ENHANCED CONCRETE PERFORMANCE WITH USE OF CARBON NANOTUBE LIQUID ADDITIVE

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ABSTRACT

Carbon nanotube (CNT) enriched liquid additives, when used in the design and construction of concrete result in improved durability and strength. Nanoparticles serve as nucleation sites during cement hydration to help create a denser, cement paste composition. Australian trials have yielded increases between 10mpa – 20mpa, equalling ~10% - 30% improvements in compressive strength gains as tested to AS1012.9 2014. Reducing the permeability of the concrete, the CNT dispersed additive significantly reduced chloride ingress in one field trial in Australia, tested at 37% reduced permeability per Method NT Build 443 1995-II. Georgia's Dept. of Transport achieved abrasion resistance and compressive strength increases by more than 30% per ASTM C779, proc. C, and ASTM C39, respectively. A trafficable concrete drainage project, in a flood zone, subject to abrasive conditions, placed concrete drain sections with and without CNT additive in the concrete. The result was a tensile strength increase of 25% and abrasion resistance 40%, and after 36 months in service it showed no cracks or pitting vs. the control mix which cracked (>0.3mm) and was deeply pitted. Edencrete is AS4020-2018 certified. Benefits of CNT technology in concrete will be detailed further in this paper.

1.0 INTRODUCTION

Enhanced Carbon nanotubes (CNTs) have been used for years in electronics, human medicine, and the automotive and aeronautics industries. In recent years, CNT-enriched liquid additives have been developed which have proven their ability to enhance a variety of properties in concrete, mortar, and shotcrete, such as compressive and split-tensile strength, and resistance to abrasion and cracking. The test results and projects supporting this paper utilized a CNT-enriched additive for concrete referred to as CNT additive, manufactured by Company E in Littleton, CO. Company E produces the CNTs and the additive in their facility in Littleton, CO., and many of the claims in this paper refer to measurements recorded either by Company E or by an accredited 3rd party laboratory.

A carbon nanotube is a sheet of graphene having a thickness equal to one atom, rolled up into the shape of a tube (Figure 1). The sp^2 bonds located at the apex of graphene's hexagonal-shaped lattice structure are very strong, providing extreme tensile capacity and a unique set of benefits to concrete (Zhang et al 1). The aspect ratio is the ratio of length to diameter and plays a large role in the CNT's effectiveness. Company E's multi-walled CNTs vary in size, with a range of diameters and lengths creating a bell-shaped distribution of aspect ratios. Using transmission electron and helium ion microscopy, the diameter of Company E's CNTs have been measured at $\approx$ 20 - 100 nm, and lengths ranging from $\approx$ 80 – 40,000 nm. Based upon the above measurements, potential aspect ratios range from 4 – 2000, with a concentration around 40 (50 nm diameter, 200,000 nm length). For the purposes of concrete, Company E's researchers believe a range of CNT aspect ratios are more effective for improving concrete performance than CNTs having a uniform dimension. Using a combination of aggregate sizes is more effective than a single diameter of rock in densifying the hardened cement paste matrix; the same theory has been applied to the range of CNT aspect ratios in concrete.

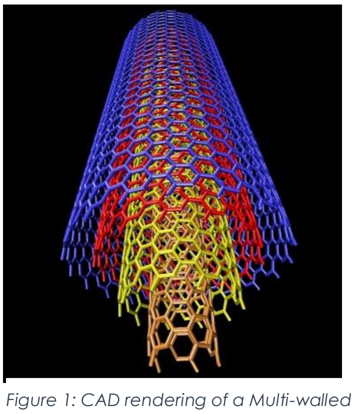


Figure 1: CAD rendering of a Multi-walled Carbon Nanotube

When effectively dispersed in concrete, CNT's function as Nano-sized pieces of carbon reinforcement, providing nucleation sites for cement hydration. In figure 2, the cement that has hydrated onto the surface of a carbon nanotube displays a dimpled surface, and shaded red for easier viewing at 75,000 x magnification. The hydration of cement onto the CNTs provides increased strength to the hardened cement paste matrix (Rashad 2). Carbon nanotubes are only 17% the weight of steel, more than 100 - 300 times stronger in tensile capacity than 60 ksi steel, and non-corrosive (Chang et al 3). Like macro fibres, the shape of CNTs help them improve the mechanical performance of concrete, including shrinkage and resistance to crack propagation (Metaxa et al 4). Unlike macro fibres, however, CNTs improve the strength and abrasion resistance of concrete. In many cases, the improved strength provided by CNT additives may allow for a reduction in total cementitious of the mix. Additionally, CNT additives have been shown to improve concrete durability by reducing permeability, which is important in combatting freeze/thaw and reducing scaling from de-icer chemicals placed by the DOT in winter conditions.

Figure 2: Helium-Ion Microscopy Image Eden Innovations CNT (75,000 x mag)

2.0 DISCUSSION

2.1 Australian project review– precast trial

Various Precast elements are subjected to harsh water, sewerage and drainage damage, caused by their environment. With an objective to increase the overall durability of their precast elements, by increasing the abrasion resistance, decreasing the permeability, whilst maintaining strength and workability, this Precast company conducted an in-house trial in Q2-2019. Their local ready-mix supplier agreed to take part in the trial, dosing the CNT additive at the concrete plant, prior to supplying the concrete to the Precast yard.

The concrete was a designed S50, ternary blend, spreadable precast mix, at a target 0.33 w/c. A total of 3 x 4m^3 loads were delivered during the trial. At a standard overhead batch plant, the concrete was batched, the cement wet out, holding back a 1:1 ratio of tail water to CNT additive dose, per m^3. The CNT additive was then dosed into truck. The truck was spun ~70 revolutions (3 minutes) before then slumping the load, prior to traveling an approx. 20 minutes to the precast yard. Dosing details, some design targets and actual results are listed in Table 1.

Table 1. Concrete Mix Details (2.1)

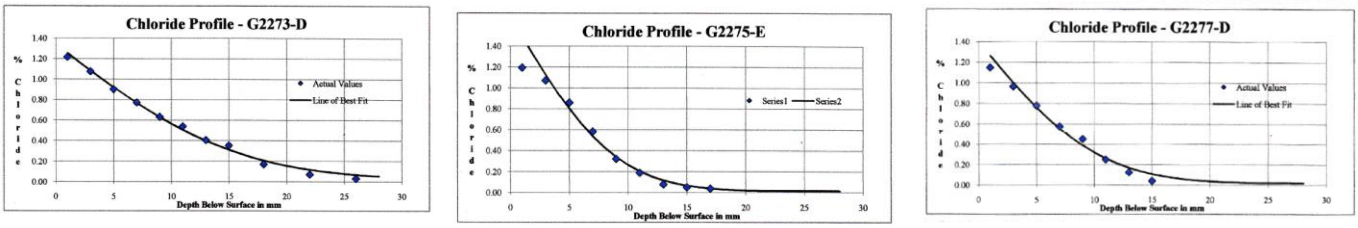
		Reference	**2.5L/m^3**	**5L/m^3**
w/c Target		0.33	0.33	0.33
w/c Actual		0.33	0.41	0.33
Slump Targets		650-720	650-720	650-720
Slump Actuals		680	650	740

Important attributes of plastic concrete for precast placement applications are flowability and workability. During the trial the precast company closely monitored the plastic concrete properties to ensure, at minimum, the addition of the CNT additive maintained the same flowability and workability, when compared to their reference mix. Table 3 shows the spreadable slump targets were met. The results in Table 3 indicate that the 3rd load with 5L/m^3 of the CNT additive, increased the water reducing properties and may have enabled further water cut during batching.

During placement other observations and comments made by the precast company were - *"plastic properties are a thicker concrete that remains spreadable and has an increased* *workability". "Looks really good, it's better than the normal stuff". "It's visually and physically thicker and not sticky"* Refer Figure 3.

Figure 3: Concrete with CNT additive, measuring the spread during the slump flow test

Testing was contracted by a 3rd party approved laboratory, to verify compressive strength to AS 1012.9:2014 conformance to 56 days and Determination of Chloride Ion Diffusion Coefficient, Nordtest Method NT Build 443 1995-II. Like the plastic properties, the precast company expected the compressive strength to be ≥ to the reference load and a decreased permeability, to reduce moisture/chloride ingress and increase the durability of the precast elements. Figure 4 indicates the effective chloride transport coefficient, *De,* stated to two significant digits in m²/s. The results indicate that the concrete loads dosed with the CNT additive both resulted in a significant reduced Chloride Ion Diffusion Coefficient when compared to the reference.



Reference:

D_e = 2.38E-11 m^2/s and 2.45E-11 m^2/s

CNT Additive: 2.5 L/m^3 :

D_e = 8.00E-12 m^2/s and 1.09E-11 m^2/s

CNT Additive: 7.5 L/m^3 :

De = 1.09E-11 m²/s and 1.10E-11 m^2/s

Figure 4: Determination of Chloride Ion Diffusion Coefficient, Nordtest Method NT Build 443 1995-II

Whilst the high early strength (HES) was slightly lower at days 1 and 3 with use of the CNT additive, the Compressive strength at 28 days was increased ~7MPa at 28 days and continued to increase to ~10mpa at 56days with use of the CNT additive. Refer Table 2.

Table 2: Compressive Strength results AS 1012.9:2014 (2.1)

Hardened Properties	Day	Reference	2.5L/m³	5L/m³
MPa	1 Day	20	19.5	17
MPa	3 Day	41.5	38	38
MPa	11 Day	57	60	59
MPa	28 Day	67	74.5	74.5
MPa	56 Day	73.5	83.25	81.25

2.2 Extended Design Life

Our industry continues to strive for increased Durability of concrete in various types of concrete structures, to extend the life of our valuable assets, whilst delivering a more sustainability solution. We continue to see concrete loads dosed with the CNT additive, in various concrete mix designs, reduce the Chloride Ion Diffusion Coefficient when compared to the reference. In May 2020 a laboratory trial was conducted in Brisbane, to determine performance results prior to a field trial. The mix was a Ternary blended mix with a total cementious of 526kg/m³, at a ratio of 55% OPC, 25% flyash and 20% slag, and a w/c of 0.37. Compressive strength of the CNT additive dosed concrete mix at 5L/m³, achieved a 10% increase when compared to the control mix. The testing program included AS 1012.9:2014 conformance to 56 days and Determination of Chloride Ion Diffusion Coefficient, Nordtest Method NT Build 443 1995-II.

The Chloride Ion Diffusion Coefficient results of both the control mix and the CNT additive dosed trial mix, were inputted into the LIFE-365 service life prediction model. This program enables various environment conditions to be chosen too, as part of the service life prediction, as indicated in the Figures 4 and 5.

Figure 4 indicates a 'Parking Garage' condition environment. This references the level of its corrosive environment. The results in Figure 4 indicate an increase of predicted total service life of ~19 years for the CNT additive dosed concrete when compared to the control mix. In addition, the reduction in repair cost prediction over a 100 year period is 67.3%.

Diffusion Properties and Service Lives

Alt name	D28	m	Ct	Init.	Prop.	Service life
Control	-> 1.12E-12 m*m/sec	-> 0.2	-> 0.08 % wt. conc.	65.2 yrs	-> 6 yrs	**71.2 yrs**
EX HC @ 5L	-> 7.70E-13 m*m/sec	-> 0.2	-> 0.08 % wt. conc.	84.4 yrs	-> 6 yrs	**90.4 yrs**

Figure 4: Control mix vs. concrete with CNT additive Chloride Ion Diffusion Coefficient results and total service life prediction in a 'Parking Garage' environment.

Figure 5 indicates a 'Marine Spray Zone' condition environment. This references a higher level of a corrosive environment. The results in Figure 5 indicate an increase of predicted total service life of >20 years for the CNT additive dosed concrete when compared to the control mix. In addition, the reduction in repair cost prediction over a 100 year period is 41.3%.

Diffusion Properties and Service Lives

Alt name	D28	m	Ct	Init.	Prop.	Service life
Control	-> 1.12E-12 m*m/sec	-> 0.2	-> 0.08 % wt. conc.	47.3 yrs	-> 6 yrs	**53.3 yrs**
EX HC @ 5L	-> 7.70E-13 m*m/sec	-> 0.2	-> 0.08 % wt. conc.	68 yrs	-> 6 yrs	**74 yrs**

Figure 5: Control mix vs. concrete with CNT additive Chloride Ion Diffusion Coefficient results and total service life prediction in a 'Marine Spray Zone' environment.

2.3 USA project review - Stormwater drainage in townhome facility (USA)

Figure 6: Concrete Company X Project – Town home Drainage System May 2015 (Left), December 2017 (Right)

In May 2015, Company E collaborated with Concrete Company X, a Denver contractor who was interested in evaluating the CNT additive in the expansion of a residential town home community. The evaluation included a new concrete system for directional flow of stormwater runoff within the asphalt parking and common areas (see figure 6).

These areas are exposed to abrasive conditions from surface water flow, passenger vehicles, and commercial vehicles such as snow plows and garbage trucks. Exposure to de-icer chemicals and waste in refuse areas was also a challenge. Within the same community, the concrete for the existing town homes had developed severe pitting from de-icer chemicals, abrasion from vehicles, and cracking in many places due to heavy loads. The project was slated to need approximately 10 cubic yards of concrete. To accommodate the

comparison, the placement was split across two 5-yard trucks and spaced at 45 minutes. The evaluation involved a five-yard load of concrete containing the CNT additive at a dosage equal to 8.3 L/m^3 of concrete, compared to a five-yard load of concrete not containing the additive, referred to as the reference. The reference and the sections containing the CNT additive were placed end to end in the newly added section of the facility, to provide identical in-service conditions during the evaluation. The goal was not to improve strength, rather it was to improve the in-service performance of the concrete after exposure to stormwater runoff and de-icer chemicals, combined with abrasion from concentrated vehicle traffic. Lab testing included split-tensile testing per ASTM C496, and abrasion resistance according to ASTM C779, proc. C.

Results from lab testing confirmed the CNT additive's ability to improve the split-tensile strength and resistance to abrasion by approximately 22% and 40%, respectively. At the end of the 20-minute test, it should be noted that test samples were abraded to a depth equal to the depth measured for reference samples after only the first 3 minutes of the test. The test program in the lab indicated that adding the CNT additive significantly improves the concrete's resistance to abrasive wear. Test results are summarized below in table 3.

Table 3: Concrete Company C Project – Town home Drainage – Laboratory Test Results (2.3)

Property and Test Standard	Reference	CNT Additive	% Improvement with CNT Additive
Abrasion Resistance (ASTM C779, proc. C)	2.8 mm	1.27 mm	~ 40%
Split-tensile Strength (ASTM C496)	2.45 mpa	2.83 mpa	~ 22%

Figure 7: Concrete Company C Project – Town home Drainage (December 2017; 31-months old); Reference (Left) and CNT Additive (Right)

Results from the concrete placed in the field demonstrate a familiar story. Relative to the reference, the sections containing the CNT additive performed significantly better than the reference from the abrasive wear created by water flow and passenger/commercial service vehicles. After 31-months in service, figure 7 shows the reference stained and pitted from de-icer chemicals, also showing signs of deterioration from snow plows and traffic. The sections containing the CNT additive were uncracked, less abraded, and in significantly better shape than the reference. The additive has helped the concrete to maintain a brighter albedo, and minimal staining or pitting from chemicals. The texture from the broom finish has diminished on the reference but is still intact on the test sections containing the CNT additive. It is anticipated that the use of the CNT additive in applications exposed to these conditions will extend the service life and reduce the maintenance schedule, ultimately increasing the customer's return on investment (ROI) and minimizing disturbances to residents for repair work.

3.0 CONCLUSION

For the projects presented herein, lab results and field performance have confirmed the ability of CNT additives to improve the durability and service life of concrete. From roadway applications and hardstand areas subjected to extreme impact, point, and rolling loads, to residential driveways and light – heavy commercial slab construction, a growing number of applications support the conclusion that using this CNT additive enhances concrete performance. Whether it is durability, strength, rheology, provides sustainability opportunities by potentially reducing the carbon footprint with reduced GP cement use. and/or material and labour costs, projects using this CNT additive continue to demonstrate superior performance against traditional concrete. It is understood that relatively speaking, the placements using CNT additives are young. However young, the benefits shown to date are extremely impressive and support their continued use and evaluation to fully understand the extent to which they improve concrete.

References

1. Zhang, Zhenhua et al. "All-carbon sp-sp2 hybrid structures: geometrical properties, current rectification, and current amplification." *Scientific reports* vol. 3 (2013): 2575. doi:10.1038/srep02575
2. Rashad, Alaa. (2017). Effect of carbon nanotubes (CNTs) on the properties of traditional cementitious materials. Construction and Building Materials. 153. 81-101. 10.1016/j.conbuildmat.2017.07.089.
3. Chia-Chi Chang, I-Kai Hsu, Mehmet Aykol, Wei-Hsuan Hung, Chun-Chung Chen, and Stephen B. Cronin. "A New Lower Limit for the Ultimate Breaking Strain of Carbon Nanotubes" *ACS Nano* 2010 *4* (9), 5095-5100DOI: 10.1021/nn100946q
4. Metaxa, Zoi S., et al. "Carbon nofiber–Reinforced Cement-Based Materials." *Transportation Research Record*, vol. 2142, no. 1, Jan. 2010, pp. 114–118, doi:10.3141/2142-17.
5. Design life Software at: http://www.life-365.org/