Continuation of Carbon Nanotubes Additives for Structural and Highway Concrete

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16. Abstract

The purpose of this project was to evaluate the performance of carbon nanotube (CNT)-reinforced concrete. Carbon nanotubes have exceptional mechanical properties and small scales. Combining them with composite material enables engineers to further modify material microstructure. Carbon nanotubes have been used extensively in modifying cement properties, but few studies have evaluated carbon nanotube's effects on concrete. A laboratory investigation into the effect of CNTs on the performance of concrete mixtures versus traditional PennDOT concrete mixtures was conducted and the benefits evaluated. The results from the laboratory testing were used to estimate the life cycle costs for both traditional PennDOT concrete and the CNT concrete. Recommendations relative to the feasibility of incorporating CNT technology for PennDOT concrete mixtures as well as any potential benefits or disadvantages have been made.

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1. Literature Review

Portland Cement Concrete (PCC) is the most widely used construction material due to its versatility, durability, and economy (Mindess et al. 2003). However, PCC is also a quasi-brittle material that has low tensile strength and ductility, as well as weak resistance to the propagation of cracks. Also, problems related to shrinkage, durability and workability have caused a multitiude of issues during construction. Consequently, there is a great desire to tailor the mechanical properties of PCC, and extensive efforts have been put forth to improve its weakness. Some of these developments include the use of chemical admixtures, supplementary cementitious materials, and fibers (Mindess et al. 2003). More recently, the use of nanomaterials, such as nano-oxides (SiO_2, Fe_2O_3, TiO_2)(Nazari and Riahi 2011)(Zhang and Li 2011) and carbon nanomaterials ((Lourie 1998)(Li et al. 2005), has been investigated. The new research area implies a transition from traditional macrostructure PCC reinforcement, such as fiber and steel reinforcement, to microstructure reinforcement. This review introduces the current knowledge surrounding the use of carbon nanotubes (CNTs) to address the issues with traditional concrete mixture problems.

1.1 Portland Cement Concrete (PCC) Background

As a brittle material, PCC has limited tensile strength, and it cracks without significant plastic deformation. Additionally, PCC shrinkage does not cause problems if the PCC is not restrained. However, concrete structures restrained by reinforcement or other layers, like base and subgrade, develop non-negligible tensile stresses due to shrinkage. Also, PCC volume variation can change a structure’s shape and influence its functionality. PCC structures are expected to have long lives and low maintenance costs. Therefore, they must have excellent durability to resist the anticipated exposure conditions, such as freezing-thawing cycles and chloride penetration. Damage due to freezing and thawing is the most potentially destructive weathering factor, especially in the presence of deicing chemicals and water, which are prevalent on roads and bridges. The freezing of ice and subsequent expansion in the paste deteriorates the concrete. Chloride presence in plain PCC (not containing steel) is generally not a durability concern. However, for steel-reinforced structures, such as bridge decks and reinforced concrete pavements, the presence of chloride ions is of greater concern due to the potential for steel corrosion. This is particularly common in Pennsylvania since deicers release a significant amount of chloride ions, which can accelerate the corrosion of steel. Many factors influence the properties of concrete, such as the water-cement ratio (or water-cementitious materials ratio), the curing and environmental conditions, and the age of the concrete (Mindess et al. 2003). However, this report focuses on factors that are pertinent to this research.

1.1.1 W/C Ratio

The water-cementitious material ratio (w/c ratio) refers to the mass ratio of water with respect to cementitious material (Portland Cement, blended cement, fly ash, slag, silica). Typically, the w/c ratio has the most significant effect on the properties of PCC, including strength, porosity, and workability. The water to cement ratio is one (1) of the primary factors that influence the strength of concrete and has been expressed as a function, as shown in the equation below (Abrams 1918).

$$\sigma_c = \frac{A}{B^{1.5\left(\frac{w}{c}\right)}}$$

Where: *A = empirical constant, usually 14,000 lb/in*^{2}

B = constant that depends mostly on the cement properties

w/c = water to cementitious materials ratio

Even though it does not incorporate other effects, such as environmental conditions, other admixtures, and aggregate type, it is still a useful tool to anticipate concrete strength in the normal range of w/c ratios. Furthermore, the American Concrete Institute (ACI) has adopted some empirical guidance for developing required average strength, in case historical data on trial mixtures are not available. Some of these guidelines are presented below in Figure 1 and Table 1.

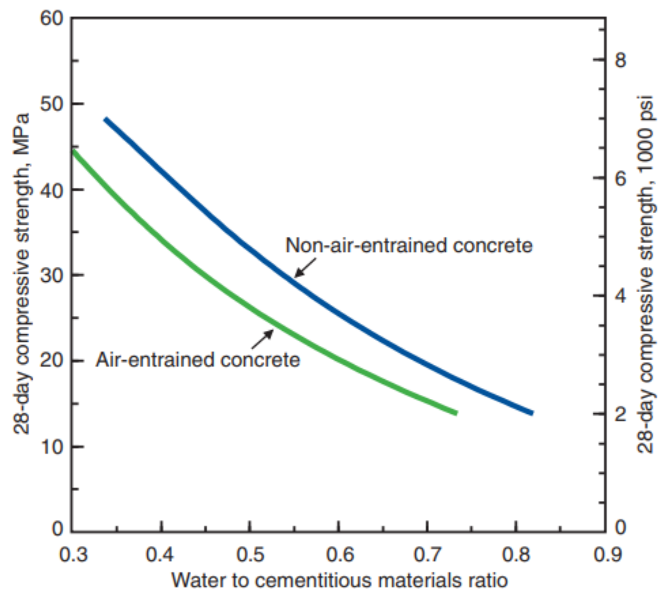

Figure 1. Relationship between compressive strength and water to cementing materials ratio for concrete using 3 ⁄4-in. to 1-in (Kosmatka et al. 2011)

Table 1. Strength is based on cylinders moist-cured 28 days (ASTM C39). Relationship assumes nominal maximum size aggregate of about 19 to 25 mm. (Kosmatka et al. 2011)

Compressive strength at 28 days, psi	Water-cementitious materials ratio by mass	
	Non-air-entrained PCC	Air-entrained PCC
7,000	0.33	-
6,000	0.41	0.32
5,000	0.48	0.4
4,000	0.57	0.48
3,000	0.68	0.59
2,000	0.82	0.74

1.1.3 Hydration

In general, cement constitutes approximately 10% of total concrete volume and acts as an adhesive matrix that binds the aggregates together (Mindess et al. 2003). Therefore, its strength and binding capacity play important roles in concrete's strength, and those paste properties are usually related to cement hydration products and paste porosity. Hydraulic cement sets and hardens by reacting chemically with water. This reaction is called hydration. During this process, two (2) main chemical products are generated, which contribute the most to the strength of cement paste (C_3S for earlier strength, C_2S for long-term strength). These effects carry through into concrete (Mindess et al. 2003).

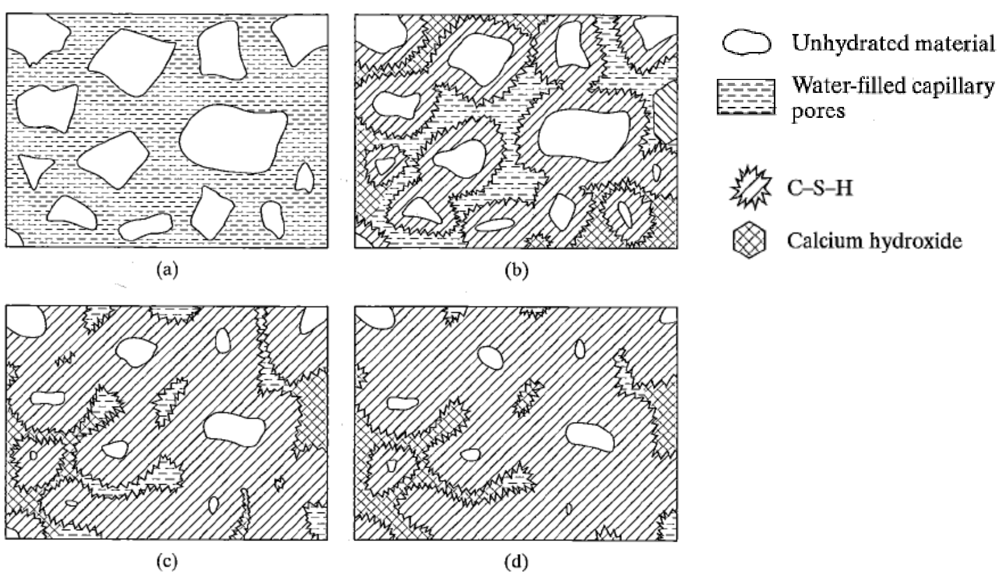

Figure 2. Schematic outline of microstructural development in Portland cement pastes: (a) initial mix; (b) 7 days; (c) 28 days; and (d) 90 days (Mindess et al. 2003)

Consequently, adjusting the hydration process and modifying the quantity, property, and interaction of hydration products improves the mechanical performance of concrete. As the hydration proceeds, some of the water is consumed and replaced with solid hydration products (Mindess et al. 2003). However, the water cannot be completly used up (the consumption depends on the initial w/c ratio) and still occupies a large fraction of the capillary pores. Moreover, these pores are filled with water and air. Therefore, they have no strength and could weaken the concrete structure (Mindess et al. 2003). In other words, the less porous the cement paste, the stronger the concrete.

1.1.4 Tensile Strength

The tensile strength of concrete is much lower than the compressive strength, and sometimes it is not considered in structural design (ACI 318). However, it is still critical for PCC because under tensile load, initial branching cracks can combine into a single macrocrack and propagate through concrete with ease. In addition, most cracking is formed due to tensile stresses, even under compressive load. An indirect means of measuring the tensile strength of concrete is to measure the flexural strength of a beam in bending (ASTM C78). Several equations describe the relationship between flexural and compressive strengths; the relationship used by ACI 318 is as follows:

$$\begin{cases} f_r' = 0.6\sqrt{f_c'} & \text{MPa} \\ f_r' = 7.5\sqrt{f_c'} & \text{lb/in.}^2 \end{cases}$$

Where: f_r' = *flexural strength of concrete*

f_c' = *compressive strength of concrete*

1.1.5 Drying Shrinkage

"Drying shrinkage" in hardened PCC is the contracted strain caused by the loss of water. Typically, PCC experiences a shkinkage strain of 400 to 800 millionths at 50% humidity. In reinforced concrete structures, with average amounts of reinforcement, drying shrinkage is assumed to be 200 to 300 millionths. The differences in magnitude of concrete shrinkage depend on the amount of restraint and reinforcement present (Kosmatka et al. 2011).

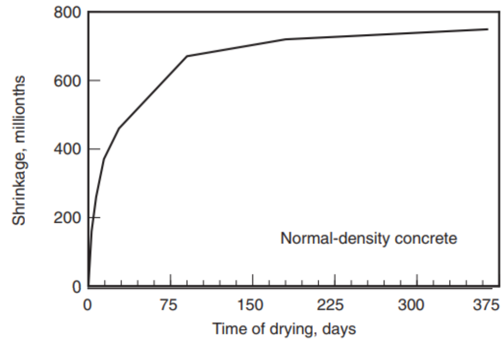

Figure 3. Relative humidity distribution at various depths, drying shrinkage, and mass loss of 150×300-mm (6×12-in.) cylinders moist-cured for 7 days followed by drying in laboratory air at 23°C (73°F) and 50% RH (Hanson 1968)

The damage of shrinkage does not just rely on the magnitude of shrinkage, but more importantly, the restraint: In case of no restraint, concrete with shrinkage is not subjected to severe tensile stress. However, when the movement is curbed, the shrinkage generates significant stress and cracks can develop. The factors that affect the drying shrinkage of PCC are w/c ratio, degree of hydration, porosity, age of paste, curing temperature, and presence of admixtures (Mindess et al. 2003).

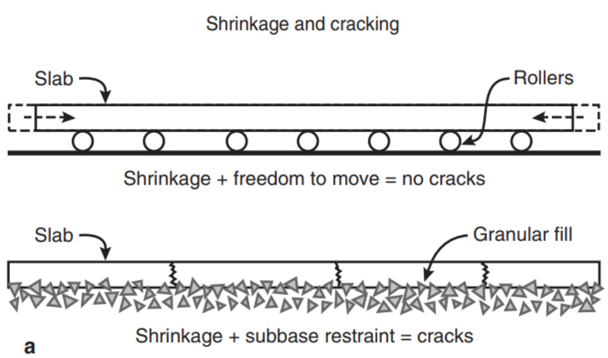

Figure 4. Illustration showing no crack development in concrete that is free to shrink (slab on rollers) (Kosmatka et al. 2011)

1.1.5 Durability

Durability is the ability of concrete to maintain its desired properties and resist weathering action and chemical attack, such as freeze-thaw cycles, alkali-silicate and carbonation reaction, chloride penetration, and abrasion (Mindess et al. 2003). Also, concretes with different functions require different degrees of durability properties, and different types of durability are influenced by different factors. But for most cases, reduced permeability enhances overall durability.

Permeability is the most important property for concrete structures with severe exposure conditions. It is defined as either the amount of water migration through concrete when the water is under pressure or the ability of concrete to resist penetration by water or other substances (Kosmatka et al. 2011). The overall permeability of PCC to water is a function of: (1) the permeability of the paste; (2) the permeability and gradation of the aggregate; (3) the quality of the paste and aggregate transition zone; (4) the relative proportion of paste to aggregate; and (5) the w/c ratio (Mindess et al. 2003). Figure 5 depicts the effect of the w/c ratio on the permeability of PCC, wherein the permeability of the concrete decreases with decresing w/c ratio. Figure 6 shows the relationship between the results of the rapid chloride permeability test (ASTM C1202) and the w/c ratio. This test indirectly estimates the permeability of concrete by measuring its electrical conductance to provide a rapid measure of the resistance to the penetration of chloride ions. As the w/c ratio decreases, the measure of the electrical conductance decreases, indicating a decrese in the permeability of the concrete.

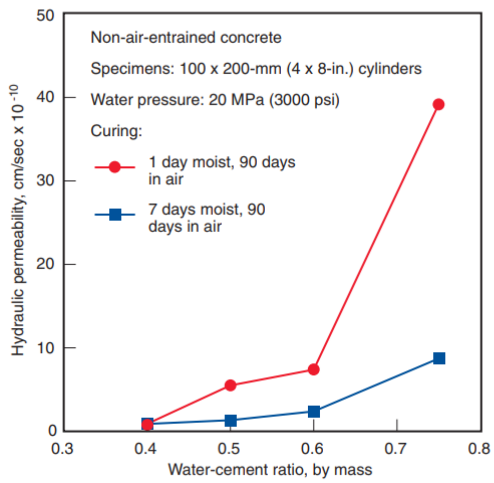

Figure 5. Relationship between hydraulic permeability, water-cement ratio, and initial curing on concrete specimen (Whiting 1988)

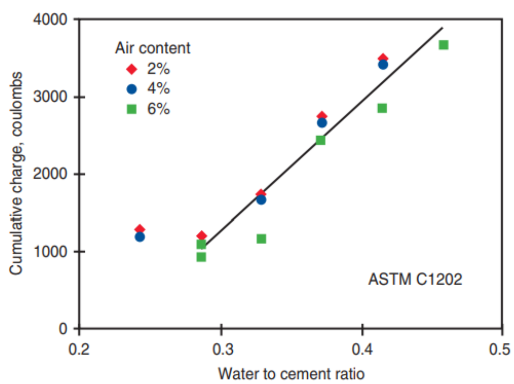

Figure 6. Total charge at the end of the rapid chloride permeability test as a function of water to cement ratio (Pinto and Hover 2001)

Freeze-thaw is the most potentially destructive weathering factor to concrete while moisture is available, particularly in the presence of deicing chemicals. This is mainly due to the freezing of water and subsequent expansion in concrete composition, especially cement paste, as shown in

Figure 7. After the moisture in concrete freezes, the transformation from liquid to solid leads to volume variation and generates osmotic and hydraulic stress in the capillary pores of cement paste. If the stress exceeds the tensile strength of the paste, cracks will initiate and propagate inside the concrete. The accumulation of freeze-thaw cycles and damage of paste can ultimately cause substantial expansion and deterioration of concrete.

Figure 7. Air-entrained concrete (bottom bar) is highly resistant to repeated freeze-thaw cycles (Kosmatka et al. 2011)

Decreased permeability improves concrete's resistance to freezing and thawing, chloride-ion penetration, and other chemical attacks (Kosmatka et al. 2011). Therefore, w/c ratio can also affect the ultimate freeze-thaw resistance since a high w/c can increase the permeability. Figure 8 shows the results of the freeze-thaw durability test for concrete with varying w/c ratio (ASTM C666).

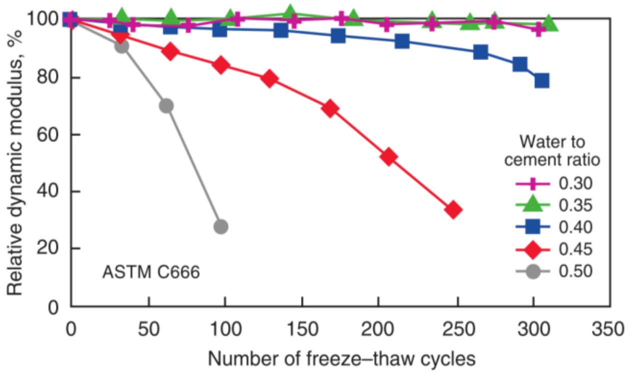

Figure 8. Durability factors vs. number of freeze-thaw cycles for selected non-air-entrained concretes (Pinto and Hover 2001)

Typically, air entrainment is used to prevent freeze-thaw damage in concrete. The microscopic air bubbles can accommodate the increased volume due to ice formation from water, thus relieving the hydraulic pressures and preventing damage to the concrete. Generally, 6-8% air entrainment guarantees the integrity of concrete in moderate exposure conditions (Mindess et al. 2003).

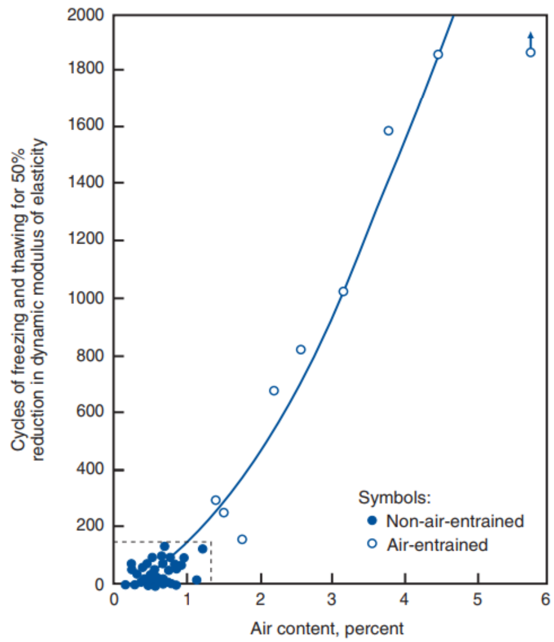

Figure 9. Effect of entrained air on the resistance of concrete to freezing and thawing in laboratory tests (Bates et al. 1952)

1.2 Carbon Nanotube (CNT) Background

1.2.1 What Are They?

Carbon nanotubes (CNTs) are cylindrical carbon allotropes composed of conjugated carbon rings. CNTs can be envisioned as tubes of one or more graphene sheets typically having diameters on the nanoscale and lengths on the micron-scale. CNTs are classified based on the number of walls in the tube structure: Either single-walled carbon nanotube (SWCNT), double-walled carbon nanotube (DWCNT), or multi-walled carbon nanotube (MWCNT). Diameters range from 0.8-2 nm for SWCNTs to 5-20 nm for MWCNTs (De Volder et al. 2013). Figure 10 shows the possible CNT orientations and configurations (Schnorr and Swager 2011). The size of CNTs relative to Portland cement and supplementary cementitious materials (SCM) found in concrete is shown in Table 2.

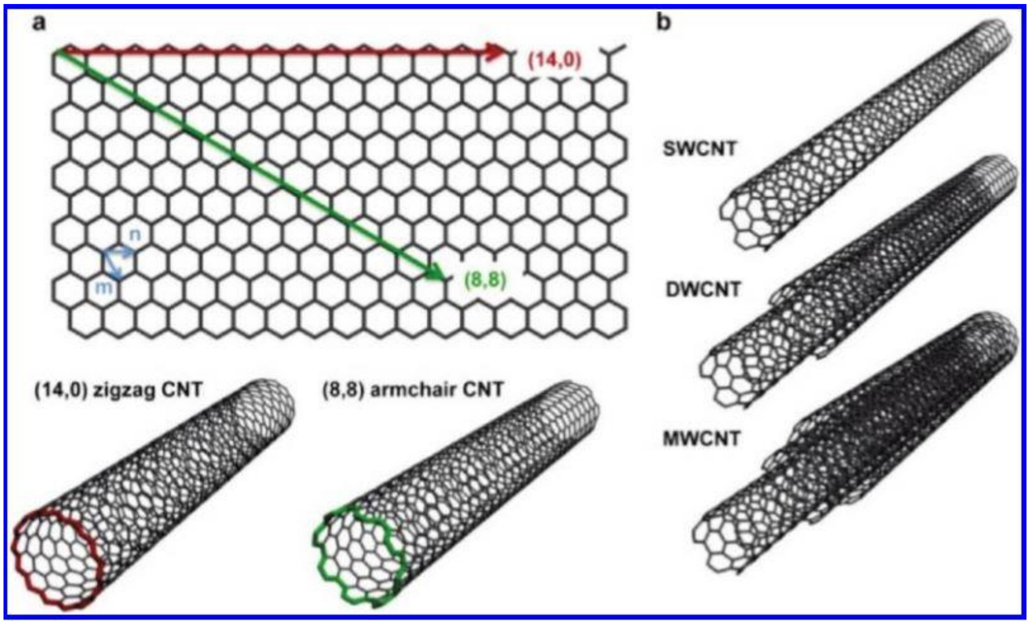

Figure 10. Carbon Nanotube Orientations (a) and Configurations (b) (Schnorr and Swager 2011)

Table 2. CNT, cement, and SCM relative dimensions (Mindess et al. 2003, De Volder et al. 2013)

		Dimensions	
		Length (μm)	Diameter
Silica fume		-	0.1 – 0.3 μm
Fly ash		-	10 – 15 μm
Cement particle		-	10 – 15 μm
CNT	MCNT	1 – 100	5 – 20 nm
	SCNT	1 – 50	0.8 – 2 nm

CNTs can have either open or closed tube ends, with closed tube ends having a fullerene-type hemisphere cap. There are differences in chemical reactivity between the ends and the side walls that can be used in selective chemical manipulation (Schnorr and Swager 2011). Their high specific surface and aspect ratio (length/diameter); their mechanical, electrical, and thermal properties; and their surfaces' ability to be manipulated in a controlled way have garnered significant attention for a wide range of applications.

1.2.2 Synthesis and Characterization

The three (3) most common techniques to synthesize CNTs are arc-discharge, laser-ablation, and catalytic growth, such as chemical vapor deposition (CVD) (Popov 2004). The most prominent CNT synthesis method is CVD, in which hydrocarbons nucleate a catalyst substrate at high temperatures (Popov 2004). The structural properties and chemical composition of CNTs are characterized using a wide range of techniques. Characterization technologies can be classified as either microscopy and diffraction techniques, spectroscopy techniques, or thermal techniques (Herrero-Lattore et al. 2015). Microscopy techniques measure properties of individual CNTs (Belin and Epron 2005). Scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM) are microscopy and diffraction technologies. SEM studies the diameter, length, and aggregation state of CNTs, while TEM and AFM study the length, number of layers, and distance between layers of CNTs (Herrero-Lattore et al. 2015). Spectroscopy techniques include Raman spectroscopy (RS), infrared spectroscopy (IR), ultraviolet-visible spectroscopy (UV-vis), fluorescence spectroscopy (FS), and x-ray photoelectron spectroscopy (XPS). RS studies purity, by-product presence, and diameter distribution; IR studies purity and functionalization; XPS assesses the elemental composition and functionalization of CNTs; and UV-vis and FS study CNT size, dispersion efficiency, and purity (Herrero-Lattore et al. 2015). Thermogravimetric analysis (TGA) is a thermal technique that measures purity, by-product presence, and quality (Herrero-Lattore et al. 2015).

1.2.3 Mechanical, Electrical, and Thermal Properties

CNTs have excellent mechanical properties such as tensile strength and elastic modulus. The elastic modulus of a CNT is on the magnitude of 1 TPa, and CNTs can be 30-100 times stronger than steel (Peng et al. 2008; Hilding et al. 2003). The tensile strength and elastic modulus can vary based on the method used to synthesize the CNT. The predominant synthesis methods include chemical vapor deposition (CVD), arc-discharge, and laser-ablation (Popov 2004). To gauge tensile strength and elastic modulus based on production method, one (1) study used a nanomanipulator inside a scanning electron microscope (SEM) and a force sensor to conduct a tensile test of a CNT (Jang et al. 2011). Arc-discharged MWCNTs were observed to have a tensile strength and elastic modulus of 30-40 GPa and 0.98 TPa respectively, and MWCNTs grown with chemical vapor deposition were observed to have a tensile strength and elastic modulus of 10-20 GPa and 0.56 TPa respectively (Jang et al. 2011).

SWCNTs can have different electrical properties (i.e., they can be conductors or semiconductors) based on their diameter and helicity (Odom et al. 1998), whereas MWCNTs are zero-band gap conductors (Schnorr and Swager 2011). In addition to having significant electrical transport properties, CNTs have significant thermal transport properties. The theoretical thermal conductivity for a SWCNT is approximated to be 2400-2900 W/mK, compared to 1000 W/Mk for graphite, an established thermal conductor (Hilding et al. 2003; Che et al. 2001). The theoretical thermal conductivity for a MWCNT is approximated to be 1980 W/Mk (Kim et al. 2001). This is particularly effective in liquid suspensions where small additions of SWCNT into a water or oil increased the thermal conductivity (Duong et al. 2008).

1.2.4 Dispersion

To use CNTs as a reinforcing agent, the nanotubes must be mixed in a liquid suspension or solvent. Dispersion of CNTs in liquids is often difficult, as the nanotubes tend to bundle together because of large aspect ratio and intermolecular forces (Hilding et al. 2003). There are several methods of enhancing the dispersion of CNTs in liquids. These methods are classified as either physical or chemical. The most common physical method of dispersion is ultrasonication. Ultrasonication applies energy to the liquid suspension to disrupt the strong inter-tube forces. This approach can shorten the tubes and enhance dispersion, but also affects the material's properties (e.g., mechanical strength) (Hilding et al. 2003). Methods of ultrasonication include the ultrasonication wand and ultrasonication bath. The following figures show MWCNT length as a function of time for both methods (Hilding et al. 2003). The ultrasonication wand, or probe, can potentially damage the mechanical properties of the CNTs during dispersion.

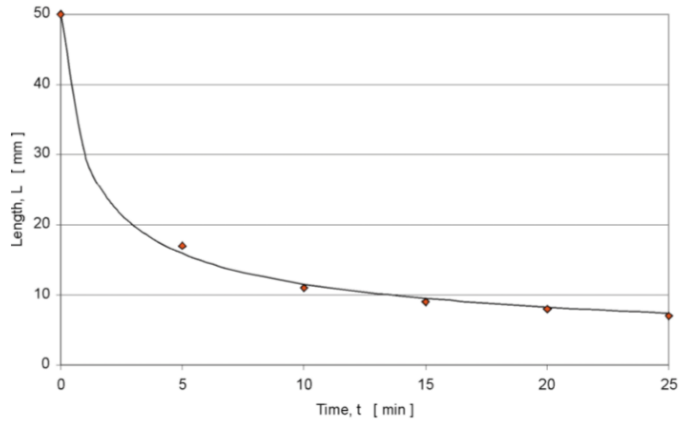

Figure 11. MWCNT length change as function of time ultrasonic bath (Hilding et al. 2003)

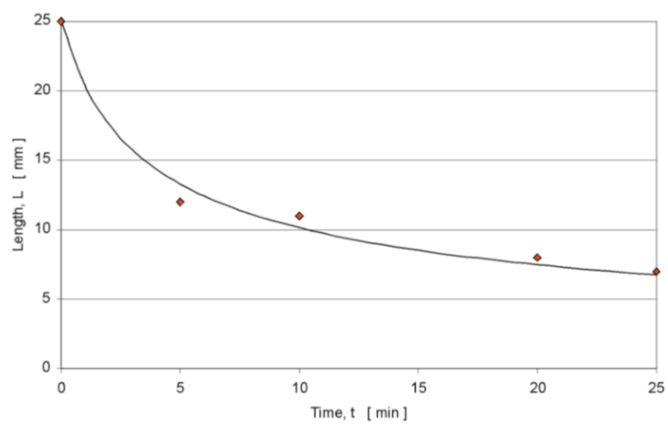

Figure 12. MWCNT length as function of time using ultrasonic wand (Hilding et al. 2003)

Chemical functionalization through covalent binding to the CNT surface effectively enhances dispersion and a wide range of functional groups have been demonstrated (e.g. carboxylic acid, -COOH, to large polyethylene glycol, PEG, molecules) (Zhang et al. 2008). Enhancing dispersion of CNT suspensions has a coupled effect of enhancing properties of the composites they are incorporated into (Hirsch 2002). Yet enhanced properties are not linearly correlated with increased level of functionalization.

One (1) example is the CNT mechanical properties, where elastic modulus was increased up to a 10% degree of functionalization, beyond which elastic modulus decreased (Zhang et al. 2008). Strength and ductility have also been shown to decrease with functionalization due to local disruption of conjugated structure (Zhang et al. 2008). Functionalization is necessary to help dispersion of CNTs in the composite matrix, but there is a trade-off with maintenance of the mechanical properties that must be considered, depending on the intended application.

1.2.5 Applications

CNTs are used in a wide variety of applications. A leading environmental application of CNTs is in drinking water and wastewater treatment, including absorbents and membranes. CNTs' high specific surface area and manipulable surface chemistry enhance adsorption of contaminants (Qu et al. 2013). CNTs are implemented into water treatment membranes because the mechanical and chemical stability and small diameter of the nanotubes lead to a quicker water permeation flux (Qu et al. 2013). CNTs also provide significant benefits in the disinfection step of water treatment. Electrical conductivity is important for electrochemical inactivation. When a small voltage is applied to a CNT filter, the bacteria and viruses present are oxidized and inactivated in seconds (Qu et al. 2013).

In addition to water treatment, CNTs are used in many electronic applications. Lithium-ion batteries are designed with CNT electrodes (Schnorr and Swager 2011; Popov 2004; Paradise and Goswami 2007). Redox reactions at the CNT surface oxygen groups lead to high gravimetric storage and power output capabilities (Lee et al. 2010). Electric double-layer capacitors are an alternative to lithium batteries that uses the large surface area of CNTs to achieve higher energy density (Schnorr and Swager 2011). Nanowires, contacts in organic transistors, and field effect transistors are among the other electronic uses of CNTs (Schnorr and Swager 2011).

CNTs are used in composite materials to provide significant coupled effects, including vehicle lightweighting. CNTs can be implemented as conductive fillers in plastics, which is important for fuel lines and filters of cars (De Volder et al. 2013). The high elastic modulus and tensile strength of CNTs are impactful in enhancing mechanical properties of composites and metals. Automobile tires are reinforced with CNTs to improve skid resistance and to reduce abrasion (Paradise and Goswami 2007). Several factors, such as diameter, aspect ratio, alignment, dispersion, and matrix interactions, determine the mechanical property enhancements of adding CNTs (De Volder et al. 2013).

1.3 Summary of Current Research into the Use of CNTs in PCC Mixtures

CNTs have been applied to cement-based materials due to their extraordinary mechanical properties. Possible reinforcing mechanisms of CNTs have been discovered and will be discussed. However, the extent of the reinforcement has varied significantly in previous experiments. This might be due to different concrete components, CNT treatments, and concrete mixing procedures. In other words, the four (4) reinforcing mechanisms described below may not be achieved simultaneously in one (1) concrete mixture (Liew et al. 2016).

1.3.1 Bridge Effects

The primary reinforcing mechanics of CNTs is the bridging effect. Prolific research has shown that CNT can bridge nano-size and micro-size pores or gaps in the range of 10–10^3 nm within hydration products (Parveen et al. 2015). In fact, CNTs are basically equivalent to micro-fibers, providing load transfer from the matrix to the CNTs and reducing the formation of micro-size pores or gaps.

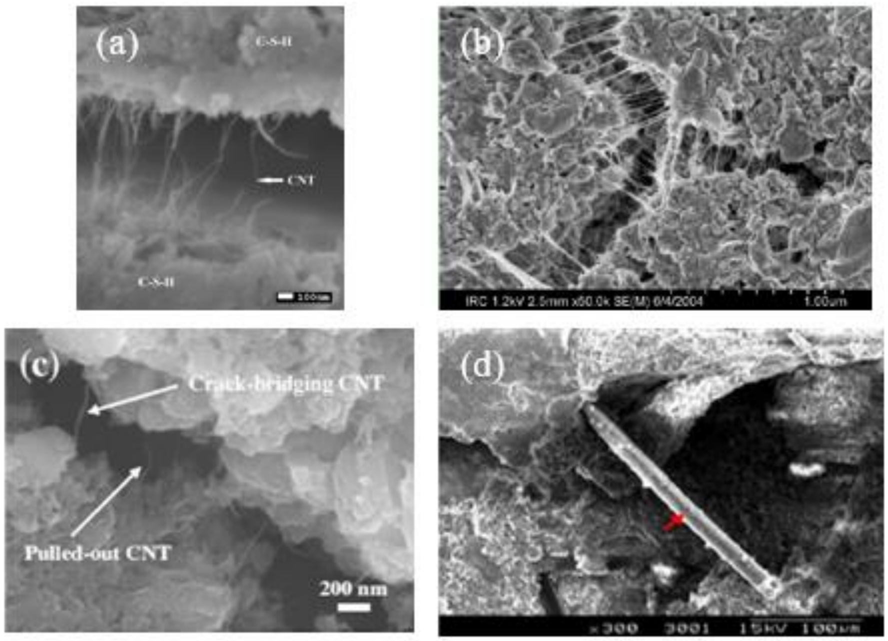

Figure 13 (a). SEM image showing the micro-crack bridging and breakage of MWCNTs within cement paste composite (Al-Rub et al. 2012) (b). Example of crack bridging in a SWCNT/hydrated OPC composite bridging structures are SWCNTs (Raki et al. 2010) (c). SEM images of pulled-out and crack-bridging CNTs in cement matrix (Zou et al. 2015) (d). Typical SEM image of carbon fiber cement matrix composites (Arrows: carbon fibers) (Li et al. 2005)

1.3.2 Nanoporosity Effects

The strength of concrete depends mainly on the capillary porosity or gel/space ratio of the paste (Kendall and Howard 1983). Li et al. observed that the addition of CNTs can refine the pore size distribution and decrease porosity (Li et al. 2005); their porosity results are shown in Table 3, tested using Mercury intrusion porosimetry. This filler effect might be analogous to finer mineral admixtures, such as silica fume and fine fly ash, since they have similar dimensions to CNTs.

Table 3. Effect of CNT on Compressive Strength, Flexural Strength, and Porosity (Li et al. 2005)

Mix	Compressive strength (MPa)	Flexural strength (MPa)	Porosity (%)	
			(d>50 nm)	(d < 50 nm)
PCC	52.27 ± 1.4%	6.69 ± 1.5%	2.67 ± 8.7%	15.09 ± 9.1%
PCC+CNF	47.51 ± 3.1%	8.14 ± 2.6%	9.89 ± 6.6%	13.48 ± 5.6%
PCC+CNT	62.13 ± 2.3%	8.37 ± 2.1%	1.47 ± 9.1%	10.13 ± 9.3%

1.3.3 Effects on Mechanical Properties

The possible utilization of CNTs' mechanical properties has been investigated extensively. The research focuses on the flexural performance (such as the tensile strength, flexural strength, toughness, ductility, and fracture performance) of concrete with CNT admixtures. A summary of research results is compiled in Table 4.

Table 4. Table Improvement of CNTs to mechanical properties of cementitious composites (Liew et al. 2016)

Properties	**Improvement**	**CNTs**			**Surfactant**
		Length	**Dia.**	**Concentration**	
Tensile Strength	34%			0.3wt.%	No
	19%	2 mm	30nm	0.5 wt.%	Acetone
Tensile Modulus	71%	2 mm	30nm	0.5 wt.%	Acetone
Compressive Strength	0%	10 mm	10 nm	0.007-0.042 wt.%	Polyacrylic acid polymers
	11%	-	8 nm	0.02 wt.%	No
	19%	30 mm	10nm	0.1% f-SWNT	Pluronic F-127
	200%	-	-	-	No
Flexural Strength	0%	10 mm	10 nm	0.007-0.042 wt.%	Polyacrylic acid polymers
	47%	-	-	0.25 wt.%	PVP
	25%	30 mm	40 nm	0.08 wt.%	Surfactant
	25%	100 mm	40 nm	0.048 wt.%	Surfactant
	36%	30 mm	20 nm	0.26 wt.%	Surfactant
	269%	1.5 mm	9.5 nm	0.2 wt.%	Polycarboxylate
	65%	30 mm	8 nm	0.1 wt.%	Polycarboxylate
	50%	1.5 mm	9.5 nm	0.075 wt.%	Polycarboxylate
Flexural Modulus	72%	30 mm	2 nm	0.1 wt.%	Pluronic F-127
	35%	1000 mm	80 nm	0.5 wt.%	Acetone
Flexural Toughness	25%	-	-	0.25 wt.%	PVP
	149%	50 mm	40 nm	0.2 wt.%	SDBS&TX10
Fracture Energy	63%	1.5 mm	9.5 nm	0.075 wt.%	Polycarboxylate
	14%	30 mm	30 nm	-	No
	50%	30 mm	40 nm	0.08 wt.%	Surfactant

Young's Modulus	37%	30 mm	20 nm	0.26 wt.%	Surfactant
	32%	1.5 mm	9.5 nm	0.075 wt.%	Polycarboxylate
	227%	20 mm	2 nm	0.1 wt.%	Gum Arabic
Ductility	0%	-	-	0.25 wt.%	PVP
	86%	1.5 mm	9.5 nm	0.2 wt.%	Polycarboxylate
	81%	30 mm	8 nm	0.1 wt.%	Polycarboxylate
	227%	1.5 mm	9.5 nm	0.2 wt.%	Polycarboxylate

1.3.4 Factors Influencing Reinforcement

From the previous summary, the reinforcement effect is not as significant as expected, considering the outstanding mechanical properties and geometrical shape of CNTs. Additionally, the previous studies diverge widely from one another in their assessments of the improvements from CNTs. These two (2) controversial phenomena might be attributed to various types, lengths, and manufacturers of CNTs, but more importantly, different CNT distribution methods and subsequent different dispersion degrees.

Inappropriate dispersion will lead to agglomerates of CNTs. In this case, CNTs are attracted to each other and aggregate into large bundles. This phenomenon decreases the homogeneity of the concrete mixture and eliminates the micro advantage of CNT. Even worse, the bundles of CNTs can act as crack initiators. Examples of CNT agglomerates can be seen in Figure 14, in suspension after different treatments in Figure 15, and under SEM in Figure 16.

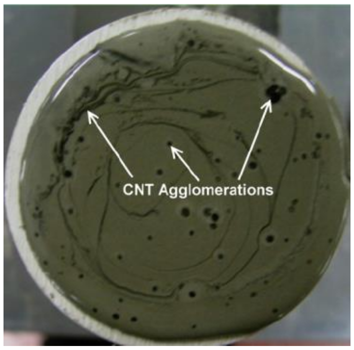

Figure 14. Fresh paste sample showing agglomerations of CNTs (w/c = 0.5, 0.5% CNT (%weight cement)) (Collins et al. 2012)

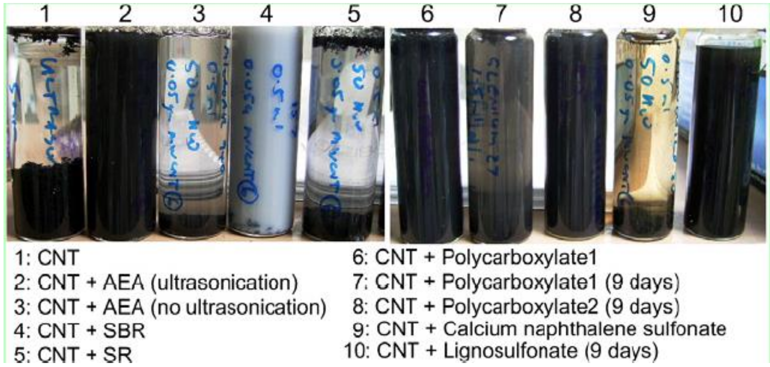

Figure BB.

Figure 15. Selected samples, following sedimentation trials of CNT in aqueous solutions. (Collins et al. 2012)

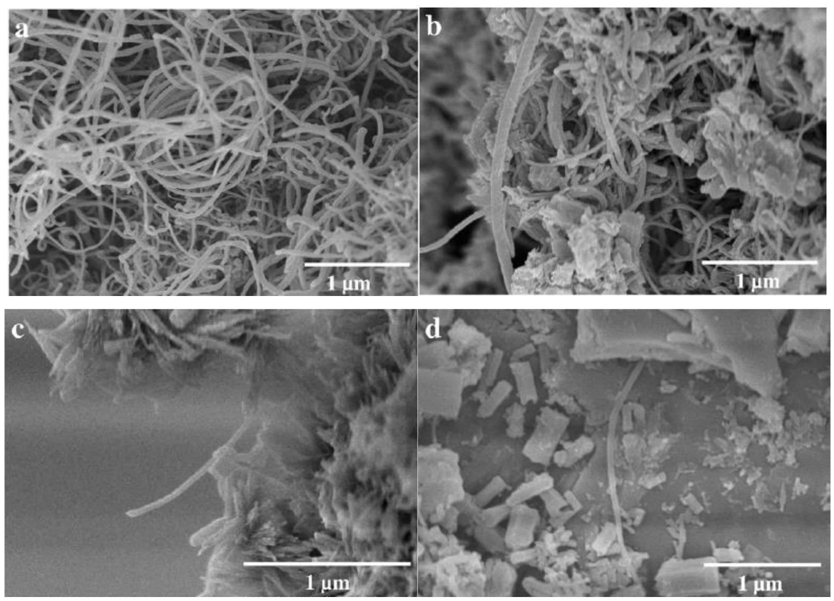

Figure 16. The SEM comparison of different degree of dispersion, dispersion with a surfactant to MWCNT ratio of (a) 0, (b) 1.5, (c) 4.0, (d) 6.25 (Konsta-Gdoutos, 2010)

1.3.5 Importance of Dispersion

Dispersion is a critical component of using CNTs as reinforcement of cementitious materials. The hydrophobicity and tubes strain of CNTs lead to van der Waals Force, which causes aggregation (poor dispersion) and can lead to weak bonds between the cement matrix and CNTs (Foldyna 2016) (Lourie 1998). These CNT bundles can further increase the effective size of the CNTs and diminish the advantages of their use. As a result, it is difficult to achieve optimal homogenous dispersion of the CNTs and overcome cohesive bonding between cement paste and the surface of CNTs. Achieving good dispersion is the first priority to ensure their maximum effectiveness, and multiple methods have been developed to improve the degrees of dispersion. A procedure to achieve dispresion is shown in Figure 17.

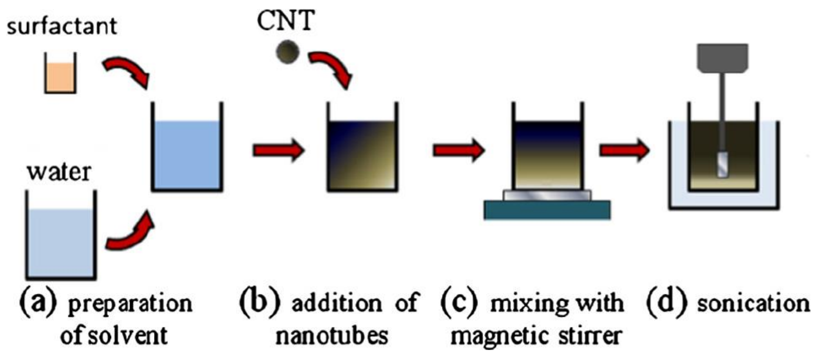

Figure 17. The dispersion procedure of CNTs in aqueous solution (Ubertini 2015)

1.3.6 Brief Summary of Sources

- Wille and Loh (2010) showed that at .022 wt% MWCNT in UHPC, there is no significant increase in compressive strength and bending strength. However, high molecular weight polyelectrolyte was successful in dispersing the nanotubes.

- Konsta-Gdoutos et al (2010) tested the mechanical properties of concrete samples based on length of nanotube and weight percentage of MWCNT. The diameter was kept consistent at 20-40 nanometers. The concentrations tested were .048 wt% and .08 wt%. The long nanotubes (10-100 micrometers) with .048 wt% had the greatest flexural strength. The short nanotubes (10-30 micrometers) with .08 wt% had the largest Young's Modulus.

- Liew et al (2016) outlined the percentage improvement of certain mechanical properties (tensile, compressive, flexural strength, Young's modulus, fracture toughness, and fracture energy) based on length, diameter, and concentration of CNTs.

- Manzur et al (2016) noted MWCNT (diameter 10-20 nanometers, length 10-30 micrometers) concentrations above .3 wt% showed lower strength values. The compressive strength was greatest at .3 wt%, and the flexural strength was greatest at .1 wt%. Both samples contained a percentage of polycarboxylate plasticizer.

- Tastani et al (2016) showed that at .1 wt% MWCNT, the toughness of the concrete sample significantly increases. There is also a synergy between polypropylene fibers and carbon nanotubes.

- Tyson et al (2011) used MWCNTs with a well-controlled diameter of 9.5 nanometers and length of 1.5 micrometers in Type I/II Portland Cement concrete. It was determined that .2 wt% MWCNT samples had larger strain capacity, ultimate strength, elastic modulus, and toughness than 1 wt% MWCNT samples. Both concentrations increased concrete performance.

- Ameri et al (2016) tested five (5) different MWCNT concentrations (.2, .5, .8, 1.2, 1.5 wt%) in bitumen to see the effects on fatigue life and strain energy. 1.5 wt% MWCNT samples had the largest fatigue and strain energy.

- Kowald (2004) used MWCNTs with diameters of 10-30 nanometers and lengths of 1-10 micrometers. Concrete samples had the largest compressive strength, with an addition of .5 wt% MWCNT. Note that the concentration of MWCNT can affect the water to cement ratio.

- Nochaiya and Chaipanich (2011) found that as the concentration of MWCNTs increases, the porosity decreases and the intruded volumes decrease.

- Mohsen et al (2016) tested concrete specimens prepared with MWCNTs. In general, it was determined that the longer the sample was mixed, the better the dispersion and the lower the porosity. Batches with .25 wt% MWCNT had the best flexural strength according to statistical analysis conducted.

- Adresi et al (2016) looked into the best surfactant to improve MWCNT dispersion in concrete. MWCNT (diameter 10-20 nanometers, length ~10 micrometers) was held constant at .05 wt%. Defoamers helped to increase flexural and compressive strengths.

- Cwirzen et al (2013) tested MWCNTs (diameter 10 nanometers, length 2-4 micrometers) in concrete mortar subjected to freeze/thaw cycles. The flexural and compressive strengths of the concrete samples lowered slightly from the reference with MWCNT addition. The addition of .23 wt% MWCNT had better strength than .5 wt% MWCNT.

- Feneuil et al (2017) tested MWCNT concrete samples (diameter 20-30 nanometers, length > 5 micrometers) for autogenous shrinkage. Above .01 wt%, autogenous shrinkage was reduced as functionalized MWCNT concentration was increased.

- Isfahani et al (2016) used functionalized MWCNTs (diameter 10-20 nanometers, length 10-30 micrometers) for compressive and flexural strength tests. For compressive strength, the optimal MWCNT concentration was found to be .1 wt%. For flexural strength, the optimal MWCNT concentration was found to be .3 wt%.

- Faramarzi et al (2015) tested MWCNT with diameter 10-20 nanometers and length 10-30 micrometers in asphalt binder. Samples with .5 wt% and 1 wt% showed increased penetration resistance.

1.4 Health, Safety, and Environmental Impact

Significant research efforts have been made to evaluate the potential health risks of CNTs, both in their raw form and once incorporated into products (NIOSH 2009). CNTs can be released as free CNTs, agglomerates of CNTs, or as particles in a composite matrix (Nowack et al. 2013). Raw CNTs can be visible to the human eye, as agglomerates can be as large as a few millimeters in diameter (NIOSH 2009). Workers with exposure to nanomaterials may be at health risk during production, pouring and mixing operations, powder handling, and mechanical disruption of the nanomaterials (NIOSH 2009). The National Institute for Occupational Safety and Health considers the release rate of inhalable and respirable CNT particles to be relatively low compared to other nanomaterials and the CNT exposure to be insignificant in large-scale nanocomposites (Nowack et al. 2013). Research into the release of CNT-concrete composites is still in its preliminary stages. Other composites, such as CNT-polypropylene composites, have been shown to emit airborne CNTs during grinding of the composite (Boonruska et al. 2016). It is important to note that free CNTs were not among the emissions, and there were no engineering controls present. The protocol for life-cycle exposures of CNT-concrete composites may be similar to CNT-polypropylene composites, but it still must be specifically assessed. The exposure pathways of CNTs to humans include inhalation, ingestion, and skin contact (Nowack et al. 2013). While handling CNTs directly poses health risks, the non-nanomaterial waste from production of CNTs is also of health concern (NRC 2012).

To identify the potential health implications of CNTs, the toxicity and carcinogenicity of CNTs must be assessed. Mesothelioma, granulomas, and lung fibrosis are among the potential health implications of CNTs (Nowack et al. 2013). CNTs damage tissue in the body as the presence of impurities or irregularities in CNTs induce reactions in the cells that create potentially dangerous species (Rendon et al. 2014). Multiple studies compiled by the NIOSH gauge the dose-response of CNT exposure on mice (NIOSH 2009). One (1) study detailed that mice experienced adverse pulmonary effects, granulomas, and interstitial fibrosis after pharyngeal aspiration of SWCNTs (Shvedova et al. 2005; Mercer et al. 2008). In another NIOSH study, mice experienced pulmonary inflammation and symptoms of interstitial fibrosis after aspiration of MWCNTs (Muller et al. 2005). Additionally, when SWCNTs were applied to the skin of nude mice, dermal irritation was observed (Murray et al. 2007). Although MWCNTs have induced carcinogenic effects, such as mesotheliomas, in mice, there has yet to be a human case of cancer induced by MWCNTs (Toyokuni 2013). Importantly, the health effects observed in mice were induced by direct and intense exposure to CNTs. The experiments on mice do show that it is important to employ methods to limit CNT exposure for worker safety, specifically regarding inhalation.

To manage exposure to CNTs, NIOSH recommends an ordered approach. The following tasks should be completed to limit exposure, if possible (in descending order of importance): (i) elimination of hazard, (ii) substitution of higher hazard to lower hazard, (iii) engineered protection from hazard, (iv) administrative policy, and (v) personal protective equipment (NIOSH 2009). Personal protective equipment is required when developing CNT composites. NIOSH states that a properly fitted facemask will stop its intended percentage of particles (NIOSH 2009). For instance, NIOSH has standardized N100 and N95 respirators as required protection against inhalation and ingestion. N100 respirators stop 99.97% of particles larger than 300 nm, and N95 respirators stop

95% of particles larger than 300 nm (Rendon et al. 2014). Long sleeve protection, gloves, and safety glasses are among other personal protective equipment used when handling CNTs. Much of the personal protective equipment recommended by NIOSH for CNT handling is needed already for concrete handling. For instance, the Occupational Safety and Health Administration (OSHA) recommends using N95 respirators to minimize the inhalation of cement dust (OSHA 2004). Also, long sleeve protection, gloves, and safety glasses are already common concrete handling protection measures. If there is a CNT spill or contamination on a surface, there are preferred cleaning methods recommended by NIOSH. HEPA-filtered vacuum cleaners and damp cleaning methods are recommended for cleaning powdered samples, and absorbent materials and liquid traps are used to clean liquid samples (NIOSH 2009). It is important for workers to continue to limit exposure to CNTs during clean-up by wearing the proper personal protective equipment. NIOSH states that disposal of the CNTs must comply with local, state, and federal regulations (NIOSH 2009).

There are properties of CNTs that cause a greater risk for health effects. If CNTs are multi-walled, of great dimension and concentration, and have a large quantity of impurities, there is an increased risk for human health effects (Rendon et al. 2014). During handling of CNTs, there is a potential increased risk for human health effects if the duration is long, the area is enclosed, there is exposure to aerosol particles, and there is a lack of aggregation of the CNTs (Rendon et al. 2014). NIOSH details good nanomaterial handling practices for management and workers in its 2009 report. Management should educate workers about nanomaterial safety and contain the presence of CNTs to the work site. Workers should properly clean areas and equipment exposed to CNTs, while avoiding inhalation of, ingestion of, and skin contact with free CNTs in open air (NIOSH 2009). If these practices are not completed, there will be a greater chance for human health effects from CNTs.

CNTs can be deposited into the environment during their life cycles in concrete composites. The environmental release of CNTs may occur during production, during the use of the products containing the CNTs, and the end of the life of the products. CNTs are released from CNT-composites after degradation, and chemical alterations of CNTs occur from environmental interactions (Nowack et al. 2013). CNTs can be deposited in soils, sediments, the atmosphere, and surface waters (Petersen et al. 2011). It is important to be aware about the release and transport of CNTs in the environment as there are several exposure pathways to organisms. The toxicity of free CNTs is generally understood to be a danger to organisms (Toyokuni 2013). Bioaccumulation and bioconcentration of these free CNTs can potentially cause health problems to organisms exposed (Nowack et al. 2013).

2. Laboratory Investigation

Two different CNT types (short and long) and two concentrations of CNTs (0.05% and 0.1% with respect to cement weight) were evaluated using a water/cementitious material ratio of 0.44. The physical properties of the multiwalled carbon nanotubes (MWCNT) can be found in Table 5. All CNTs in the laboratory investigation were functionalized with -COOH and had an outer diameter of less than 8 nm.

Table 5. Physical properties of CNTs

	Long MWCNTs-COOH	*Short MWCNTs-COOH*
Out Diameter	<8 nm	<8 nm
-COOH	3.86wt%	4-5wt%
Length	10-30 um	0.5-2.0 um

The concrete mixture design is shown in Table 6, including Type I/II cement from CEMEX Co Inc., as well as coarse limestone and fine concrete sand aggregate from Neville Aggregates Co Inc. The mixture design meets the requirements of Class AAA-P bridge deck concrete outlined in Section 704, Table A of PennDOT Publication 408 (2016) (while also satisfying the requirements of Class AA paving concrete). All specimens were cast and cured in accordance with ASTM C129.

Table 6. Concrete mixture design: batch weights for one cubic foot of concrete

Material ingredients	*Water (lb.)*	*Cement (lb.)*	*Coarse Aggregate (Dry) (lb.)*	*Fine Aggregate (Dry) (lb.)*	*Super-Plasticizer (ml)*	*CNT (g)*	*w/c*
0.1% CNTs	11.56	23.98	61.94	44.82	43.56	10.88	0.44
0.05% CNTs	11.56	23.98	61.94	44.82	21.78	5.43	0.44

The most fundamental properties of concrete were evaluated with traditional concrete tests, which target the mechanical and durability properties of concrete. They are well correlated to in-site concrete performance and therefore indicate the basic feasibility of CNT-reinforced concrete. Four replicate specimens were cast on each mixture (the traditional PennDOT mixture and the same mixture with the addition of CNTs) for each of the tests performed.

Mechanical tests:

- ASTM C39: Standard Test Method for **Compressive Strength** of Cylindrical Concrete Specimens - (4-in. by 8-in. cylindrical specimens)
- ASTM C496: Standard Test Method for **Splitting Tensile Strength** of Cylindrical Concrete Specimens - (4-in. by 8-in. cylindrical specimens)
- ASTM C78: Standard Test Method for **Flexural Strength** of Concrete (Using Simple Beam with Third-Point Loading) - (6-in. by 6-in. by 24-in. beam specimens)

Durability tests:

- ASTM C157: Standard Test Method for **Length Change** of Hardened Hydraulic-Cement Mortar and Concrete - (4-in. by 4-in. by 11.25-in. prism specimens)
- ASTM C666: Standard Test Method for **Resistance of Concrete to Rapid Freezing and Thawing** - (4-in. by 8-in. cylindrical specimens)
- ASTM C1202: Standard Test Method for Electrical Indication of Concrete's Ability to **Resist Chloride Ion Penetration** - (4-in. by 2-in. cylindrical specimens)

2.1 Results

2.1.1 Compressive Strength

Compressive strength testing was carried out on 4 in. x 8 in. cylinders according to ASTM C39. A total of 4 replicates were tested for each mixture and yielded the results in Table 7 below. Testing was carried out at both 7 and 28 days. The control produced higher compressive strengths than those cylinders which contained the CNTs. The shakedown testing yielded similar results. Tukey’s range test, a single-step multiple comparison procedure and statistical test, was utilized to compare all possible pairs of means (Montgomery 2012). At 7 days, none of the treatments were statistically different at a confidence level of 95%. At 28 days, the same statistical test showed that 0.05% - Short, 0.1% - Short, and 0.05% - Long had slightly lower compressive strengths than the control at a confidence of 95%.

Table 7. Results from compressive strength testing

	7 day		**28 day**	
Mixture	**Average Compressive Strength (psi)**	**Standard Deviation (psi)**	**Average Compressive Strength (psi)**	**Standard Deviation (psi)**
Control	5280	194	7220	130
0.05% - Short CNT	5200	45	6230	201
0.1% - Short CNT	5110	189	6220	11
0.05% - Long CNT	4780	186	5950	229
0.1% - Long CNT	5536	49	6540	390

2.1.2 Split Tensile Strength

Split tensile strength testing was carried out on 4 in. x 8 in. cylinders according to ASTM C496. A total of 4 replicates were tested for each mixture and yielded the results in Table 8 below. Testing was carried out at 28 days. Even though the compressive strengths of the mixtures with CNTs fell slightly, the split tensile strengths of all the mixtures were comparable. Statistical testing using Tukey's range test yielded that none of the treatments were statistically different at a confidence level of 95%. Even though compressive strength fell slightly, the similarity in split tensile strength appears to have improved the tensile capacity of the mixtures with CNTs.

Table 8. Results from split tensile strength testing

	28 day	
Mixture	**Average Split Tensile Strength (psi)**	**Standard Deviation (psi)**
Control	601	130
0.05% - Short CNT	581	201
0.1% - Short CNT	557	11
0.05% - Long CNT	571	229
0.1% - Long CNT	625	390

2.1.3 Flexural Strength

Flexural strength testing using a beam in third-point loading was carried out on 6 in. x 6 in. x 24 in. beams according to ASTM C78. Table 9 summarizes the flexural strength data. In general, the flexural strengths were comparable across all mixtures. A slight decrease was noted over the control, but no statistically significant difference was discerned.

Table 9. Results from flexural strength testing

	28 day	
Mixture	**Average Flexural Strength (psi)**	**Standard Deviation (psi)**
Control	846	52
0.05% - Short CNT	844	88
0.1% - Short CNT	783	110
0.05% - Long CNT	790	121
0.1% - Long CNT	834	73

2.1.4 Drying Shrinkage

Drying shrinkage is determined using ASTM C157. 3-in. by 3-in. by 11.25-in. prism specimens were used to determine the drying shrinkage (Figure 18). Figure 18 shows the specimens, the shrinkage mold, and studs, as well as the testing apparatus. The average ultimate drying shrinkage values are presented below in Table 10.

Figure 18. 3-in. by 3-in. by 11.25-in. prism drying shrinkage specimen, drying shrinkage molds, and measurement apparatus

Table 10. Results from drying shrinkage testing

Mixture	**Average Ultimate Drying Shrinkage (με)**
Control	623
0.05% - Short CNT	587
0.1% - Short CNT	572
0.05% - Long CNT	536
0.1% - Long CNT	551

2.1.5 Freeze-Thaw

Freeze-thaw testing using the freezing and thawing procedure from ASTM C666 was used to test the elastic modulus of cylindrical specimens using ASTM C469. The initial elastic modulus was determined before initiating the cycling. The results presented below show the stiffness after 4 months of freeze-thaw cycling. There was no observed or statistical difference between the CNT mixtures and the control.

Table 11. Freeze-thaw testing results

Mixture	**Initial Average Elastic Modulus (psi)**	**Average Elastic Modulus after completion of freeze-thaw cycling (psi)**
Control	$5.17*10^6$	$4.71*10^6$
0.05% - Short CNT	$5.44*10^6$	$5.28*10^6$
0.1% - Short CNT	$5.03*10^6$	$4.89*10^6$
0.05% - Long CNT	$5.06*10^6$	$4.92*10^6$
0.1% - Long CNT	$5.17*10^6$	$4.84*10^6$

2.1.6 Resistivity

Resistivity was evaluated with the Rapid Chloride Ion Penetration (RCIP) test, which can evaluate concrete resistance to chloride penetration and steel corrosion. It can also be an indicator of concrete permeability and durability performance. This test was conducted in accordance with

ASTM C1202. A potential difference of 50 V dc was used instead of the standard 60 V dc. When the standard 60 V dc was used, the current went beyond the capacity of the Ammeter.

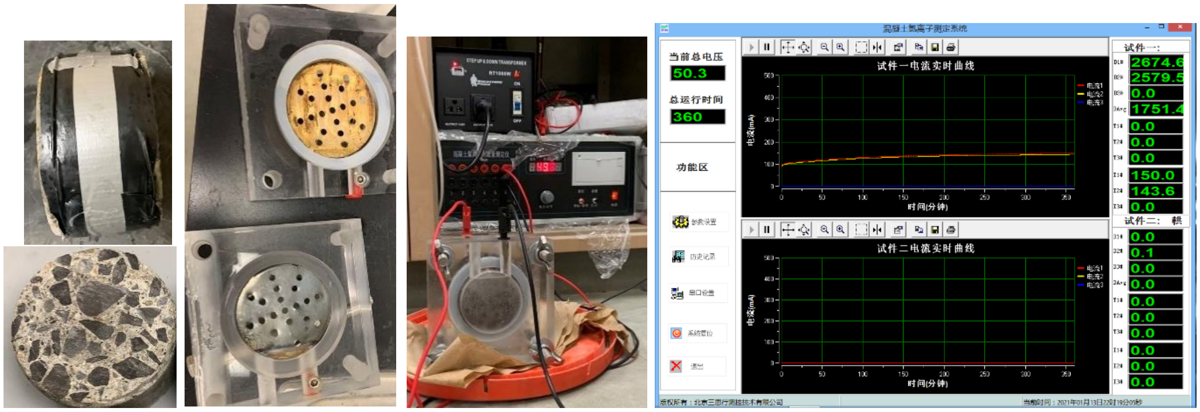

Figure 19. RCIP specimen, Applied Voltage Cell, Apparatus setup, monitor interface

For the RCIP test, CNT-reinforced concrete performed similarly to the control group. All specimens performed moderately well within a range expected for conventional Portland cement concrete (~ 2000 – 4000 Coulombs). A slight reduction was observed for 3 of the 4 CNT mixtures, but no statistical difference was observed across the replicates of the different mixtures.

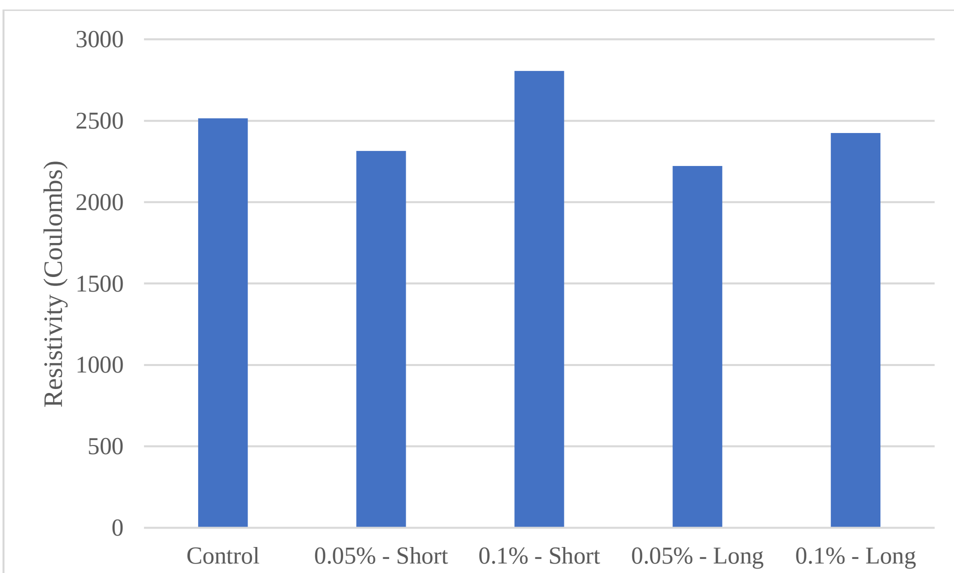

Figure 20. Rapid Chloride Ion Penetration test results of CNT-reinforced concrete specimens

Many of the tests did not conclusively show an increase in either the mechanical or durability performance. These results informed the recommendations and life cycle costs to be examined in the next sections.

3. Performance and Life Cycle Cost Analysis

The life cycle costs for traditional PennDOT concrete with CNTs are determined in this chapter. In particular, the added materials/concrete costs are weighed against the anticipated cost savings realized through the addition of CNTs, based on extrapolations and expected benefits identified from the laboratory testing. For example, the change in the design life of a traditional PennDOT concrete pavement is estimated from the measured parameters in the laboratory coupled with the planned rehabilitation schedule. The first step is to determine the overall unit cost difference of concrete with CNTs, which is then used to determine the potential benefits of a hypothetical paving project.

3.1 Unit Cost of Concrete with CNTs

Based on current prices, the average market cost of large-scale Multiwalled CNT production is approximately \$0.10 - \$15.00 per gram (*Nanotechnology* 2022, *The Global Market for Nanotechnology and Nanomaterials* 2016). With roughly two orders of magnitude difference in cost, it will be assumed that a highway construction project would minimize costs by purchasing CNTs at the lower end of the cost range. Therefore, the study will assume that CNTs cost \$200 per kg, which is double the minimum, to help account for additional costs associated with shipping and transportation of the material.

The dosage of CNTs which was established for the laboratory investigation included 0.05% and 0.1% by weight of cement. It will be assumed that the concrete used will satisfy the requirements of PennDOT Class AA paving concrete with a cement content of 600 lbs. per cubic yard (PennDOT Pub 408). This results in approximately 0.132 kg of CNTs for a dosage of 0.05% by weight of cement and 0.272 kg of CNTs for 0.1% by weight of cement. The increase in cost per cubic yard will then be \$27 and \$54 per cubic yard of concrete for a 0.05% and 0.1%, respectively.

The cost of concrete per cubic yard is highly variable and dependent on many factors, including location, raw material, and transportation costs. The material cost of concrete ranges from \$110 - \$200 per cubic yard (RSMeans, 2019). Note that this is only the cost of the material and does not include any of the labor to place and finish the material. Using a value of \$150 per cubic yard gives an increase in material cost of 18% and 36% with a CNT dosage of 0.05 and 0.1%, respectively.

Up to this point, the cost estimate has not considered the effort, equipment, and labor needed to disperse the CNTs into solution to be introduced into the concrete. This is difficult, if not impossible, to quantify accurately. A bath or probe sonicator is required to disperse the CNTs in an aqueous solution. Sonicators often cost several thousand dollars and require training to use. Then, someone must disperse the material ahead of time, which can take several hours. This significantly raises the overall cost to produce CNT concrete and makes it exceptionally difficult to keep up with the rate of production needed for a paving project. However, for the purposes of this cost estimate, equipment and labor will be assumed to double the cost of the CNT material needed. This is most likely a significant underestimate of the unit cost but will at least provide some basis for comparison.

3.2 Pavement Life Cycle Cost Analysis

A life cycle cost analysis is performed on a hypothetical pavement project of a 4-mile-long new concrete pavement with a design thickness of 12 inches. The project is a 4-lane divided highway with a 15 ft. joint spacing and 1.5 in. diameter dowel bars. The life cycle cost analysis uses the maintenance schedule for newly constructed concrete pavement from Chapter 3 of PennDOT Publication 242 (PennDOT Pub 242). The schedule is shown in Table 12.

PennDOT's life cycle cost analysis uses the Discount Rate. The Discount Rate is the five-year rolling average of the annual 30-Year Real Interest Rate on Treasury Notes and Bonds posted by the Executive Office of the President, Office of Management and Budget (OMB) Circular A-94, which is 0.5% for the year 2022 (PennDOT Pub 242). This percentage is used to convert future cash flows to a present valuation for use in a direct comparison.

The only difference in initial cost is the cost of the concrete. Approximately 37,500 yd^3 of concrete is used in the 4-mile length of roadway. For the hypothetical pavement structure, the 0.05% CNT concrete costs approximately $2.03 million more than conventional concrete. The 0.1% CNT concrete costs approximately $4.06 million more than conventional concrete. This calculation is summarized in Table 13.

Introducing CNTs into the concrete may change the cost of some maintenance items from Table 12, such as the amounts of concrete patching that are scheduled to occur at 15 years, 25 years, and 35 years. Currently, 2, 4, and 6% of the pavement area will be patched at 15, 25, and 35 years, respectively. Since minimal performance increase was shown in the laboratory investigation, a half percent reduction in patched pavement area is specified to observe the difference in overall cost. The future costs of patching will be brought back to a present value so that a direct comparison can be made to the increase in the initial cost of the CNT concrete. A unit cost of $150 per square yard of patching area is used for the calculation, and it is assumed that the same patching material will be used for each alternative. The present value of an alternative is calculated using the equation below, where i = discount rate and n = number of years.

$$Present\ Value = \frac{Future\ Value}{(1+i)^n}$$

A summary of these calculations denoting the differences in the costs is shown in Table 14. The calculations yield a savings of $224,000 for the CNT-reinforced concrete.

Table 12. Rehabilitation Schedule for Pavement Life Cycle Cost Analysis (PennDOT Pub 242)

Concrete New Construction, Reconstruction (including construction on fractured concrete pavement), Unbonded Concrete Overlay – 50 Year Pavement Life (Analysis Period)	
10 years	Clean and Seal, 25% of longitudinal joins including shoulders Clean and Seal, 25% of transverse joints Maintenance and Protection of Traffic User Delay
15 years	Concrete Patching, 2% of pavement area Diamond grinding, 50% of pavement area Clean and Seal, all longitudinal joints including shoulders Clean and Seal, all transverse joints Maintenance and Protection of Traffic User Delay
25 years	Concrete Patching, 4% of pavement area Diamond grinding, 100% of pavement area (full width) Clean and Seal, all longitudinal joints including shoulders Clean and Seal, all transverse joints Maintenance and Protection of Traffic User Delay
35 years	Concrete Patching, 6% of pavement area Clean and Seal, all longitudinal joints including shoulders Clean and Seal, all transverse joints Scratch Course, 60 pounds per square yard Asphalt Overlay, 4 inches or 4.5 inches Saw and Seal, all transverse joints Type 7 Paved Shoulders Adjust guide rail and drainage structures, if necessary Maintenance and Protection of Traffic User Delay
40 years	Clean and seal, 25% of longitudinal joints Clean and seal, 25% of transverse joints Crack seal, 500 lineal feet per mile Seal coat or Micro surface shoulders User Delay
45 years	Crack seal, 500 lineal feet per mile Partial Depth Asphalt Surface Patching, 2% of pavement area Clean and Seal, 25% of all longitudinal joints, including shoulders Clean and Seal, 25% of all transverse joints Micro surface roadway Maintenance and Protection of Traffic User Delay

Table 13. Initial Pavement Concrete Cost Calculation

	Unit Cost ($/yd^3)	Required Volume (yd^3)	Cost ($)
Conventional Class AA Concrete	150	37547	$5,632,000
0.05% CNT Concrete	204	37547	$7,659,520
0.1% CNT Concrete	254	37547	$9,687,040

Table 14. Summary of Pavement Maintenance Calculations

	Conventional Class AA Concrete	Unit Cost ($/yd^2)	Area (yd^2)	Future Cost	Present Cost
15 years	2% of pavement area	150	2252.8	$337,920	$313,562
25 years	4% of pavement area	150	4505.6	$675,840	$596,612
35 years	6% of pavement area	150	6758.4	$1,013,760	$851,379
			TOTAL	$2,027,520	$1,761,553
	CNT Concrete	Unit Cost ($/yd^2)	Area (yd^2)	Future Cost	Present Cost
15 years	1.5% of pavement area	150	1689.6	$253,440	$235,171
25 years	3.5% of pavement area	150	3942.4	$591,360	$522,036
35 years	5.5% of pavement area	150	6195.2	$929,280	$780,431
			TOTAL	$1,774,080	$1,537,638

The final overall comparison can be found in Table 15. The savings in the maintenance costs do not overcome the overall initial investment; the additional project expenses are still $1.8 and $3.8 million dollars more for the 0.05% and 0.1% CNT concrete, respectively, compared to the conventional Class AA concrete. Also, the unit cost of concrete is most likely underestimated, resulting in an even larger initial cost. In order for the life cycle costs of the CNT and conventional concrete to be comparable, the CNT concrete would need to eliminate essentially all patching, which is unrealistic. Therefore, the initial cost would have to decrease significantly in order to be financially feasible.

Table 15. Pavement Life Cycle Costs

	Conventional Class AA Concrete	0.05% CNT Concrete	0.1% CNT Concrete
Initial Maintenance Cost	$5,632,000	$7,659,520	$9,687,040
Maintenance Cost	$1,761,553	$1,537,638	$1,537,638
Total	$7,393,553	$9,197,158	$11,224,678

3.3 Bridge Life Cycle Cost Analysis

A 4-lane bridge with a 50 ft. span and an 8-inch-thick concrete deck was chosen for the life cycle cost analysis. As many components of the bridge superstructure and substructure can be made from concrete, the use of CNT concrete will be restricted to the bridge deck. The initial volume of concrete required is then 1600 ft^3. Since the volume of concrete for the bridge deck is relatively small, the initial materials cost $3200 and $6400 more, respectively, when the 0.05% and 0.1% CNT concrete are used than when conventional concrete is used.

The bridge is assumed to be maintained according to the guidelines specified in PennDOT Publication 23 Chapter 16. A 50-year design life will be used, with both alternatives being washed, cleaned, and sealed at regular intervals. 10% of the pavement area will be patched every 10 years before an overlay is placed at 30 years.

Since minimal performance increase was shown in the laboratory investigation, a half percent reduction in patched bridge deck area will be specified to observe the difference in overall cost. The future costs of patching will be brought back to a present value so that a direct comparison can be made to the increase in the initial cost of the CNT concrete. A unit cost of $50 per square foot of patching area is used for the calculation, and it is assumed that the same patching material will be used for each alternative. The present value of an alternative is calculated using Equation 1. The estimated maintenance savings amount to a present value of $1,114 for the CNT-reinforced concrete. These costs are summarized in Table 16. Similar to the pavement life cycle cost analysis, the savings in maintenance cost do not overcome the initial investment needed upfront for the CNTs. Since the quantities are smaller, there is a smaller difference in overall cost.

Table 16. Bridge Deck Life Cycle Costs

	Conventional Bridge Deck	0.05% CNT Concrete Deck	0.1% CNT Concrete Deck
Initial Material Cost	$8,889	$12,089	$15,289
Maintenance Cost	$22,277	$21,163	$21,163
Total	$31,166	$33,252	$36,452

It was found that for both a hypothetical pavement and bridge, it is not cost-effective to implement CNT concrete at this time. The cost of the CNT concrete is most likely underestimated, and more work needs done to better approximate the overall cost in a large-scale operation. One other issue not addressed is that special care will be needed to dispose of the CNT-reinforced concrete which will be another additional cost.

4. Recommendations

This section provides recommendations based upon the results from the laboratory testing and the life cycle cost analysis. The recommendations address current applicability and future research directions. The life cycle cost analysis found that for both a hypothetical pavement and bridge, it is not cost-effective to implement CNT concrete at this time. The cost of the CNT concrete is currently too high, and more work needs done to better approximate the overall cost in a large-scale operation. Additionally, many of the laboratory tests did not conclusively show an increase in either the mechanical or the durability performance of CNT concrete. Given the effort needed for dispersion prior to mixing, the results of the current and previous investigations on the topic, and the health hazards associated with handling nanomaterials, it is not recommended at this time to adopt this technology. Further advances are required to glean the benefits necessary to outweigh the costs.

CNT-reinforced cement materials will need mature preparation processes, including dispersion and distribution of the CNTs, as well as uniform specifications and standards which are not currently available. CNTs have a propensity to agglomerate, especially at higher dosages, making dispersion quite difficult and time-consuming. If CNTs are not dispersed adequately, the agglomerations can result in weak spots in the concrete matrix, which can increase the porosity and damage the mechanical properties. These difficulties would make performing quality control on CNT concrete in a field application an immense challenge at this time. Therefore, more work would need done to establish a set of standards for the introduction of CNT material into a concrete matrix.

The following research is needed to supplement the current research and fill the knowledge gaps on CNT-reinforced cementitious composites (Ramezani et al. 2022).

1) Developing and optimizing dispersion techniques. Despite extensive experimental research, obtaining a uniform and stable dispersion of high CNT concentrations is still a major challenge.
2) Conducting research on alternative dispersion solutions, such as the direct synthesis of CNTs onto the cement particles.
3) Introducing quantitative standards for describing the dispersion/agglomeration of CNTs.
4) Conducting more profound and systematic research to understand and characterize the CNT mechanisms via novel nano/micro-structural techniques. This fundamental research could establish the relationships between the underlying mechanisms of CNTs and various properties of CNT-reinforced cementitious composites.
5) Further studying the environmental impacts and toxicity of new cementitious products containing CNTs. Limited studies have been conducted on the environmental and health impact of the CNT-reinforced cementitious composites. Additionally, standards for handling materials and wearing personal protective equipment should be defined for professionals working with nanomaterials.

6) Researching the health, safety, and environmental impacts of CNT concrete material associated with disposal at the end of life, as well as during rehabilitation of structures. This is, along with handling during construction, a major concern.

Summary and Conclusions

This study was conducted under two Work Orders. The first task was to conduct a literature review, which informed the remainder of the study. In a laboratory investigation, two different CNT types (short and long) and two concentrations of CNTs (0.05% and 0.1% with respect to cement weight) were evaluated using a water/cementitious material ratio of 0.44. All CNTs in the laboratory investigation were functionalized with -COOH and had an outer diameter of less than 8 nm. CNT-enhanced concrete specimens were then tested for compressive strength, split tensile strength, flexural strength, drying shrinkage, freeze-thaw, and rapid chloride ion penetration. Many of the tests did not conclusively show an increase in either the mechanical or durability performance.

A life cycle cost analysis was performed, which found that for both a hypothetical pavement and bridge, it is not cost-effective to implement CNT concrete at this time. The cost of the CNT concrete was most likely underestimated, and more work needs to be done to better approximate the overall cost in a large-scale operation. One other issue not addressed is that special care will be needed to dispose of the CNT-reinforced concrete, which will be another additional cost. At this time, it is not recommended to adopt this technology until further advances are made to outweigh the additional cost.

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