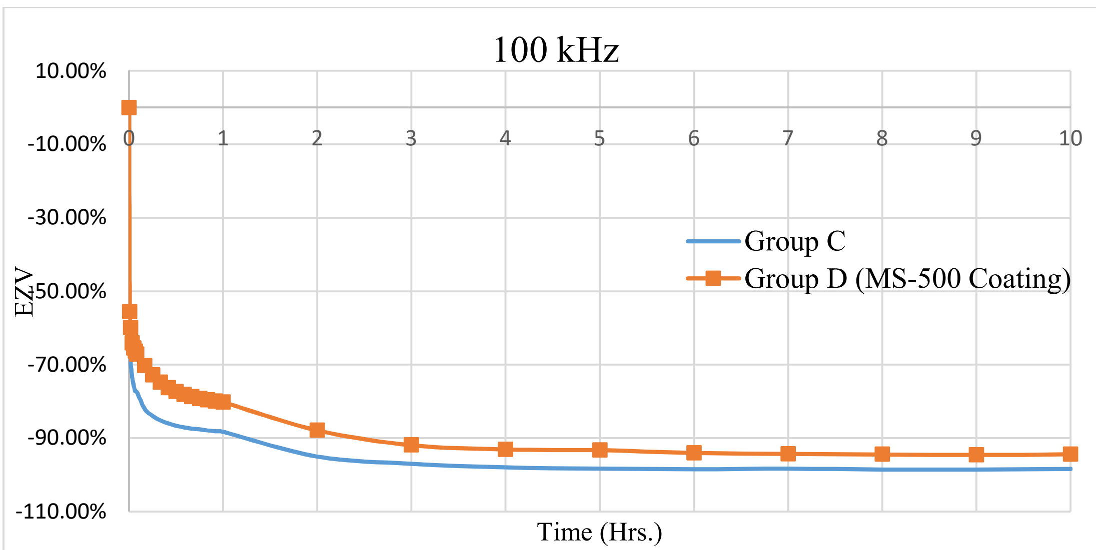

Figure 5.3 EZV for 100kHz vs. Time for Groups C and D with MS-500 Coat

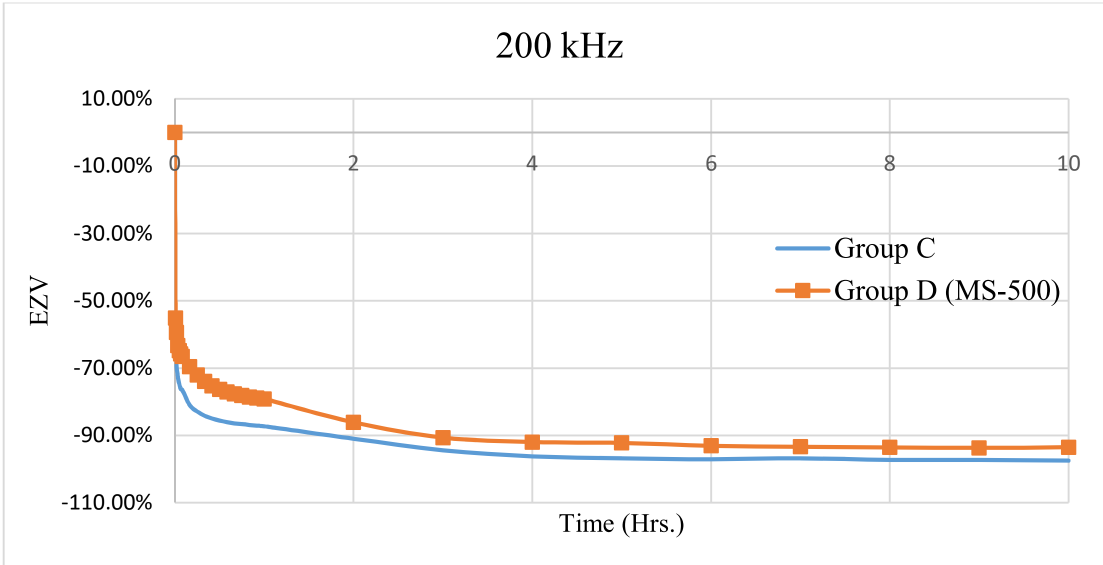

Figure 5.4 EZV for 200kHz vs. Time for Groups C and D with MS-500 Coat

The third cementitious coating studied for this experiment was Xypex. Unfortunately, this waterproof coat also failed. When group D with Xypex coating was exposed to water, the EZV dropped to -95% within an hour. Figure 5.5 and Figure 5.6 demonstrates the mean EVR for group D in comparison with group C for 100kHz and 200kHz of AC frequencies.

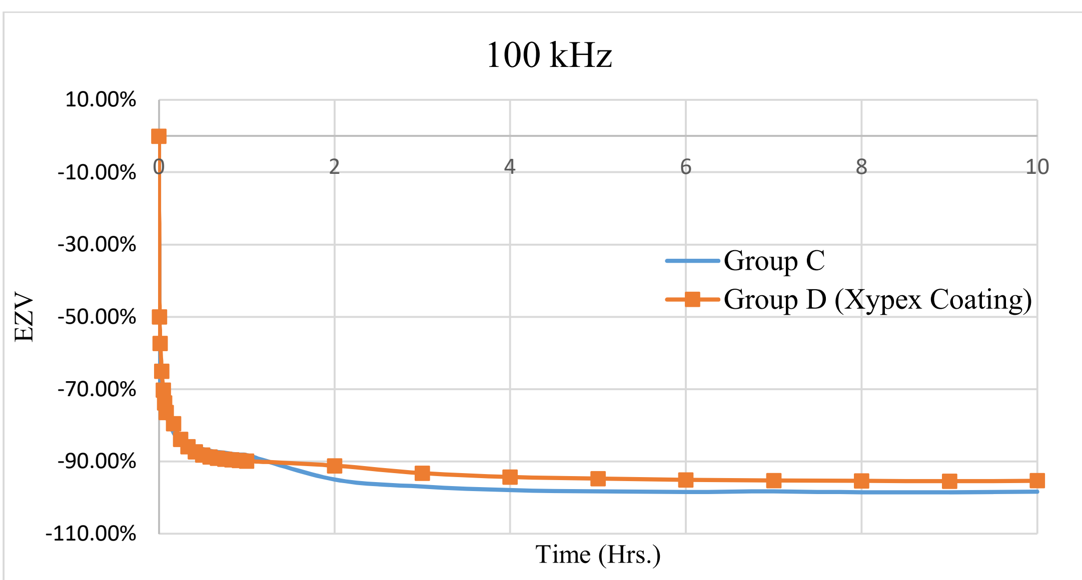

Figure 5.5 EZV for 100kHz vs. Time for Groups C and D with Xypex Coat

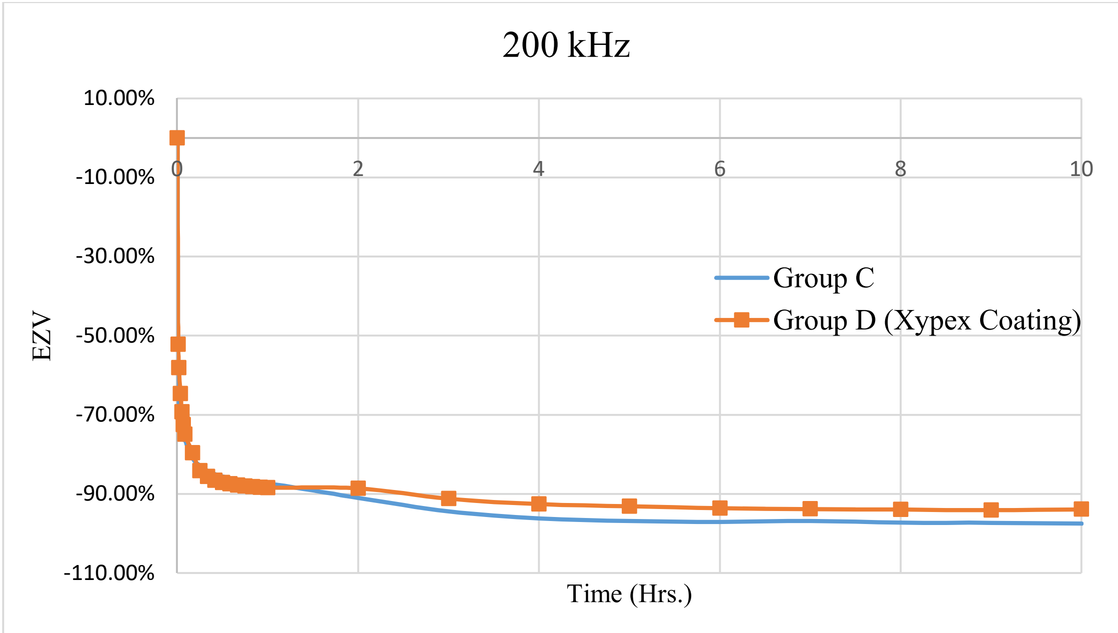

Figure 5.6 EZV for 200kHz vs. Time for Groups C and D with Xypex Coat

The final coat that was studied was epoxy. Figure 5.7 and Figure 5.8 shows the effectiveness of epoxy in the waterproofing of CNFAs. If this waterpr0ofing coat worked, it was expected that their EZV would not have a significant change. The mean EZV for group D (epoxy coated in this case) was quite stable with no sudden drop. The minor sinusoidal behavior of EZV is likely due to the temperature of the water the specimens were subjected. The water temperature would have changed with the room temperature with passing hours, so was the EZV of epoxy coated specimens in water. The EZV of group D specimens were observed for 48 hours, and there was no significant drop in EZV indicating that the epoxy coating was successful in waterproofing the CNFAs.

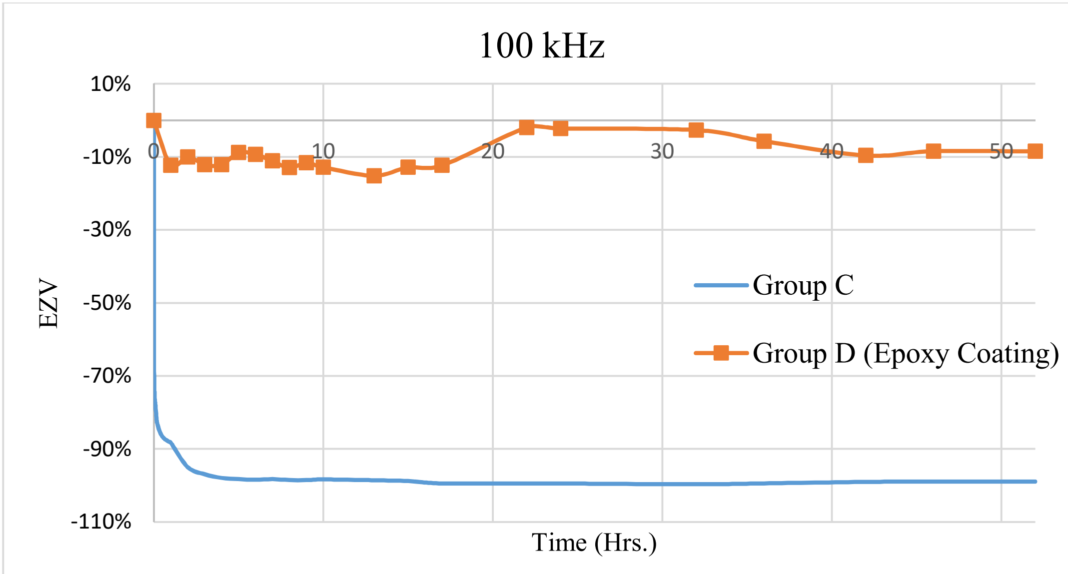

Figure 5.7 EZV for 100kHz vs. Time for Groups C and D with Epoxy-Coat

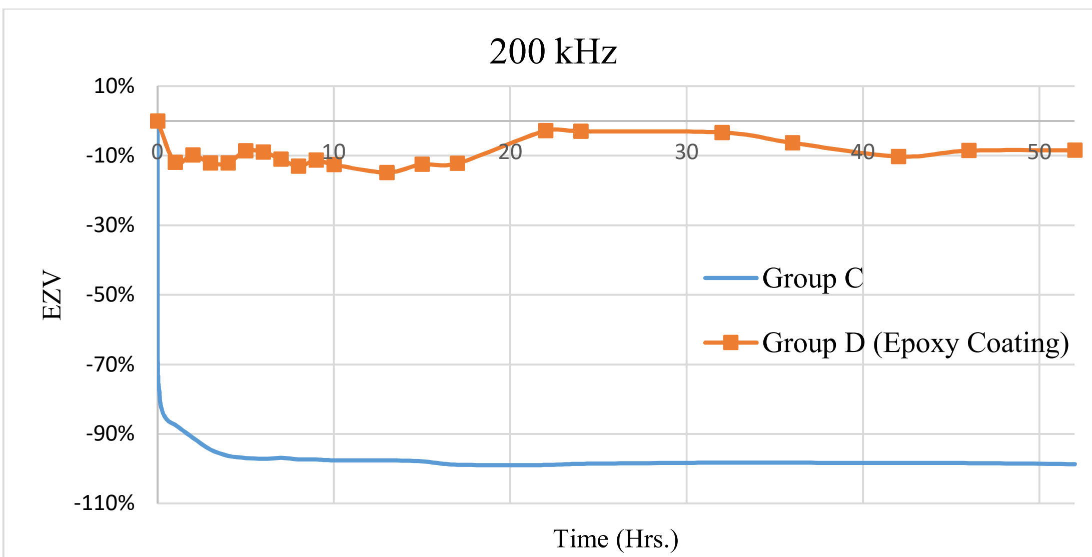

Figure 5.8 EZV for 200kHz vs. Time for Groups C and D with Epoxy-Coat

With the success of epoxy to be used in CNFAs as waterproofing coat, the comparative study of group A (without any coat), B (with an epoxy coat in the air) and C (with an epoxy coat in water) was made. There was no significant change in EZV of all three specimens except some minor sinusoidal variation due to a temperature change of ambiance in each case. The EZV for these three groups is as shown in Figure 5.7 and Figure 5.8 for 100kHz and 200kHz of AC frequencies respectively.

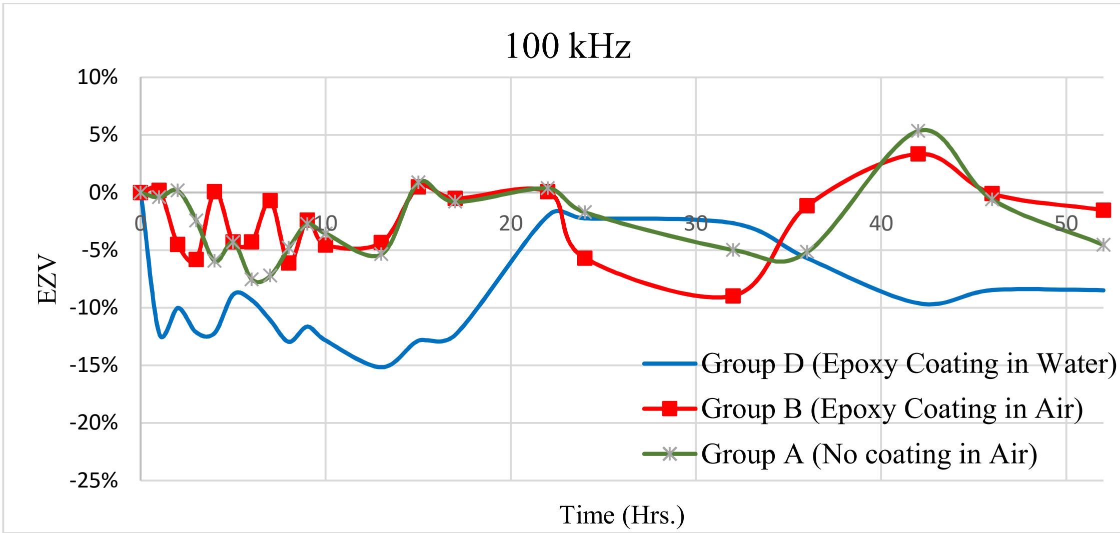

Figure 5.9 EZV for 100kHz vs. Time for Groups A, B, and D

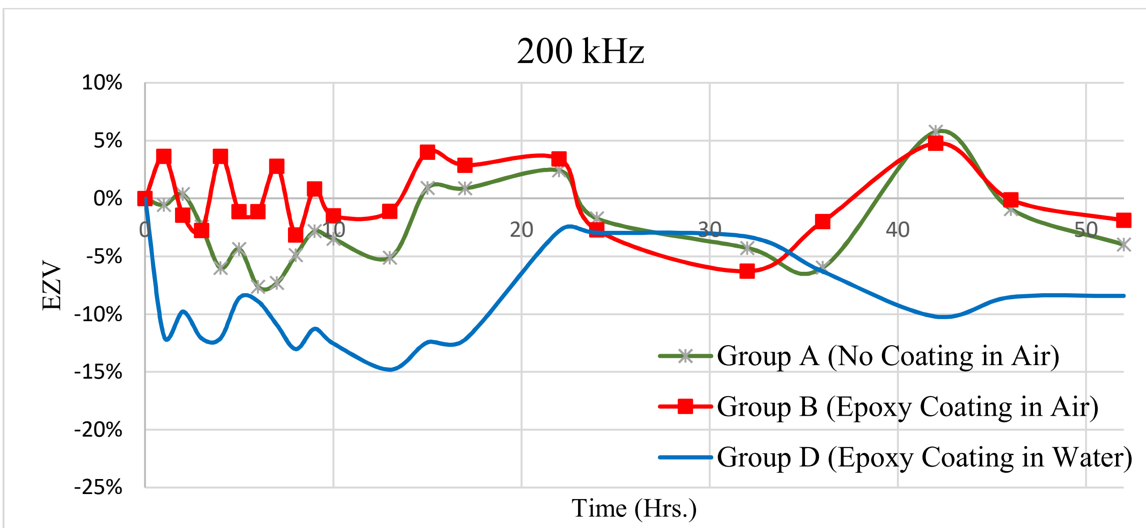

Figure 5.10 EZV for 200kHz vs. Time for Groups A, B, and D

Form Figure 5.9 and Figure 5.10, it is evident that the EZV of epoxy coated specimen behaves quite similar to uncoated CNFA under no stimulus in addition to an excellent waterproofing advantage. The EZV is very negligible when submerged in water for quite a long time (52 hours in the above case), and this insignificant change is also because of ambiance temperature change.

5.5 Summary

The response of carbon nanofiber aggregates (CNFAs) subjected to water with and without external coating was examined. Four waterproof coats were tested for the CNFAs of which three were cementitious coatings that are commercially available to waterproof concrete structures by the surface application. The fourth coat studied was epoxy adhesive whose primary application is to create a good bond between the substrate and superstrate. The CNFAs proposed in this thesis has Kim krystol as waterproofing admixture was insufficient to check the entry of water into CNFAs, dropping electrical impedance variation (EZV) immediately and significantly when plunged into the water. Surface coat of three different cementitious materials studied in this experiment checked entry of water very insignificantly in CNFAs. But the commercially available epoxy coating studied here was successful in checking the entry of water into CNFAs for the studied period. Also, the behavior of epoxy coated CNFAs in the air and water were quite similar to that of uncoated CNFAs in the air.

CHAPTER 6. CONCLUSIONS AND FUTURE WORK

6.1 Introduction

With the successful implementation of self-consolidating carbon nanofiber concrete (SCCNFC) as a strain sensor (Gao et al., 2009; Howser et al., 2011), a carbon nanofiber aggregate (CNFA) was developed (Howser et al., 2013). The developed CNFA was 16.39 cm^3 cubic aggregates made up of CNF mortar with four steel mesh and was implemented for strain, hydration, and temperature study using four probe electrical resistance measurement technique in the DC circuit. The CNFAs can be embedded in reinforced or Prestressed concrete structures for real-time structural health monitoring. In this study, the development of CNFAs with CNFAs' response in DC and AC circuits were investigated. The study was further extended with the optimization of AC frequency and carbon nanofiber (CNF) content of CNFAs for practical implementation. The optimized CNFAs were then tested to develop waterproof CNFAs with the external coating.

6.2 Conclusions and Future Works

6.2.1 Carbon Nanofiber Aggregate in DC and AC Circuits

A carbon nanofiber aggregate (CNFA) with two and four meshes was developed. The response of CNFA was measured in terms of electrical resistance and impedance for DC and AC circuits, respectively. The CNFAs were studied in no-loading study-state for both DC and AC configuration using two probe and four probe techniques. The DC resistance was not stable and continuously was increasing with time even in the no-loading stage. But, in the AC circuit, the electrical impedance of CNFAs change became very insignificant for higher frequencies, i.e., greater than 500 Hz. Also, the polarization effect was evident in the DC circuit which was studied by switching the terminal. This effect was not observed in AC circuits adopting frequencies higher than 500Hz. It was concluded to implement two mesh CNFAs in AC circuit with AC frequency greater than 500 HZ for future study.

The future works in the modification, development, and study of CNFA behavior include:

- A modified or improved design with vertical grooves into the side plates of the formwork so that the meshes would slide down into the vertical slots and be held perfectly aligned.
- Different electrode material with more conductivity was unsuccessful in being implemented in our study due to misalignment of soft copper mesh. Stronger and welded or and nickel mesh can be explored.
- Cement based material is heterogeneous translating to variable electrical properties. Each CNFA has different initial impedance because of variability. Thus more homogenous material like silicon or another polymer with more consistent material behavior can be studied.

6.2.2 Optimization of CNFA

The impedance of CNFA in no-loading conditions was studied for different frequencies from 20Hz to 300kHz. It was noted that the variation of impedance with time without any stimuli is insignificant with an increase in frequency. It was also noted that the impedance magnitude decreases with increase in AC frequency of study. The impedance for different loading stages was also studied with time and observed that the frequencies of 100kHz and 200kHz could be selected for optimization of CNF in CNFA. The compression study revealed that the CNFAs with CNF content 0.8% to the cement weight had a maximum response. Maximum electrical impedance variation (EZV) was above 30% at peak load making CNFA suitable for load or stress monitoring in 2-probe AC circuit.

The future works in the optimization of CNFA study include:

- Due to instrumental limitations, frequencies higher than 300kHz could not be studied for steady-state response in loaded and no load cases. Higher frequencies research can be done to inspect the behavior of CNFAs.
- Dispersion of CNFs in mortar has always been an issue while making CNFA. Increasing the CNF content above 1% to the weight of cement did not give dispersed CNF in CNFA which were visible by naked eyes. Higher dosage of CNFs with higher dispersive techniques can be explored.
- Scanning electron microscope (SEM) images of CNFA mortar should be taken. These should include pictures of the fibers during casting to make sure the uniform dispersion of CNFS at a microscopic level making CNFA more sensitive. Also, SEM images for post-testing to capture the pull-out behavior and pictures of the mesh-fiber interaction can be done to understand the behavior of CNFAs
- CNFAs' electrical model for AC circuit should be explored to obtain the mathematical model and calibration for different stress levels.

- The study has shown that the CNFA have dominant behavior is in the axial direction when loaded in perpendicular to the mesh layer. The use of CNFAs oriented in all three principal directions should be explored.

6.2.3 Waterproofing of CNFA

Four different waterproofing coats were studied of which three were cementitious coats. Even though CNFA developed contained waterproofing admixture; it was unable to check the water entry into the CNFA. The cementitious coated CNFAs also failed unexpectedly as the electrical impedance variation (EZV) dropped immediately when plunged into the water. The fourth coat studied, i.e., the epoxy coat was able to check the entry of water into CNFA in observable 72 hours.

The future works in the study for waterproofing of CNFA may include:

- The epoxy coated CNFAs can be tested inside the concrete cylinders, to study the bond behavior and appropriateness to be used for strain sensing.
- A long term waterproofing study with softer CNFA is necessary for its implementation to monitor water-level in low-water crossing and bridges.
- The early properties of CNFA during casting and curing should be tested to observe the correlation between initial strengths and EZV.
- There was an observable temperature effect that noised the observable EZV during sensing. Proper heat insulation method should be explored for the noise-free study of CNFAs in different stimuli.

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