INVESTIGATING THE INFLUENCES OF INGREDIENTS, W/C RATIO AND DISPERSION METHODS FOR CNT MODIFIED SMART CONCRETE

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Tofatun Jannat

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The Supervisory Committee certifies that this ***disquisition*** complies with North Dakota State University's regulations and meets the accepted standards for the degree of

MASTER OF SCIENCE

SUPERVISORY COMMITTEE:

Dr. Ying Huang
Chair

Dr. Jerry Gao

Dr. Danling Wang

Approved:

July 8, 2022
Date

Dr. Xuefeng (Michael) Chu
Department Chair

ABSTRACT

Carbon nanotubes (CNT) have excellent electromechanical properties and can be added into cement using appropriate dispersive means to produce CNT-modified cement-based smart materials (CNTCS). This study investigates how the ingredients, W/C ratio and dispersion methods influence the sensing ability of the smart concrete. Three different dispersion methods were investigated: direct mixing, surfactant surface treated with NaDDBS, and the Carboxymethyl cellulose (CMC) surface modification. CMC surface modification method showed consistency for modified cement paste and cement-sand composite material. For CMC surface treatment method, 0.6 w/c ratio was found to be optimal compared to 0.4 and 0.5. Coarse aggregate was added with cement and sand for 0.6 w/c ratio, and consistent piezo electric response was observed under dynamic loading for CMC surface treated smart concrete. However, significant reduction of sensitivity was observed between the CMC surface treated CNT modified smart concrete compared to smart cement-sand composite and the smart cement paste.

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LIST OF ABBREVIATIONS

CMC...Carboxymethyl Cellulose

CNTs...Carbon Nanotubes

SWCNT..Single-Walled Carbon Nanotubes

MWNTs ....Multi-Walled Carbon Nanotubes

CNTCS... Carbon Nanotube Cement-based Sensor

NaDDBS ....Sodium Dodecyl benzenesulfonate

W/C..Water-cement Ratios

1. INTRODUCTION

Concrete is the most widely used construction materials and takes our civilization upwards. Around the world, concrete structures are exposed to numerous environmental conditions such as erosion, impact loads, weather, and pollution. Smart concretes and structures are an intelligent system having additional properties such as self-sensing and self-healing properties. They can react to external stimuli, such as stresses and temperatures. Self-sensing concrete (also called self-monitoring concrete, intrinsically smart concrete, and piezoelectric or pressure-sensitive concrete) is a branch of smart concrete. It is fabricated by adding functional fillers (carbon fibers, steel fibers, carbon nanotubes, nickel powder, etc.) into conventional concrete to enable its ability to sense strain, stress, cracking, or damage while maintaining or even improving mechanical properties. The functional fillers need to be well-dispersed in a concrete matrix to form an extensive conductive network inside the concrete. In this chapter, various methods to develop self-sensing concrete will be reviewed. Future challenges in the development and applications of smart concretes are also discussed.

1.1. Background

Civil infrastructural systems age and deteriorate during their service life due to factors such as aging of materials, excessive use, overloading, environmental conditions, and deficient maintenance. Concentrated loads cause concrete cracking and delamination, which can be hard to detect and has long-term impacts on the structure's performance (H. Zhang, Bilotti, and Peijs 2015; Thostenson and Chou 2008), as shown in Figure 1. As a result, structural health monitoring of civil infrastructures is of considerable importance. The unique features of the enormous size and complexity of most civil infrastructures renders visual inspection very tedious, expensive, and sometimes unreliable. Previously local damage monitoring and health warning of the structures were acquired by several types of attached or embedded sensors such as shape memory alloy, resistance strain gauge, and fiber optical grating. However, these traditional sensors often have limitations such as poor compatibility with concrete and local measurements (Dong, Xing, and Li 2011).

Figure 1. A bridge with serious damages (https://www.fprimec.com/testing-damaged-bridges/).

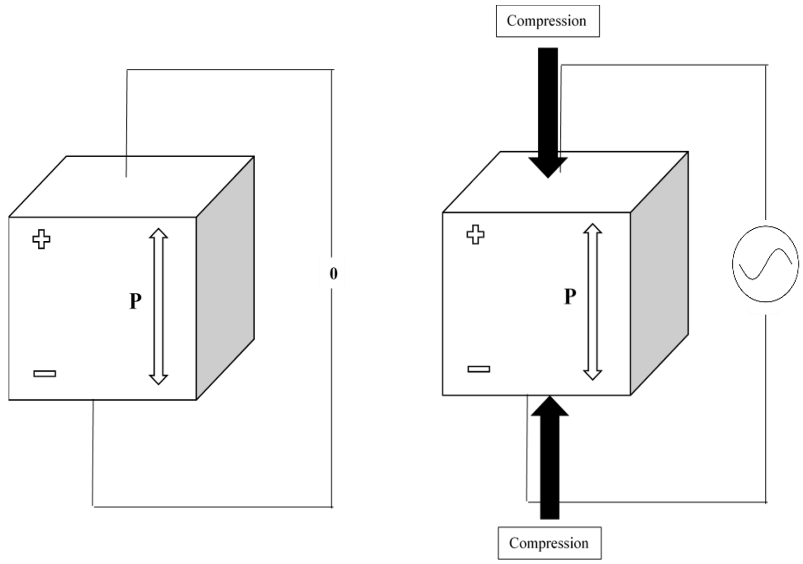
The needs for quick assessment of the state of health of civil infrastructures have necessitated research for the development of an automated, real-time, and in situ health monitoring technique. Such kind of technique allows the system to monitor its structural integrity while the infrastructures are in service, and the monitoring can be performed throughout the service life of the infrastructures. Therefore, the research and development of smart cement-based materials with intrinsic piezo resistive and/or piezoelectric self-sensing capability have crucial engineering significance for the better achievement of SHM (Teng et al. 2021). Such a structural health monitoring system is useful not only to improve reliability but also to reduce the costs of maintenance and inspection for infrastructural systems (Dong, Xing, and Li 2011).

1.2. Literature Review

Various techniques have since been developed to convert mechanical displacements into electrical signals. Piezoelectricity is the charge created across certain materials when mechanical stress is applied (J.X.J. Zhang and Hoshino 2018). They are very robust and are used in a wide range of industrial applications. It is the most common property which smart concrete tends to use upon. In this section, literature review on the piezo-electric effects, material selection, and the piezo-electric properties of CNT modified cementitious materials were discussed.

1.2.1. Working Principle of Piezo-electric Effect

The piezoelectric effect, discovered in 1880 by French physicists Jacques and Pierre Curie, is defined as the linear electromechanical interaction between the mechanical and electrical state (in a crystalline material with no inversion symmetry) such that electric charge is accumulated in response to the applied mechanical stress (Figure 2). The piezoelectric effect is a reversible process in that the direct piezoelectric effect (generation of electrical charge under an applied mechanical strain) can be reversed to generate a mechanical strain via the application of an electrical charge (reverse piezoelectric effect) (Egorov et al 2019).



(a) (b)

Figure 2. Schematic of direct piezoelectric effect: (a) piezoelectric material; electrical charge generation under (b) compression.

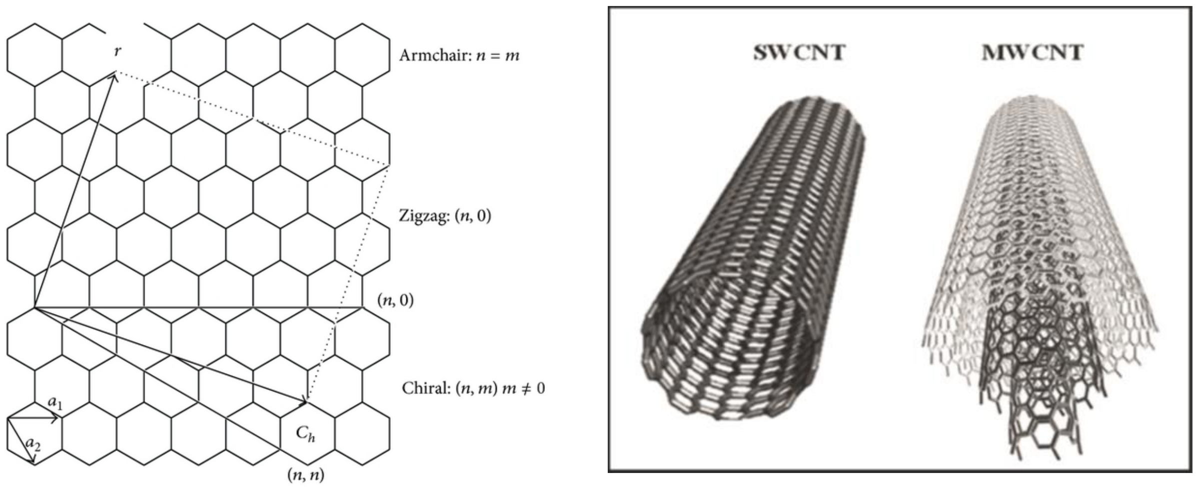
Piezoelectric-based transducers rely on the piezoelectric effect, which occurs when a crystal reorients under stress forming an internal polarization. This polarization results in the generation of charge on the crystal face that is proportional to the applied stress (Cullinan et al. 2012). Piezoelectric sensor elements generate an output signal directly from the applied strain. There is also an inverse piezoelectric effect where applying a voltage to the material will cause it to change shape. A given static force results in a corresponding charge across the sensor. This dynamic sensitivity means they are good at measuring slight changes in pressure, even in a very high-pressure environment.

The main advantages of piezoelectric sensors are toughness, low power, and insensitive to electromagnetic interference. The piezoelectric elements can be small with an extremely fast response to changes in pressure. Some devices can measure rise times in the order of 1 millionth of a second. The sensors are simple to construct and can be made from inexpensive materials. They function over a wide range of pressures and temperatures so there are suitable sensors available for every application.

1.2.2. Piezo-electric Materials Selection

Some of the piezoelectric materials found include: 1) naturally occurring biological piezoelectric materials such as human bone, tendon, cellulose, collagen, and deoxyribonucleic acid; 2) naturally occurring piezoelectric crystals such as quartz (SiO2), Rochelle's salt (NaKC4H4O6 · 4H2O), topaz, tourmaline group minerals, etc.; 3) synthetic piezoelectric ceramics such as lead zirconium titanate, PZT (Pair of lead Zirconate Titanate) (Pb [ZrxTi1 − x] O3 $0 \leq x \leq 1$), barium titanate (BaTiO3), potassium niobate (KNbO3), bismuth ferrite (BiFeO3), zinc oxide (ZnO), etc.; and 4) synthetic piezoelectric polymers such as poly (vinylidene fluoride) ((CH2-CF2) n), co-polymers of PVDF such as poly (vinylidene fluoride-co-trifluoroethylene) P(VDF-TAFE), polyimide, odd-numbered polyamides, cellular polypropylene, etc. Among the examples of piezoelectric materials shown above, for wearable and body-worn applications, where repeated substantial amounts of strain are encountered, ceramic materials are not amenably owing to their brittleness, low strain capabilities, and the toxicity of lead-containing materials such as PZT.6,10 These factors, coupled with the increasing demand for flexible electronics, have inspired scientists to develop increasingly efficient flexible energy harvesting materials. Piezoelectric polymers offer huge advantages over piezoelectric ceramics, including low material density, flexibility, biocompatibility, and lower costs (N. Soin, T.H. Shah 2016). However, these traditional piezo-electric materials usually are applied to develop sensors with needs for small sizes and local measurements.

In recent decades, studies in Nano piezotronics have indicated that strained graphene may exhibit abnormal flexoelectric and piezoelectric properties. Similar assumptions have been made regarding the properties of carbon nanotubes (CNTs). Experiments were carried out confirming the occurrence of a surface piezoelectric effect in multi-walled CNTs under a non-uniform strain (Il'ina et al. 2018). CNTs are described as a long cylinder formed by rolling a graphene sheet and then closing it on both sides by fullerene hemispheres, which were discovered by Iijima in 1991. There are two types of CNTs, single-walled carbon nanotubes (SWCNT) and multi-walled carbon nanotubes (MWCNTs). In addition to the two different basic structures, there are three distinct types of carbon nanotubes. These three types of CNTs are armchair carbon nanotubes, zigzag carbon nanotubes, and chiral carbon nanotubes. The difference in these types of carbon nanotubes is created depending on how the graphite is “rolled up” during its creation process. The choice of the rolling axis relative to the hexagonal network of the graphene sheet and the radius of the closing cylinder allows for several types of SWCNTs (single-walled carbon nanotube) (Figure 3a) (Saifuddin, Raziah, and Junizah 2013). The SWCNTs are the fundamental cylindrical structure of a graphene sheet defined by its diameter (about 0.43 nm) and chirality. The MWCNTs are made of coaxial cylinders (Figure. 3b), which have interlayer spacing close to that of the interlayer distance in graphite. The inner nanotube has a smaller diameter than the outer nanotube. These cylindrical structures are only a few nanometers in diameter, but the cylinder can be tens of microns long, with most end-capped with half of a fullerene molecule. The SWCNTs have equivalent properties as SWCNTs, yet the outer walls on MWCNTs could protect the inner CNTs from chemical interactions with outer ones. The CNTs have an extremely high tensile strength of 100 GPa and excellent elasticity. The MWCNTs have an even higher tensile strength than the SWCNTs (Min et al. 2010).



(a) (b)

Figure 3. (a) Schematic representation of formation of single-walled carbon nanotubes by rolling of a graphene sheet along lattice vectors which leads to armchair, zigzag, and chiral tubes(Saifuddin, Raziah, and Junizah 2013) and (b)Diagrams of the SWCNT and the MWCNT (Veena).

Because of the covalent bonding of carbon atoms to form CNTs, it delivers excellent mechanical properties, such as extremely high aspect ratios as reinforcing fibers for stronger and tougher cementitious materials as well as decreasing the porosity of the composite to reduce crack growth. Since the CNTs are tube-shaped and made of carbon atoms on a nanometer scale and have a much finer scale than common fibers, it is more efficient for crack bridging at the very beginning stage of crack propagation within composites (Foldyna, Foldyna, and Zeleňák 2016).

Cement as the main ingredient of cementitious materials has no sensing capability. Therefore, the addition of functional fillers can enable electrical conductivity in cementitious materials. As CNTs possess excellent electrical conductivity and are known as the most promising self-sensing material in cementitious materials to assist with achieving piezo-resistive effect (Reales and Filho 2017). The piezoelectric sensing characteristics of CNT favor the development of CNT modified cement paste into an intrinsic sensor for concrete structure (Ubertini et al. 2014) and it had been used as a concrete embedded sensor for the identification of the fundamental frequency of footprint-reinforced concrete beams. The CNT modified cement paste also had been employed as the cementitious sensor for repair works, and its piezoresistive response under stress changes was captured which could provide an early warning failure (Metaxa et al. 2016). In addition, it had been developed as a two-end wire connected with a pair of lead zirconate titanate (PZT) wafers to evaluated the feasibility of a non-destructive monitoring method for concrete strength detection (Tareen et al. 2021). Further efforts had been made to establish an intelligent traffic monitoring through embedded CNT modified cement paste sensors, which can be used for vehicle weighing and traffic flow detection under high-speed movement (J. Zhang et al. 2015).

1.2.3. Current State-of-Practice of Investigation on W/C, Components, Mechanical and Piezo-electric Properties of CNTs Modified Cementitious Materials

The additive of CNTs in cement mortars would dramatically enhance the electrical conductivity, flexural and compressive strength as well as failure strain. In particular, it could increase the compressive strength up to 19%, and flexural strength up to 25% as well as possessing the highest Young's modulus (1.4 TPA), tensile strength (above 100GPa), current density (109 A/cm^2), thermal conductivity (above 3000 W/mK), and high aspect ratios, 0.5 nm to 5 nm diameters (Ganesh 2013).

The percentage of CNTs used in cementitious materials is a critical parameter for strength improvements (Leonavičius et al. 2017). Previous studies demonstrated that the optimum percentage of CNTs in cementitious materials is approximately 0.1% of CNTs by mass of cement, which will increase electrical conductivity and almost double the compressive strength (Reales and Filho 2017).

Moreover, modified CNTs cementitious materials have been found that the electrical conductivity and piezo-electric effect were also significantly improved because the CNTs create larger surface contact with cementitious materials than other potential nanoparticles (Spires and Brown 1996). The presence of microcracks could be indicated with stable increases in the conductivity, which would change to a sudden peak when micro cracks coalesce, and failure occurs (Rausch and Mäder 2010).

These electromechanical characteristics of CNTs open new potential applications for cementitious nanocomposites with enhanced mechanical properties and added multi-functionality in stress monitoring of cementitious structures, detecting damage (Konsta-Gdoutos and Aza 2014). Meanwhile, it has been revealed that the self-sensing capability of nanotube-cement composites could be utilized in various applications, such as under dynamic load and impact, in the elastic and plastic ranges of deformation, and for crack development sensing (Reales and Filho 2017).

But it has not been studied yet the influence of CNTs in cementitious materials with different water-cement ratios. The water to cement ratio largely determines the strength and durability of the concrete when it is cured properly. The w/c ratio refers to the ratio of the weights of water and cement used in the concrete mix. Based on the exposure conditions and requirements, the w/c ratio is selected. As concrete is composed with cement, sand and coarse aggregate, so the effect of CNTs for stress sensing can be affected by the concrete components as well as different water cement ratios.

1.2.4. CNTs Dispersion Methods

As composites are multifunctional materials made of two or more materials with different properties, which can be regarded as two parts including matrix and functional phases. A good dispersion of added phase in the matrix is a key prerequisite to ensure the functionality of composites (Chia and Huang 2017b). Although CNTs can be a potential candidate for self-sensing in cementitious materials, it also has drawbacks. The biggest problem of applying CNTs into cementitious materials is that they tend to form into a group due to a considerable amount of Van der Waals force functioning in between CNTs. Therefore, it is necessary to identify the practical means of dispersion to ensure good dispersion of CNT in the cement matrix (Chia et al. 2021). Effective dispersion methods for functional fillers in cementitious materials are necessary to form consistent and optimized conductivity. The current dispersion methods for CNT include mechanical stirring, ball milling, ultrasonic treatment, electric field induction, surfactant treatment, strong acid oxidation, etc. (Ping ZHU 2018) and some of them are listed in Table 1 (Parveen, Rana, and Fangueiro 2013).

Table 1. Comparison of current dispersion methods

Methods	Procedures	Time
Direct Mixing	Easy (Direct Mixing with Water)	5 Minutes Plus
Surfactant	Medium (Add 0.5% NaDDBS & 0.25% Defoamer)	2 Hours Plus
Acid Treatment	Medium (Add Sulphate & Nitric Acid)	10 Minutes Plus

NaDDBS: Sodium Dodecylbenzen Sulfonate

The direct mixing method is easy to conduct and very time-efficient, however, studies have shown that direct mixing CNTs in water without any dispersing agent would not effectively disperse CNTs into the cement mortars. The piezo-electric effect changes from dynamic loadings are minor compared with Surfactant and Acid Treatment methods. CNTs dispersed more evenly in a cement mixer with less water (Materazzi, Ubertini, and D'Alessandro 2013). A cement mixture with less water increases the piezo-electric sensitivity in CNTs (Kim, Park, and Lee 2014).

More recently, the piezo-electric response of two different dispersion methods of CNTs in cement was studied, including the use of acid surface treatment and surfactant Sodium Dodecylbenzene Sulfonate (NaDDBS) surface modification. The experimental results showed that the acid treatment method had a much stronger and more accurate response compared to the surfactant method (Kim, Park, and Lee 2014). However, it was difficult to scale up for larger samples. The use of strong acid also made it difficult to implement as it would pose a danger in the field.

Though not as good as an acid-treated method, the piezo-electric response from the surfactant dispersion method was also tested to be promising (Chia and Huang 2017b). Studies performed on two different surfactants for surface modifications including Sodium Dodecyl Sulfate (SDS) and NaDDBS also showed that the NaDDBS dispersed CNTs are more stable and sensitive to the external force compared with SDS in dispersing the CNTs (Yu and Kwon 2009). In addition, superplasticizers and silica fumes have also been used as surfactants to mix CNTs into cement. However, the researchers claimed that these methods were not effective due to the lack of consistency of dispersion(Yu 2012). In all these investigations, MWNTs were adopted as they are more sensitive to stress changes compared with SWNTs.

CNTs can be added to cementitious materials to create a multifunctional nanocomposite with excellent strain-sensing properties but it requires uniform dispersion on the cementitious material to achieve such quality. Recent studies shows that, CMC surface modification significantly improves the dispersion effectiveness and significantly increased the stress detection sensitivity and consistency (Chia et al. 2021). But the research was only conducted for smart cementitious materials. Influence of sand and coarse aggregate on cement as concrete has not been investigated.

1.3. Problem Statements

From the above literature reviews, the following findings and gaps in knowledge can be identified to achieve effective self-sensing concrete materials:

1) Currently there are limited studies on how the concrete ingredients and water-cement ratio influencing the sensing properties of the smart concrete;

2) For CNTs modified cementitious materials, a proper dispersion is challenging. There are currently several dispersion methods available such as direct mixing, the surfactant method, and the acid treatment method, but none of them can produce a uniform, consistent, and optimized dispersion. Recent studies show that CMC surface treatment method significantly improves the dispersion effectiveness in cementitious materials, but it has not been studied yet the dispersion effectiveness with all the concrete ingredients with different water cement ratios.

1.4. Objectives and Arrangement of This Thesis

To meet the challenges mentioned above, the objective of this study is to develop an effective co-polymer dispersing method that could achieve a uniform and consistent dispersion for CNTs in smart concrete materials. The specific tasks of this study to address these challenges are listed below:

1) Investigating the influences of dispersion methods on smart cementitious and concrete materials to achieve better dispersion of CNTs.
2) Investigating the influence of concrete ingredients on the sensing ability of smart cementitious materials;
3) Comparing various water-cement ratios for surface treatment methods for cementitious material and defining the better stress sensitivity for concrete materials.

Thus, the remaining thesis is organized as follows: in Chapter 2, different dispersion methodology are introduced, and sample preparations are presented to include all three dispersion methods for three different combinations of smart cementitious materials with different three water-cement ratios; in Chapter 3, experimental results are illustrated; in Chapter 4, the results are discussed to show the influences of concrete ingredients, water-cement ratio, and dispersion methods for smart concrete materials; in Chapter 5, conclusions and future work, which have been demonstrated based upon the findings from this study.

2. METHODOLOGY AND SAMPLES PREPARATION

To validate the effectiveness of the CMC surface treatment dispersion method, this chapter introduces the dispersion methods of the CNTs in water by utilizing three different dispersing methods, including direct mixing, surfactant method, and the CMC surface treatment method. MWCNTs were used throughout the study (supplied by SkySpring Nanomaterials, Inc.). After dispersing CNTs in water solution using the three different methods, cement mortar, samples with cement-sand, and cement-sand-aggregate cubic samples with dimensions of 2 in. × 2 in. × 2 in. × 2 in. × 2 in. were made for further testing. All the samples were prepared at room temperature (22°C ± 2°C).

2.1. Selection of Water Cement Ratio

To investigate the influences of water-cement (w/c) ratio on sensing properties of smart concrete material, three water cement ratios including 0.4, 0.5, and 0.6 are used in this study as they are the typical w/c ratios used in fields. A mix ratio of 0.35 may not mix thoroughly, and may not flow well enough to be placed, on the other hand too much water will result in segregation of the sand and coarse aggregate components from the cement paste (Kishan Mudavath, 2017). In addition, to investigate the influence of concrete ingredients, three cementitious materials composites are studied including cement paste, cement-sand composite, and concrete with cement, sand, and coarse aggregate.

2.2. Dispersion Methodology

To investigate the influence of dispersion methods, in this study, three dispersion methods are studied including direct mixing method, surfactant surface treatment method, and the CMC surface treatment method. Although the acid treatment method had a much stronger and more accurate response compared to the surfactant wrapping method (Han and Yu 2014), it is not used in this study because previous studies showed that the use of acid treatment was difficult to scale up for larger samples and it also made the treatment difficult to implement, as it would pose danger in the field. In addition, the super plasticizer and silica fume are not included in this study as literatures showed that these methods were relatively not effective (Yu and Kwon 2012).

2.2.1. Direct Mixing Method

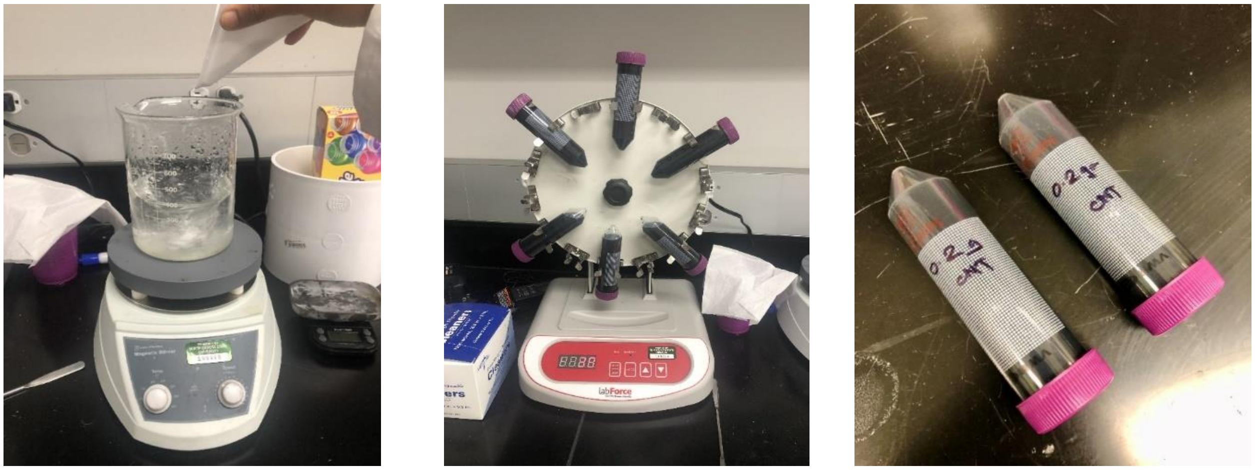
The direct mixing method was the most common method for mixing CNTs into cement mortar. This method directly mixes the CNTs (0.1% of cement) in cement, sand, and water, without any treatment of CNTs. Three steps are followed by using the direct mixing method as below:

1) First, 0.2 g CNTs is added to 120 ml of water to have a 0.1% CNTs solution.
2) Second, 0.1% CNTs solution is fully mixed with a stirring bar on the magnetism stirrer for 5 minutes.
3) Last, 0.1% CNTs solution is mixed with 200 g cement and 400 g of sand (1:2 design mix ratios) to make a 2-inch by 2-inch by 2-inch cement block for 0.6 water-cement ratio.
4) The same procedure was followed for 0.5 and 0.4 water-cement ratios for 1:2 cement-sand design mix respectively.

2.2.2. CMC Surface Treatment Method

For CMC surface treatment method, based on the literature review, it is shown that 0.1% of CNT with 0.5% of CMC had the better sensitivity in cement mortar samples compared to other ratios (Chia et al. 2021). Thus, this study adopted 0.5% of CMC for 0.1% CNTs by weight. The methodology to disperse CNTs using CMC surface treatment and fabricating cement mortar samples is described below:

1) CMC water solution was prepared by mixing 5 g of dry CMC (0.5% of water) with 1000 mL of water. Since CMC is water–absorbent and has high water retention, it clumps easily. To prevent this, CMC should be slowly added to the center of the vortex. The solution was stirred at 1600 rpm for 30 minutes until CMC completely dissolved into water as shown in Figure 4(a).
2) The CMC water solution was further mixed with CNTs (0.1% of cement) in 50 ml test tubes and placed into a tube rotator for at least 72 hours rotating to make sure a proper coating of CMC on the CNTs as seen in Figure 4(b).
3) Last, the CMC-treated CNTs sediment was mixed with 400 g of cement with 240 ml, 200 ml, and 160 ml of water respectively to make cement mortar samples with 0.6, 0.5, and 0.4 of water-cement ratios for sensing testing.
4) For samples with sand, a 1:2 design mix ratio was followed. 400 g of sand was added with 200 g of cement with 240 ml, 200 ml, and 160 ml of water respectively. And for the coarse aggregate 1:2:3 design mix ratio was followed. 400 g of sand and 600 g of coarse aggregate was added with 200 g of cement with 240 ml, 200 ml, and 160 ml of water respectively for 0.6, 0.5, and 0.4 water-cement ratios.



(a) (b) (c)

Figure 4. (a) Preparation of the CMC solution under mixing; (b) The test tubes with carbon nanotubes wrapped with CMC being placed in the rotator; (c) Fully dispersed CNTs solution with 0.5% CMC using CMC surface treatment method after 72 hours of rotating.

2.2.3. Surfactant Dispersion Method

For surfactant dispersion method, there are two different surfactants for surface modifications including sodium dodecyl sulfate (SDS) and NaDDBS. Among these two, the NaDDBS was found out to be more stable and sensitive to the external force compared with SDS when dispersing the CNTs (Yu and Kwon 2009). Thus, in this study, the NaDDBS is used as surfactant for the surface treatment on CNTs. The NaDDBS was provided by Sigma-Aldrich Co., USA. A critical micelle concentration of NaDDBS in water, 1.4×10-2 mol/L, was taken as the input surfactant concentrations. Four steps were needed to prepare the surfactant solution with CNTs as follows:

1) First, 1.17g of NaDDBS was mixed with 240ml of water using a stirring bar for up to 5 minutes.
2) Secondly, the 0.2 g CNTs (0.1% of cement) were added to the aqueous solution and utilized a sonicator for 2 hours to make a uniformed dispersion solution as shown in Figure 5.

3) Thirdly, NaDDBS treated CNTs solution was mixed with 200 g of cement and 400 g of sand and 200 g of cement, 400 g of sand, and 600 g of coarse aggregate till the solution was dispersed into cement very well for 0.6 water-cement ratio.
4) Last, due to the properties of NaDDBS, air bubbles would appear in the cement mortars. Therefore, 0.25% of defoamer (by volume) was utilized to decrease the air bubble in CNTs filled cement mortars and mixed till NaDDBS treated CNTs solution with defoamer dispersed well. The defoamer was provided by Tributyl phosphate supplied by Sigma-Aldrich Co., USA.

Figure 5. The test tubes with carbon nanotubes with NaDDBS being placed in the sonicator.

2.3. Samples Preparation

All the CNTs solutions from the three different methods with three different water-cement ratios prepared in Section 2.1 were mixed with cement, cement-sand, and cement-sand coarse aggregate and placed into 2in. × 2 in. × 2 in. molds to make samples as shown in Figure 6. The samples were kept in molds for 24 hours at room temperature (22°C ± 2°C). An exception would be that all the cement mortars and concrete samples with 0.5% CMC, needed 30 hours of sitting time in the molds to stay intact. Electrical wires were placed half-inch deep and half-inch apart from each other in each sample before the samples were cured. The samples were demolded and put into water for 7 days to cure followed by 10 days of air drying at room temperature. Figure 7 demonstrates a ready-mixed sample.

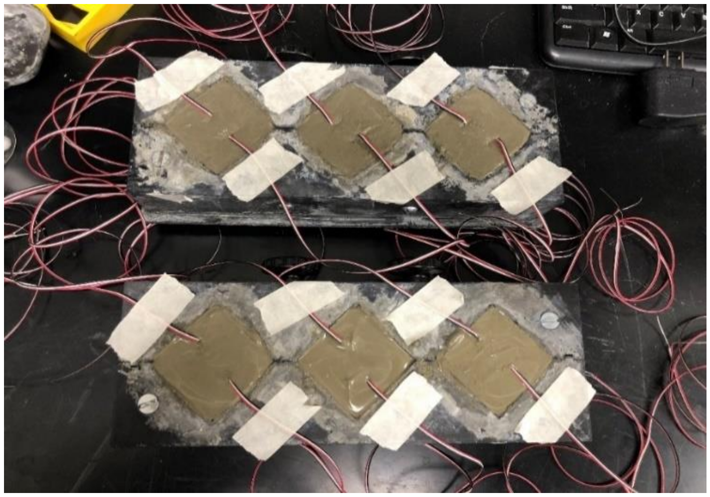


Figure 6. The 2 inches cubic molds for fabricating samples.

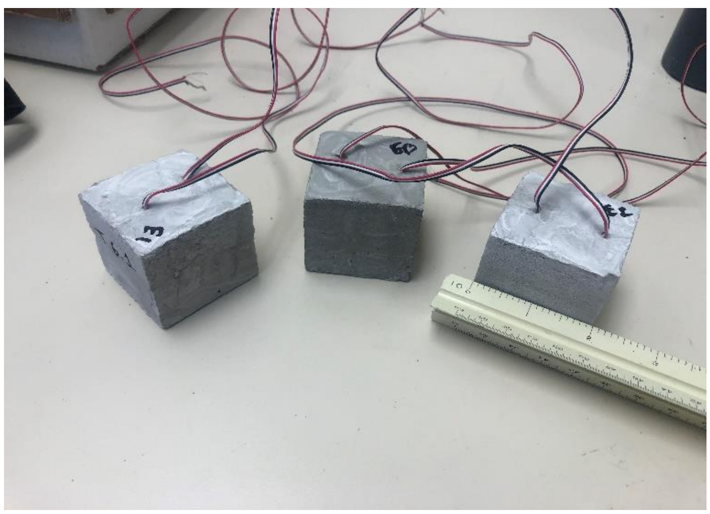


Figure 7. The sample embedded with electrical wires after curing.

Table 2 below shows the testing sample matrix. Various samples were made based on the three different dispersion methods and water-cement ratios. Figure 8 shows the samples made for this study. Group A is control samples, which are simply made of water, cement, and sand. Therefore, no electric changes are expected. Group B, C, and D used 0.1% CNTs solution directly mixed into cement and cement- sand samples for 0.6, 0.5, and 0.4 water-cement ratios respectively.

The purpose of this design is to make comparisons between direct mixing and the CMC surface treatment method with a fixed percent of CNTs content. Group E to J is also designed as control samples as well as for testing how CMC itself affects the property of the cementitious and concrete material with different water-cement ratios. Group K represents the samples made with cement-sand and coarse aggregate with the most consistent water-cement ratio. Group L and M are samples from the surfactant method with NaDDBS.

Table 2. Testing sample matrix

Dispersion Method	Group	Sample No.#	Description	W/C Ratio	Design Mix
None	A	3	Control (No CNTs and CMC)	0.6	1:2 Cement: Sand
Method #1 Direct Mixing	B	3	0.1% CNTs	0.6	1:2 Cement: Sand
	C	3	0.1% CNTs	0.5	1:2 Cement: Sand
	D	3	0.1% CNTs	0.4	1:2 Cement: Sand
Method #2 CMC Surface Treatment Method	E	3	0.1% CNTs + 0.5% CMC	0.6	Cement
	F	3	0.1% CNTs + 0.5% CMC	0.5	Cement
	G	3	0.1% CNTs + 0.5% CMC	0.4	Cement
	H	3	0.1% CNTs + 0.5% CMC	0.6	1:2 Cement: Sand
	I	3	0.1% CNTs + 0.5% CMC	0.5	1:2 Cement: Sand
	J	3	0.1% CNTs + 0.5% CMC	0.4	1:2 Cement: Sand
	K	3	0.1% CNTs + 0.5% CMC	0.6	1:2:3 cement: sand: coarse aggregate
Method #3 Surfactant Method	L	3	0.1% CNTs + 0.5% NaDDBS + 0.25% deformer	0.6	1:2 Cement: Sand
	M	3	0.1% CNTs + 0.5% NaDDBS + 0.25% deformer	0.6	1:2:3 cement: sand: coarse aggregate

Figure 8. The sample groups from three different dispersion methods with different water-cement ratios.

2.4. Summary

In this chapter, the dispersion methodology of three different methods was introduced to investigate CNTs dispersion, as well as the samples, were prepared. The direct mixing method is directly mixing CNTs with distilled water. The surfactant method is mixed with NaDDBS and defoamer to disperse the CNTs in cementitious materials. Last, the proposed CMC surface treatment method utilizes CMC solution to mix with CNTs. The water-cement ratios remain the same for all three methods. The laboratory testing of these prepared samples will be further explained in Chapter 3.

3. EXPERIMENTAL SETUP AND RESULTS

This chapter presents the laboratory experimental setup and the experimental results by using the direct mixing method, surfactant method, and CMC (Carboxymethyl Cellulose) surface treatment dispersion methods for different water-cement ratios mentioned in Chapter 2 to validate the statistically experimental data for cement mortar samples and samples made with cement and sand. Also, to further prove the experimental data, comparisons between various water-cement ratios and dispersing methods are conducted.

3.1. Experimental Setup

The prepared samples were tested under dynamic loads to test their sensing capacity. Figure 9 illustrates the laboratory test setup. Dynamic loading tests were applied on each cement and concrete sample by utilizing MTS 809 Axial/Torsional Test Systems, Inc., USA. The piezoelectric response was measured by a digital bench multi-meter (BK 5492B, B&K Precision Inc., USA). Samples were subjected to dynamic loading as shown in Figure 10 with an average load of 1,912 N and a range from 166 to 2,078N in 10-12 cycles. The frequency of the loading was set to be 0.1 Hz. All the samples were tested at room temperature.

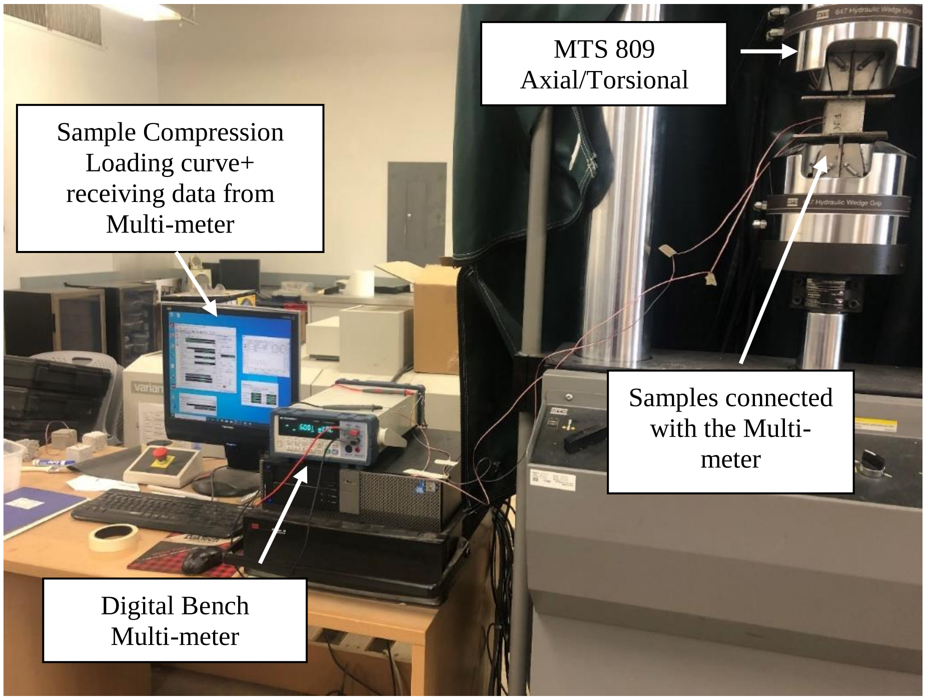


Figure 9. Laboratory setup for full experimental setup.

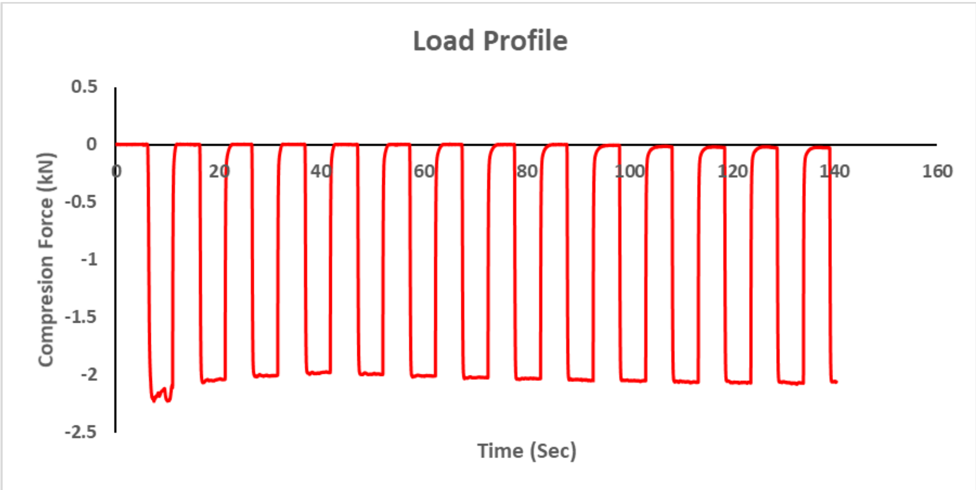


Figure 10. Dynamic loading curve.

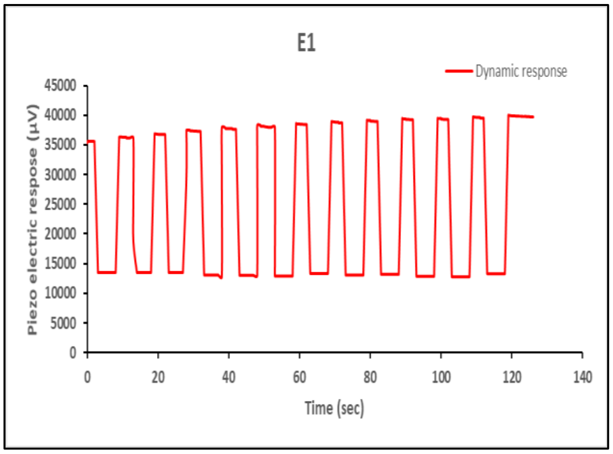
3.2. Experimental Results

This section shows the experimental results of base piezo-electricity and sensitivity of the smart cementitious materials and samples made with cement and sand under dynamic loads in Figure 10 from the samples prepared using the three different dispersion methods, including the direct mixing method, the surfactant method, and the CMC surface treatment method. In addition, it also illustrates the test results from samples made from the CMC surface treatment method with three different water-cement ratios of 0.6, 0.5, and 0.4 under dynamic loading, to validate an effective and reproducible method for CNTs (carbon nanotubes) dispersion in concrete materials.

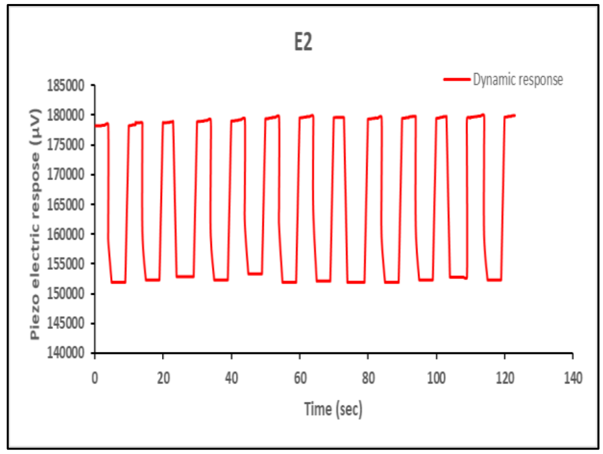
3.2.1. The CMC Surface Treatment Method

3.2.1.1 Cementitious Samples

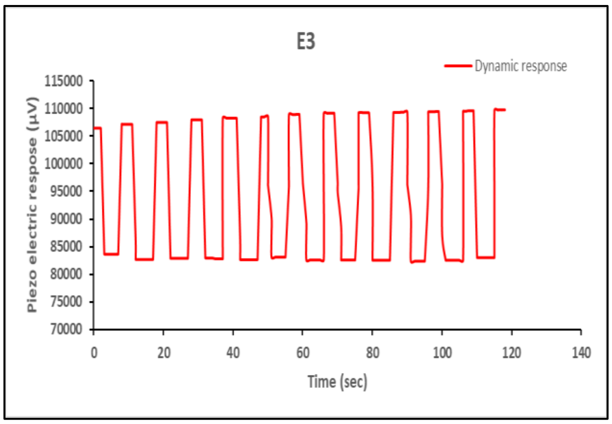
Figure 11 (a), (b) and (c) provide the dynamic responses from sample E1 to E3. The samples are made with 0.6 water-cement ratios. The responses are presented in μV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 11 (d) shows the average response is 12 μV/N and the responses are constant for all the three samples.



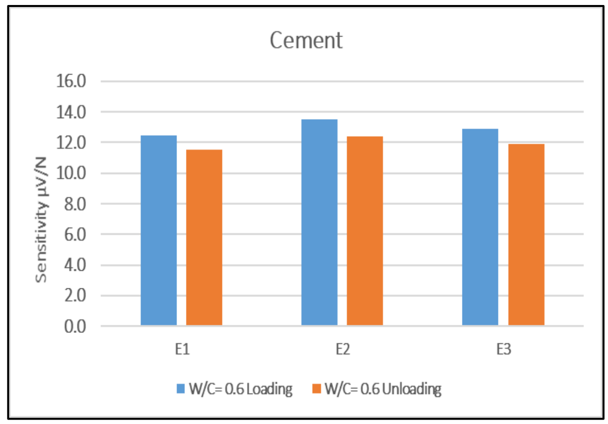
(a)



(b)



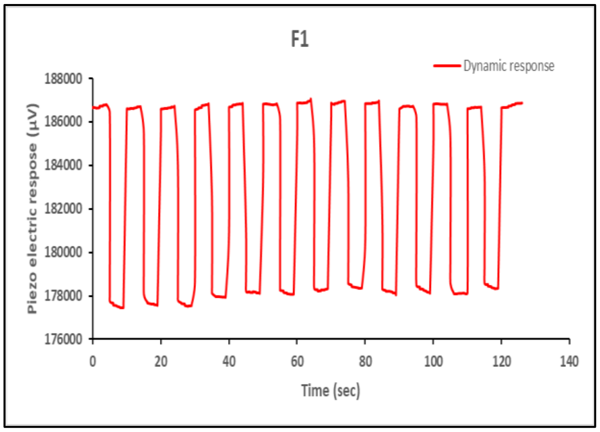
(c)



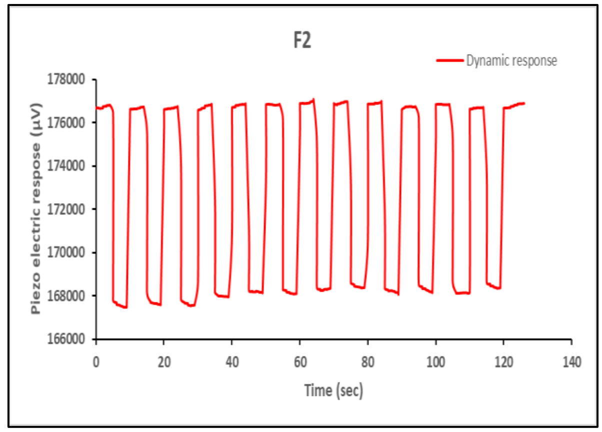
(d)

Figure 11. Piezo-electric responses for CMC surface treatment method: sample (a) E1, (b) E2, (c) E3, (d) samples summary.

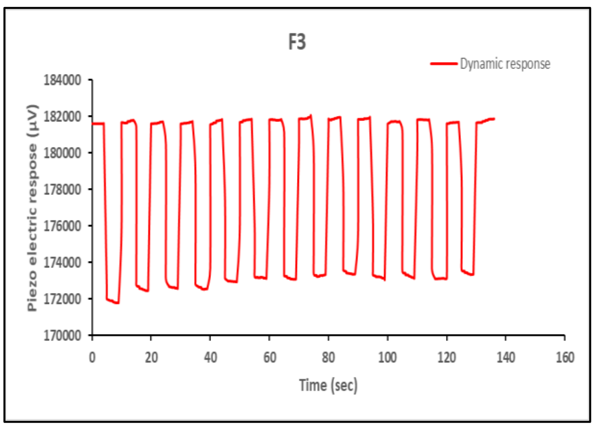
Figure 12 (a), (b) and (c) provides the dynamic responses from sample F1 to F3. The samples are made with 0.5 water-cement ratios. The responses are presented in µV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 12 (d) shows the average response is 4.4 µV/N and the responses are constant for all the three samples.



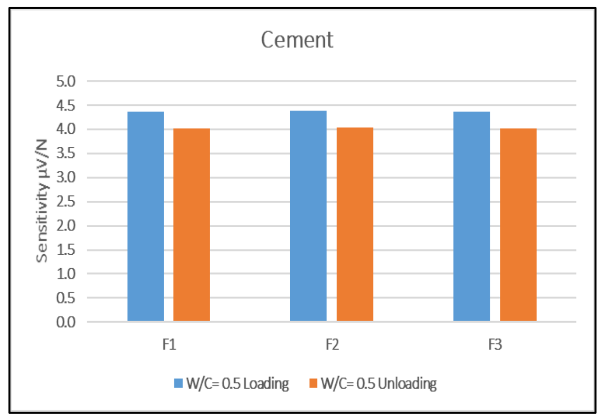
(a)



(b)



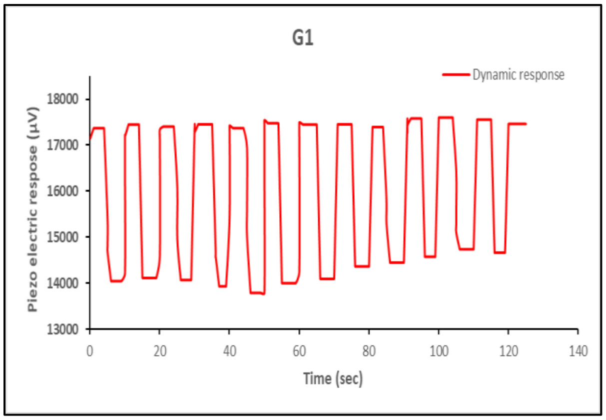
(c)



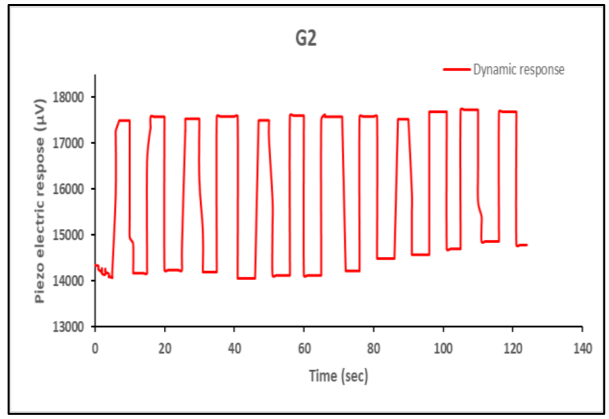
(d)

Figure 12. Piezo-electric responses for CMC surface treatment method: sample (a) F1, (b) F2, (c) F3, (d) samples summary.

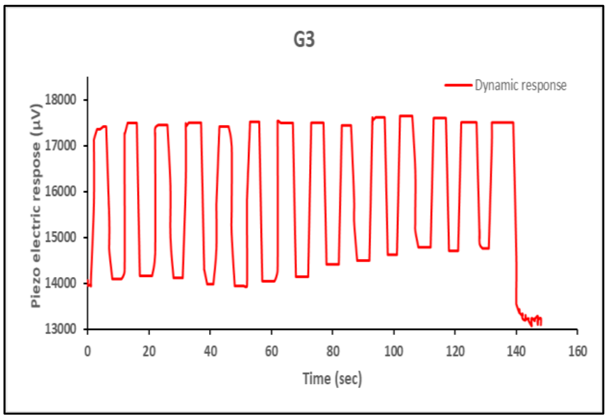
Figure 13 (a), (b) and (c) provide the dynamic responses from sample G1 to G3. The samples are made with 0.6 water-cement ratios. The responses are presented in µV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 13 (d) shows the average response is 1.6 µV/N and the responses are constant for all the three samples.



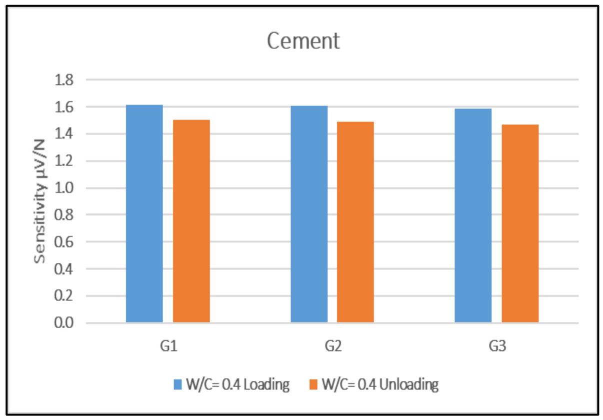
(a)



(b)



(c)

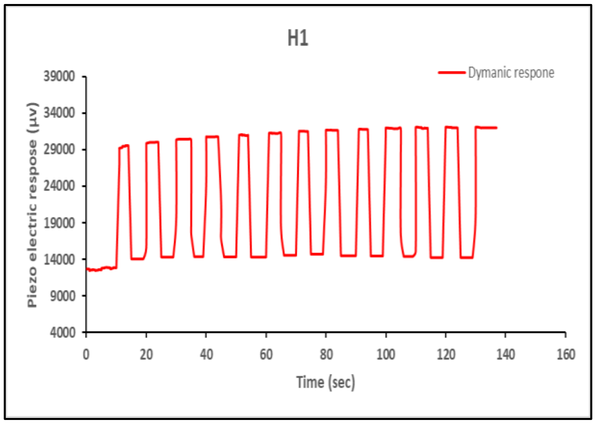


(d)

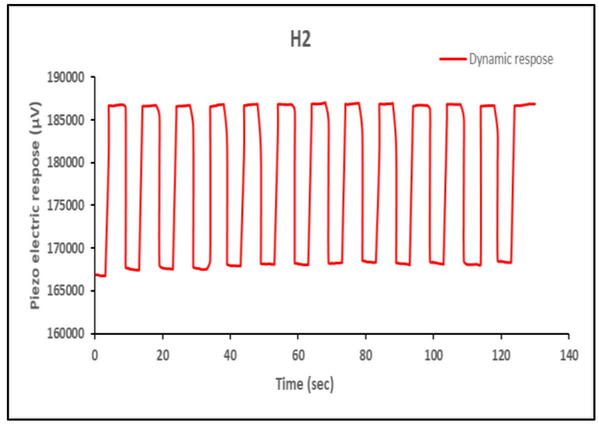
Figure 13. Piezo-electric responses for CMC surface treatment method: sample (a) G1, (b) G2, (c) G3, (d) samples summary.

3.2.1.2 Samples with Sand and Cement

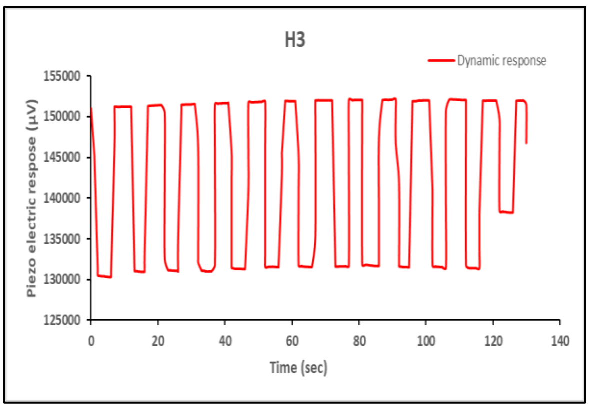
Figure 14 (a), (b) and (c) provides the dynamic responses from sample H1 to H3. The samples are made with 0.6 water-cement ratios and sand was added with 1:2 cement: sand ratios. The responses are presented in µV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 14 (d) shows the average response is 9.3 µV/N and the responses are constant for all the three samples.



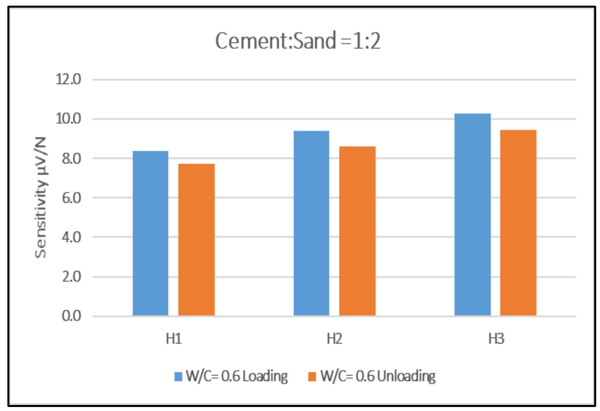
(a)



(b)



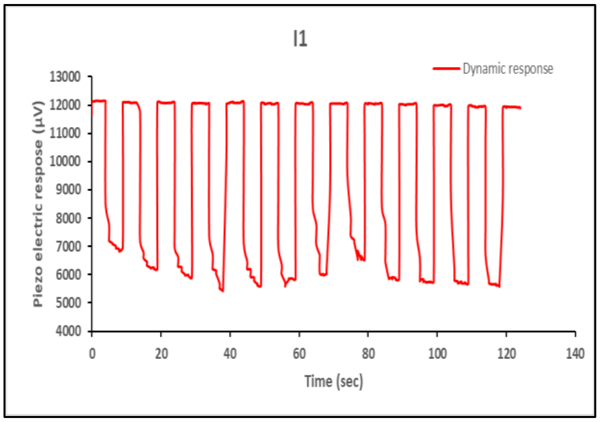
(c)



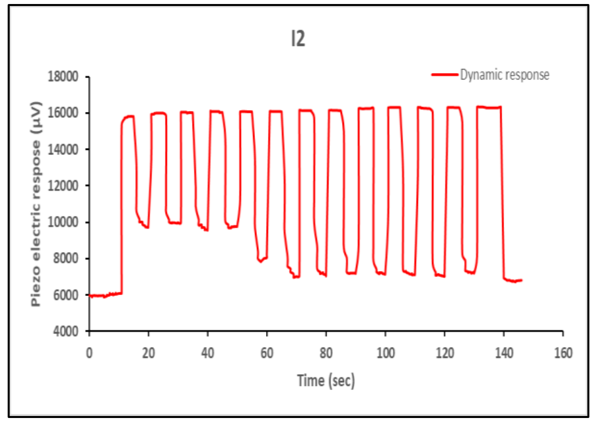
(d)

Figure 14. Piezo-electric responses for CMC surface treatment method: sample (a) H1, (b) H2, (c) H3, (d) samples summary.

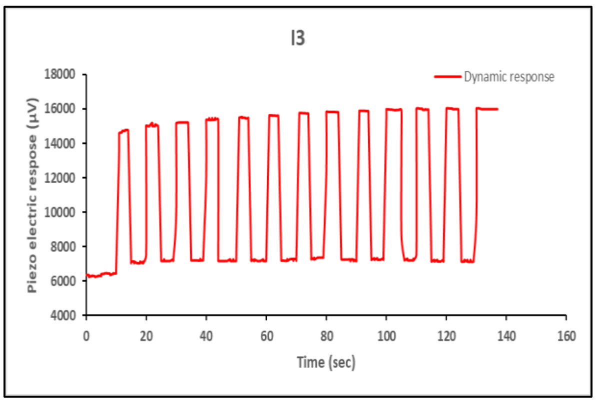
Figure 15 (a), (b) and (c) provides the dynamic responses from sample I1 to I3. The samples are made with 0.5 water-cement ratios and sand was added with 1:2 cement: sand ratios. The responses are presented in µV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 15 (d) shows the average response is 3.8 µV/N and the responses are constant for all the three samples.



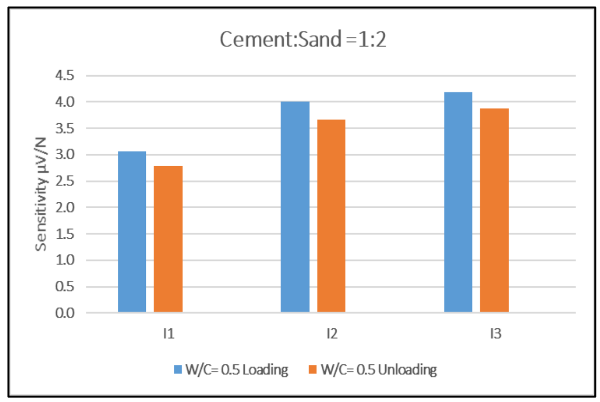
(a)



(b)



(c)



(d)

Figure 15. Piezo-electric responses for CMC surface treatment method: sample (a) I1, (b) I2, (c) I3, (d) samples summary.

Figure 16 (a), (b) and (c) provide the dynamic responses from sample J1 to J3. The samples are made with 0.4 water-cement ratios and sand was added with 1:2 cement: sand ratios. The responses are presented in µV (x10^6) corresponding to the applied load of 2000 N. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 16 (d) shows the average response is 1.8 µV/N and the responses are constant for all the three samples.

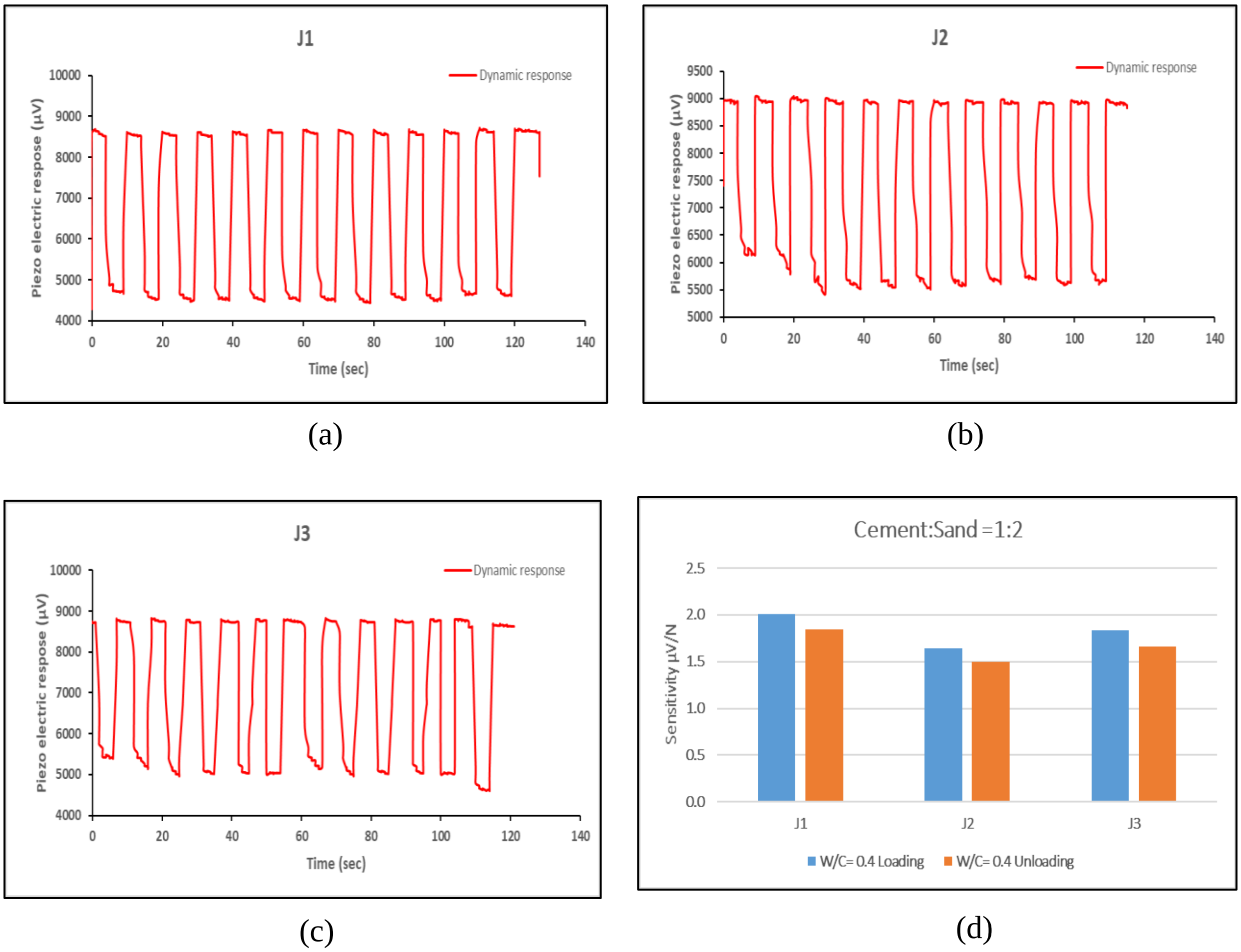
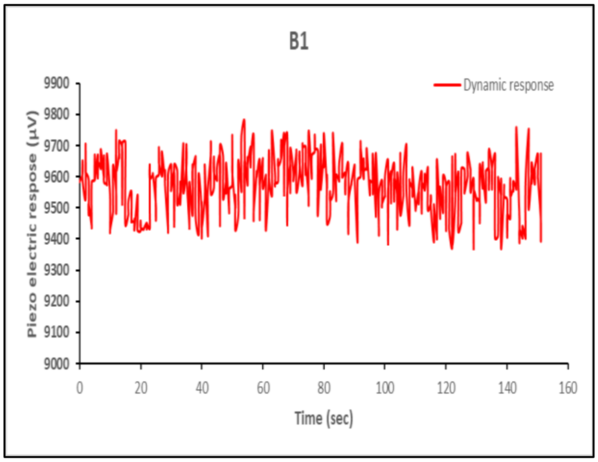


Figure 16. Piezo-electric responses for CMC surface treatment method: sample (a) J1, (b) J2, (c) J3, (d) samples summary.

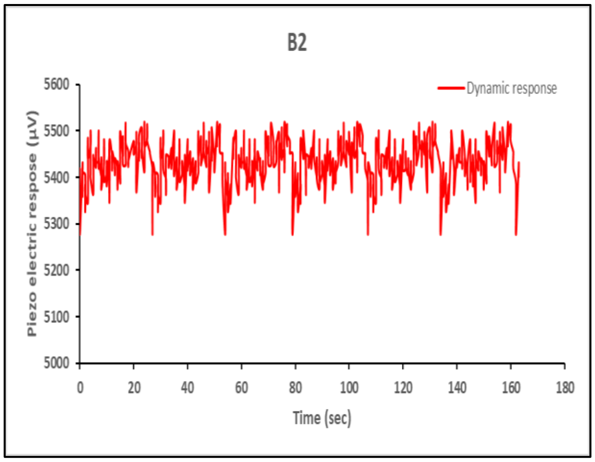
3.2.2. Direct Mixing Method

3.2.2.1 Samples with Sand and Cement

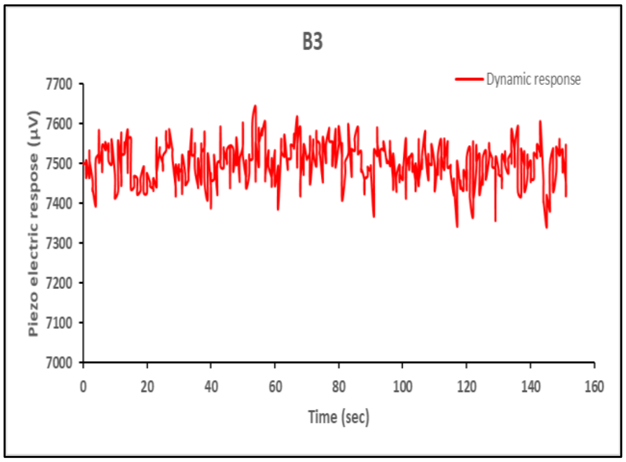
In this study sand was added with cement to observe the responses with different water-cement ratios as previous studies show that direct method cannot uniformly disperse CNTs in cementitious materials (Chia and Huang 2017a).



(a)



(b)

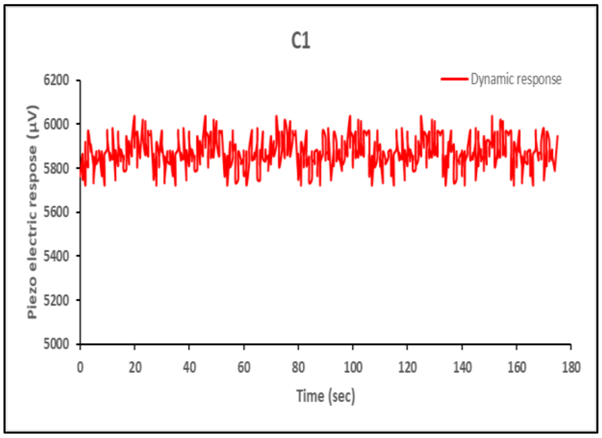


(c)

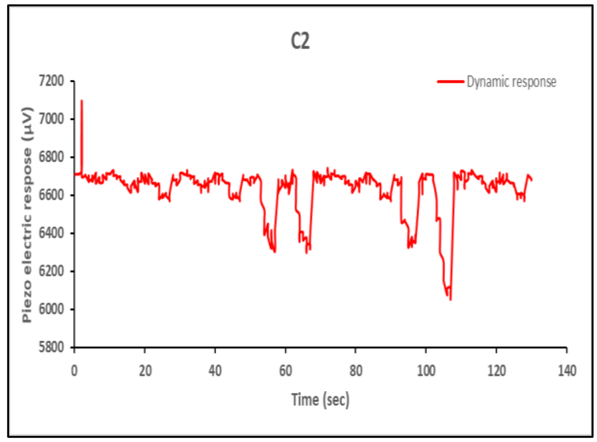
Figure 17. Piezo-electric responses for direct mixing method: sample (a) B1, (b) B2, (c) B3.

Figure 17 (a-c) depicts the piezo-electric responses of three samples B1 to B3 prepared using direct mixing method with 0.6 water-cement ratios and 1:2 cement: sand ratios. The dynamic responses do not change linearly with the compressive stress and the changes are not proportional to the stress levels for 12 consecutive cyclic loads. The responses are presented in µV (x10^6) corresponding to the applied 2000 N of load. As there were no noticeable changes in voltage corresponding with the loading and unloading so further analysis was not done.

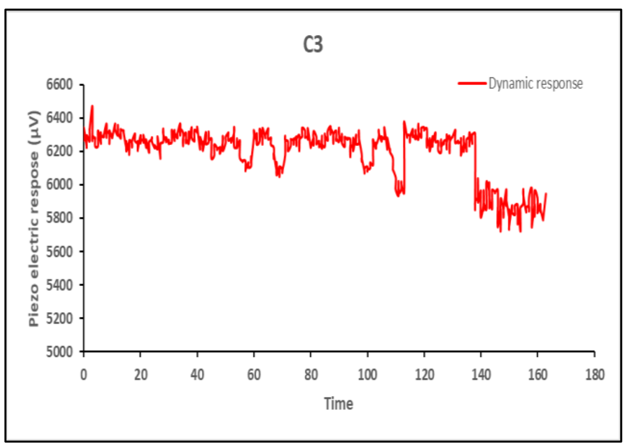
Figure 18 (a-c) depicts the piezo-electric responses of three samples C1 to C3 prepared using direct mixing method with 0.5 water-cement ratios and 1:2 cement: sand ratios. The dynamic responses do not change linearly with the compressive stress and the changes are not proportional to the stress levels for 12 consecutive cyclic loads. The responses are presented in µV (x10^6) corresponding to the applied 2000 N of load. As there were no noticeable changes in voltage corresponding with the loading and unloading so further analysis was not done.



(a)



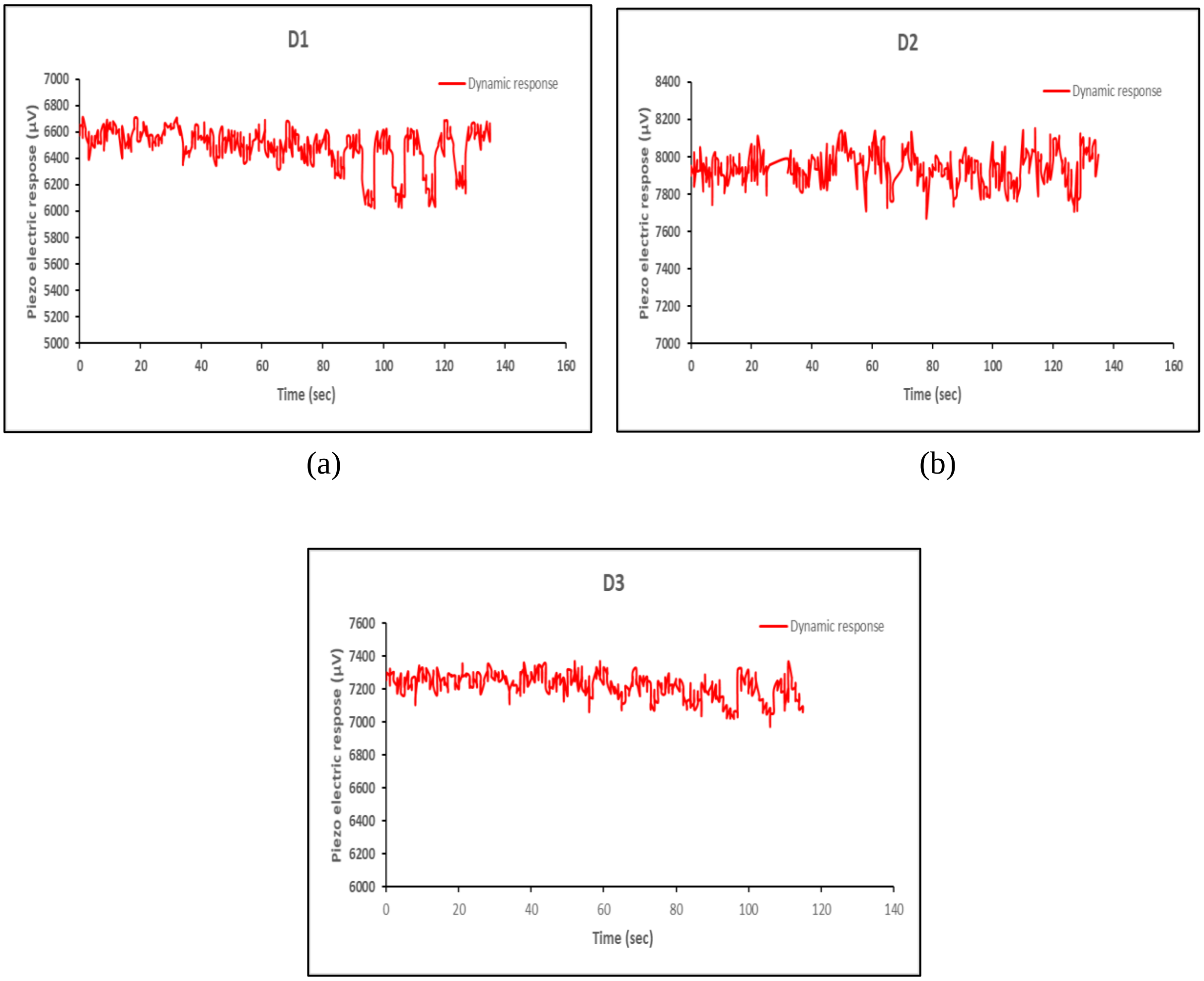
(b)



(c)

Figure 18. Piezo-electric responses for direct mixing method: sample (a) C1, (b) C2, (c) C3.

Figure 19 (a-c) depicts the piezo-electric responses of three samples D1 to D3 prepared using direct mixing method with 0.4 water-cement ratios and 1:2 cement: sand ratios. The dynamic responses do not change linearly with the compressive stress and the changes are not proportional to the stress levels for 12 consecutive cyclic loads. The responses are presented in µV (x10^6) corresponding to the applied 2000 N of load. As there were no noticeable changes in voltage corresponding with the loading and unloading so further analysis was not done.



(a) (b)

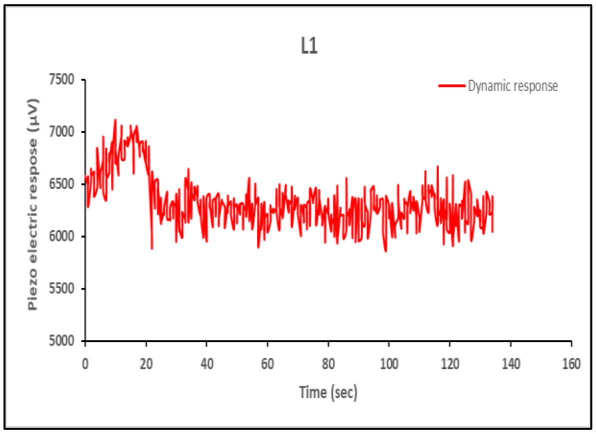
(c)

Figure 19. Piezo-electric responses for direct mixing method: sample (a) D1, (b) D2, (c) D3.

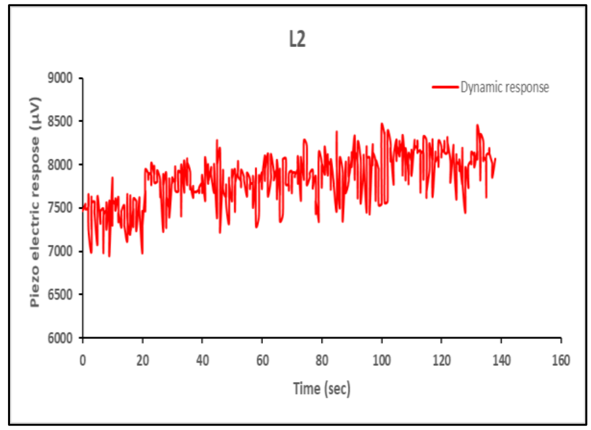
3.2.3. Surfactant Method

3.2.3.1 Samples with Sand and Cement

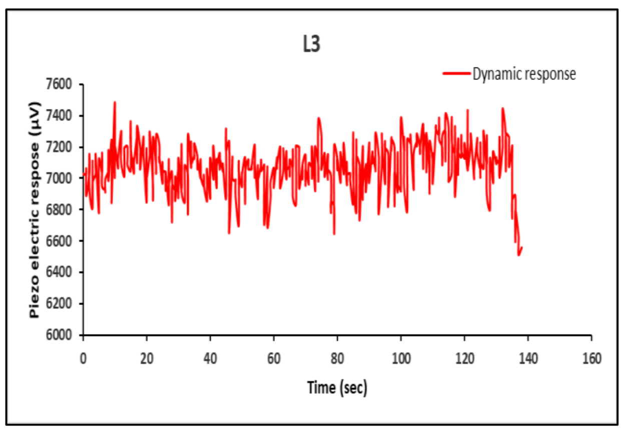
Figure 20 (a-c) depicts the piezo-electric responses of three samples L1 to L3 prepared using surfactant method with 0.6 water-cement ratios and 1:2 cement: sand ratios. The dynamic responses do not change linearly with the compressive stress and the changes are not proportional to the stress levels for 12 consecutive cyclic loads. The responses are presented in µV (x10^6) corresponding to the applied 2000 N of load. As there were no noticeable changes in voltage corresponding with the loading and unloading so further analysis was not done.



(a)



(b)



(c)

Figure 20. Piezo-electric responses for surfactant method sample (a) L1, (b) L2, (c) L3.

4. ANALYSIS AND DISCUSSION

This chapter represents the comparison of the experimental data of different water-cement ratios for CMC surface treatment dispersion methods and validates a water-cement ratio to add coarse aggregate to the samples for smart concrete material. Also, to further prove the experimental data, a comparison was made with samples made with the surfactant method for smart concrete material.

4.1. Comparison of Dispersion Methods

Figure 21 shows the responses from all the three dispersion methods adopted in this research to observe the piezo electric responses from samples made with cement and sand. Here one of the samples made with 0.6 water-cement ratio sample group from each dispersion method has been considered for this comparison. CMC Surface treatment method showed consistency in responses and the responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loading. Where, direct mixing method and surfactant method didn't show any changes in responses with the dynamic loading.

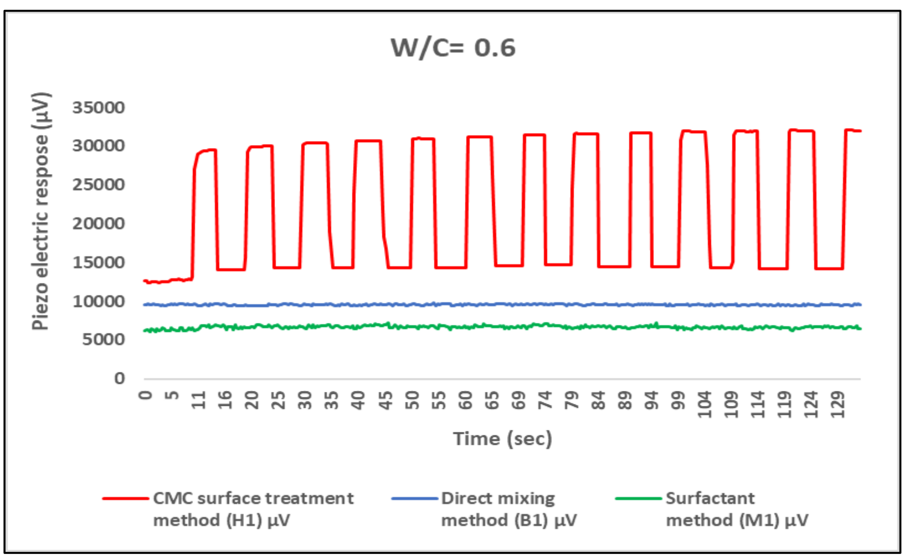


Figure 21. Summary of all three dispersion methods with 0.6 w/c ratio.

4.2. Comparison of The Water Cement Ratios

Table 3 shows the average responses from the sample group made with cement mortar for different water-cement ratios for CMC surface treatment method. Figure 22 provides the summary for three sample groups made with cement mortar with different water-cement ratios, where samples made with 0.6 water-cement ratio have an average response of 13 µV/N with a standard deviation of 0.5. Similarly, samples made with 0.5 and 0.4 water-cement ratios have the average responses of 4.5 µV/N and 1.8 µV/N with a standard deviation of 0.009 and 0.015, respectively. The error bars represent the standard deviation for each sample group.

Table 3. Average dynamic responses from the sample group made with cement mortar with the CMC surface treatment method

W/C= 0.6			W/C= 0.5			W/C= 0.4		
Sample ID	Loading	Unloading	Sample ID	Loading	Unloading	Sample ID	Loading	Unloading
E1	12.476	11.543	F1	4.369	4.017	G1	1.616	1.503
E2	13.490	12.402	F2	4.378	4.042	G2	1.606	1.493
E3	12.883	11.904	F3	4.361	4.025	G3	1.585	1.471
Average	12.950	11.950		4.369	4.028		1.602	1.489
Standard Deviation	0.510	0.431		0.009	0.013		0.016	0.016

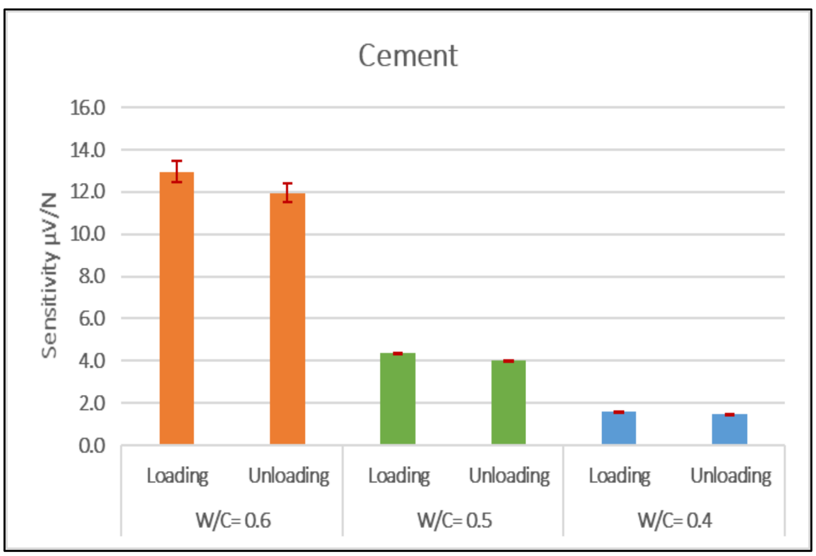


Figure 22. Summary of the responses from the sample group made with cement mortar with CMC surface treatment method.

Table 4 shows the average responses from the sample group made with cement and sand for different water-cement ratios for CMC surface treatment method. Figure 23 provides the summary for three sample groups made with cement and sand with different water-cement ratios, where samples made with 0.6 water-cement ratios have an average response of 9.2 µV/N with a standard deviation of 0.94. Similarly, samples made with 0.5 and 0.4 water-cement ratios have 3.8 µV/N and 1.8 µV/N with a standard deviation of 0.6 and 0.18, respectively. The error bars represent the standard deviation for each sample group.

Table 4. Average dynamic responses from the sample group made with cement and sand with the CMC surface treatment method

W/C= 0.6			W/C= 0.5			W/C= 0.4		
Sample ID	Loading	Unloading	Sample ID	Loading	Unloading	Sample ID	Loading	Unloading
H1	8.380	7.742	I1	3.059	2.791	J1	2.009	1.845
H2	9.378	8.609	I2	4.012	3.672	J2	1.644	1.494
H3	10.259	9.433	I3	4.190	3.871	J3	1.832	1.664
Average	9.339	8.595		3.754	3.445		1.829	1.667
Standard Deviation	0.940	0.846		0.608	0.575		0.183	0.176

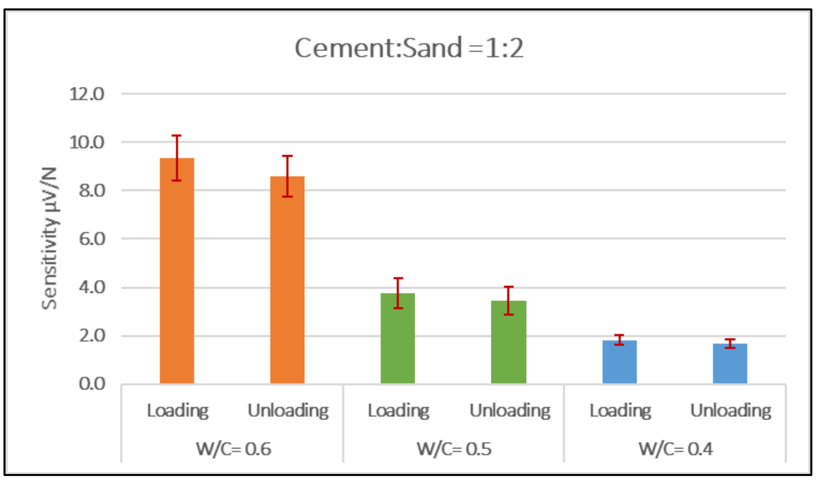
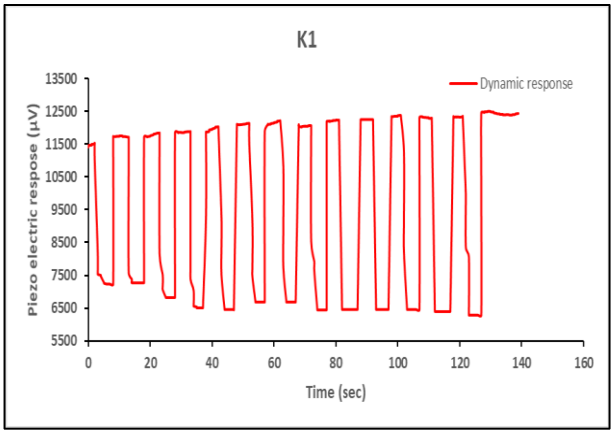


Figure 23. Summary of the responses from the sample group made with cement and sand with the CMC surface treatment method.

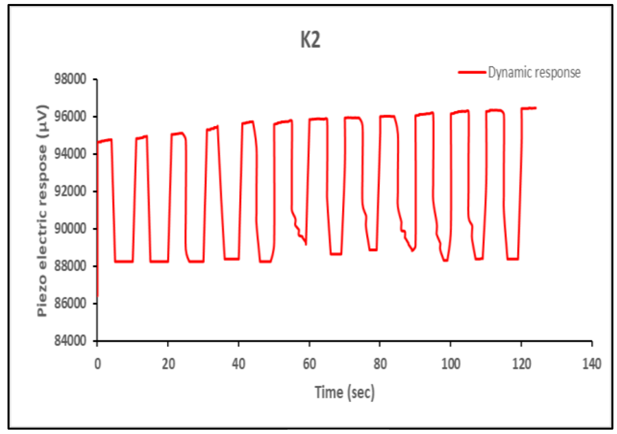
In both cases 0.6 of the water-cement ratios sample group has a bigger dynamic response compared to other water-cement ratios. So, for further analysis as smart concrete material coarse aggregate was added with cement and sand with 0.6 of water-cement ratio with other properties remaining the same as before.

4.3. Samples with Cement, Sand, and Coarse Aggregate

Figure 24 (a), (b), and (c) provides the dynamic responses from sample K1 to K3. The samples are prepared with CMC surface treatment method with 0.6 water-cement ratio and coarse aggregate was added with a 1:2:3 cement: sand: coarse aggregate ratio. The responses are presented in µV (x10^6) corresponding to the applied load. Figure 24 (d) represents the average loading and unloading responses of the sample group per 2000N of loading. The dynamic responses change linearly with the compressive stress and the changes are proportional to the stress levels for 12 consecutive cyclic loads. Figure 24 (d) shows the average response is 2.75 µV/N and the responses are constant for all three samples.



(a)



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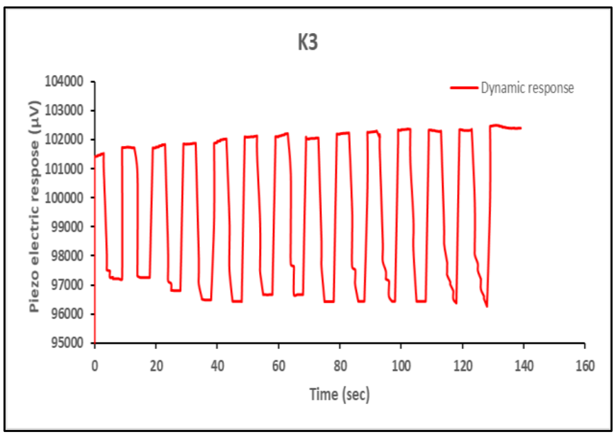

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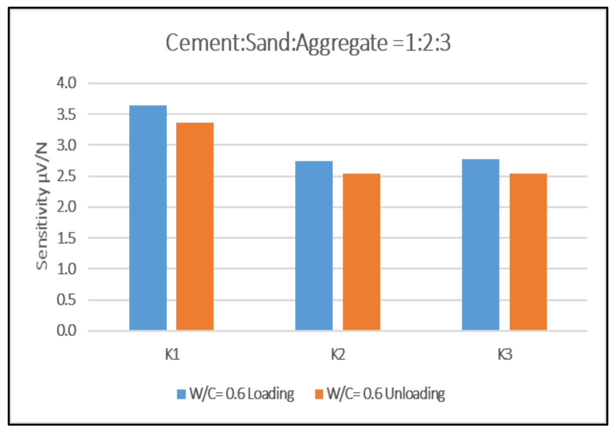


(d)

Figure 24. Piezo-electric responses for CMC surface treatment method: sample (a) K1, (b) K2, (c) K3, (d) samples summary.

Table 5 shows the average responses from the sample group made with cement sand and coarse aggregate for CMC surface treatment method with different water-cement ratios. Figure 25 provides the summary for three sample groups made with cement sand and coarse aggregate with 0.6 water-cement ratio, which have an average response of 2.7 µV/N with a standard deviation of 0.016.

Table 5. Average dynamic responses from the sample group made with cement, sand, and coarse aggregate with the CMC surface treatment method

	W/C= 0.6	
Sample ID	Loading	Unloading
K1	3.634	3.368
K2	2.748	2.537
K3	2.770	2.542
Average	2.759	2.540
Standard Deviation	0.016	0.004

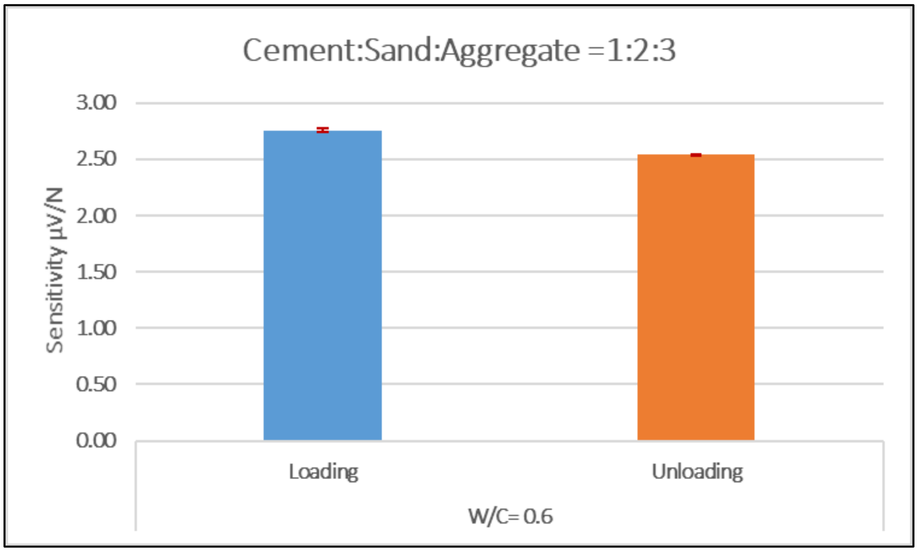
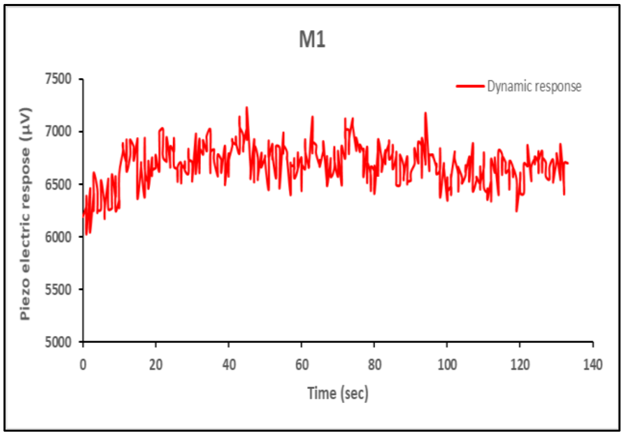
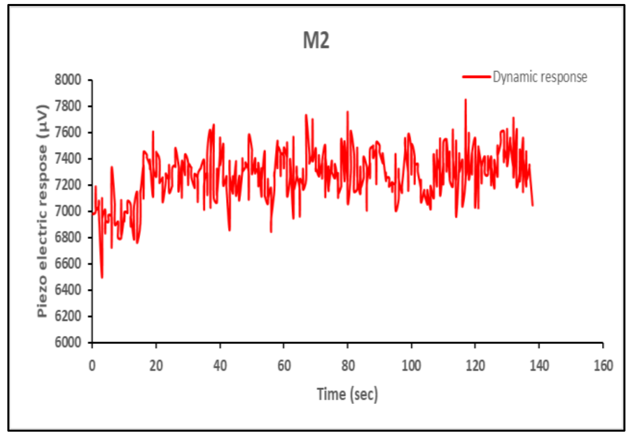


Figure 25. Responses from the sample group made with cement sand and coarse aggregate with CMC surface treatment method.

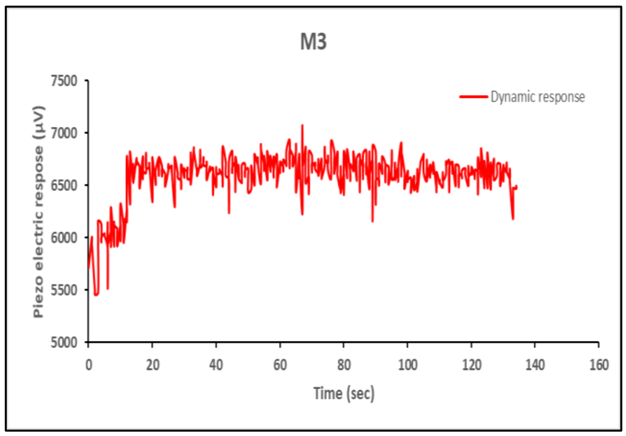
Coarse aggregate was also added to the samples in the surfactant method to see if there is any response as smart concrete. Figure 26 (a-c) depicts the piezo-electric responses of three samples M1 to M3 prepared using the surfactant method with 0.6 water-cement ratio and 1:2:3 cement: sand: coarse aggregate ratio. The dynamic responses do not change linearly with the compressive stress and the changes are not proportional to the stress levels for 12 consecutive cyclic loads. The responses are presented in µV (x10^6) corresponding to the applied 2000 N of load. As there were no noticeable changes in voltage corresponding with the loading and unloading so further analysis was not done.



(a)



(b)



(c)

Figure 26. Piezo-electric responses for surfactant method sample (a) M1, (b) M2, (c) M3.

4.4. Influence of Concrete Ingredients

Figure 27 represents the summary of the responses from the sample group made with CMC surface treatment method with 0.6 water-cement ratio. Here it can be seen that, the sensitivity reduces progressively when sand and coarse aggregate was added with cement. The Cement mortar samples have the sensitivity of 12 µV/N which reduces to 9 µV/N when sand was added and reduces to 3 µV/N when sand and coarse aggregate was added with cement. So, sand and coarse aggregate together has the influence in the sensitivity which reduces the sensitivity 4 times compared with the cement paste samples.

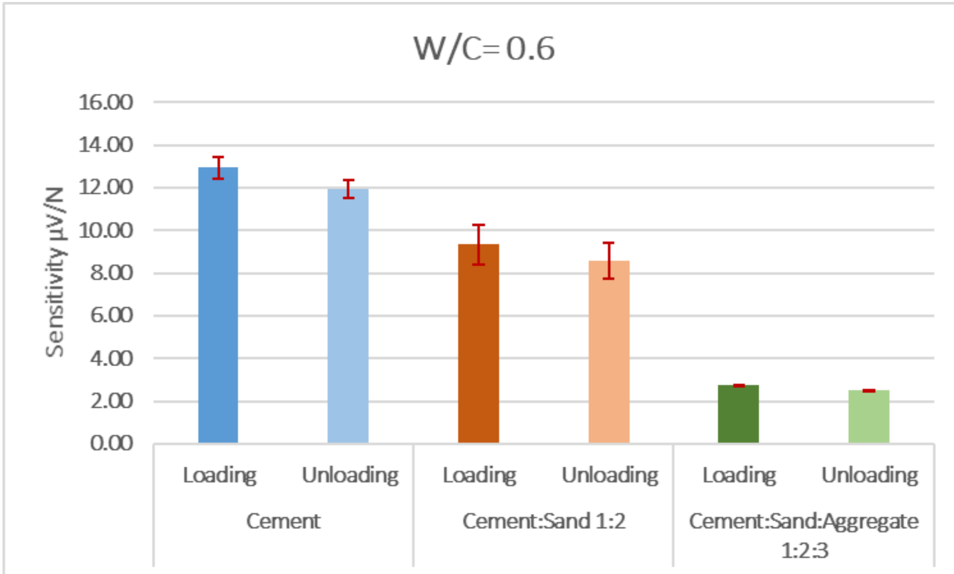


Figure 27. Responses from the sample group made with CMC surface treatment method with 0.6% water-cement ratio.

4.5. Summary

In this chapter, the experimental results from the dynamic loading tests are presented from testing the samples in all the three dispersion methods including the direct mixing method, surfactant method, and the CMC surface treatment dispersion method. CMC surface treatment method dramatically increased the dispersion effectiveness by showing uniform, consistent, and optimized responses. Where samples made with 0.6 water-cement ratios with the CMC surface treatment dispersion method has a better response in stress sensing. By comparing range mean, minimum mean and standard deviation from each dispersion method, the CMC surface treatment method showed consistency in sensitivity hence can be adopted to develop smart concrete material.

5. CONCLUSIONS AND FUTURE WORK

5.1. Conclusion

This study investigates the influences of dispersion methods of CNTs, w/c, and concrete ingredients on the sensing ability of smart cementitious materials. The following conclusions can be drawn based on the findings from this study:

- The comparison between three different dispersion methods showed that the CMC surface treated CNTs has an improved dispersion of CNTs in smart cementitious materials and can enhance stress sensing with better consistency of cementitious and concrete materials.
- The surfactant method showed inconsistency with the dynamic loading for cementitious and concrete materials.
- 0.6 water-cement ratio shows better stress sensitivity compared to other water-cement ratios for concrete materials.
- Smart concrete behavior can be achieved using a proper dispersion method with CNT such CMC surface treatment method, however, the adding of coarse aggregate and sand will significantly reduce the sensing ability and will need to be accounted in practical applications if the lab experiments were performed on cement paste only.

5.2. Future Work

This study was focused on developing smart concrete with proper dispersion of CNTs with various water-cement ratios to find a better water-cement ratio for smart concrete material. The following ideas can also be tested:

- In this study, a 1:2:3 design mix was used which has a compressive strength of 4000 psi. Various design mix ratios such as 1:2:4, 1:3:3, and 1:2:2 can be used to develop smart concrete with CNT.
- New dispersion methods can be adopted with CNT for smart concrete materials.
- Further, investigate the optimal mixing progress, the dispersion effectiveness, chemical reactions, bonding mechanisms, and the mechanical property of the smart concrete materials made with the CMC coated CNTs.
- In this study, all the samples were made at room temperature. Temperature sensitivity could be tested on the samples with extremely high and extremely low temperatures to see any temperature sensitivity of the samples.

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