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# Coupling effect of salt freeze-thaw cycles and cyclic loading on performance degradation of carbon nanofiber mortar

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ABSTRACT

This paper aims to investigate the coupling effect of salt freeze-thaw cycles and cyclic loading on weight loss, relative dynamic elasticity modulus and electrical resistance degradation of carbon nanofiber mortar. Three types of salt solutions with NaCl concentrations of 0%, 1.5% and 3.0% were adopted and two freeze-thaw temperatures cycles were carried out at −10 °C ~ 10 °C and −20 °C ~ 20 °C respectively. Cement mortars with water to cement (w/c) ratios of 0.5, 0.45, 0.4 and 0.35 were prepared by incorporating carbon nanofibers (CNFs) with 2.25% of cement volume. On the other hand, cyclic loading was applied to selected specimens before the freeze-thaw cycle test. Experimental results show that all specimens behaved little mass loss after exposure to the salt freeze-thaw cycles under temperature of −10 °C ~ 10 °C and a significant mass loss was induced by the freeze-thaw cycles in 1.5% NaCl and 3.0% NaCl solutions with temperature of −20 °C ~ 20 °C. On the other hand, no visible difference can be detected for the electrical resistance variation and the relative dynamic elasticity modulus under the two freeze-thaw temperatures for every salt solution. The cyclic loading treatment had an accelerating degradation of cement mortar induced by the salt freeze-thaw cycles. The electrical resistance increase of carbon nanofiber mortar reveals a similar tendency to the relative dynamic elasticity modulus loss. Therefore, carbon nanofiber mortar behaves a potential self-sensing performance for salt freeze-thaw cycles induced damage.

## 1. Introduction

Concrete as a construction material is widely used in many climate regions such as extremely cold environments, terrible hot regions, oceans, frequent earthquake prone areas and other disaster areas. The reliability of civil structures built by concrete is relatively low due to the complex application environment. For the purpose of hazard mitigation, reinforcement and maintenance, it is significant to monitor the damage of concrete structures (Kordell et al., 2017). The intrinsic self-sensing concrete provides a new sensing tendency for health monitoring of concrete structures. This type of concrete is normally fabricated by some conductive fillers with high conductivity such as carbon fibers, carbon nanotubes and carbon nanofibers (CNFs) (Chen and Chung, 1996; Konsta-Gdoutos and Aza, 2014; Sun et al., 1999). The intrinsic self-sensing concrete (ISSC) can monitor damage, displacement, stress and strain by the fractional variation of electrical resistance without any other sensors (Wang et al., 2017; Hammel et al., 2004).

CNFs are elegant engineered functional fillers with hollow cylinders. The diameters of CNFs are around 100 nm and their lengths are a few microns. Being compared with carbon nanotubes (CNTs), CNFs show numerous exposed edge planes along the surface, which are advantageous to chemical or physical interaction. Moreover, CNFs are produced at a lower cost than carbon nanotubes (CNTs) (Konsta-Gdoutos and Aza, 2014). Some researchers reported that CNFs cement-based materials behaved a good self-sensing ability (Wang et al., 2017; Hammel et al., 2004), being able to well responds to the applied stress, strain and damage by recording electrical resistance (Hammel et al., 2004). Furthermore, CNFs cement-based material provides a possible method for diagnosing the damage status of concrete structures exposed to environmental or/and mechanical loading damage. This diagnosed result provides a reliable basis for selecting reasonable rehabilitation or repairing plans (Li et al., 2017).

When being applied to constructions in northern regions of China, CNFs cement-based materials will have to undergo freeze-thaw (F-T) cycles. Moreover, a real concrete structure always works under mechanical loads including its self-weight action. On the other hand, concrete structures in the pavement system are exposed to salt freeze-thaw conditions due to the application of deicing salts in winter or

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marine environments (Shi et al., 2010; Fabbri and Fen, 2006). The coupling effect of mechanical load, salt and free-thaw cycles leads to an accelerating deterioration for cement concrete materials (Fabbri and Fen, 2006). The freeze-thaw cycles may result in the acceleration of inner damage of concrete and ion concentration variation of pore solution (Shi et al., 2010). The conductive performance of CNFs cement-based materials depends on ionic conduction, electric phenomena, electric polarization and macroscopic tunneling effect (Sun et al., 1998). Therefore, the conduction of CNFs cement-based materials varies with freeze-thaw cycles (Gao et al., 2015). Consequently, the evolution of electrical resistance of CNFs cement-based materials can provide some information about the freeze-thaw cycles induced damage of concrete structures, which is seldom reported.

Many methods were used to investigate the damage evolution of concrete with freeze-thaw cycles (Tang and Petersson, 2004; UNE-CEN/TS 12390–9:2008 EX., 2008; Molero et al., 2012). The external damage is evaluated by mass loss, whereas the internal damage is usually evaluated by some nondestructive testing technologies such as ultrasonic measurement, nuclear magnetic resonance and electrical methods (Setzer et al., 2001; Wang et al., 2013; Ding et al., 2013). Of which, the relative dynamic elasticity modulus is the most popular one due to the satisfactory reliability and repeatability.

This paper aims to investigate the coupling effect of salt freeze-thaw cycles and mechanical loading on the degradation of CNFs mortars. CNFs added mortar specimens were prepared with four different water to cement ratios. Freeze-thaw cycles were performed in three NaCl solutions with temperature of −10 °C ∼ 10 °C and −20 °C ∼ 20 °C respectively, and cyclic loading was applied to selected samples before the freeze-thaw test. The evolution of mass loss, relative dynamic elasticity modulus (*RDME*) and electrical resistance were monitored for evaluating the degradation of mortar samples with different freeze-thaw cycles.

## 2. Experimental

### 2.1. Raw materials

The PR-19-XT-LHT-OX CNFs with a density of 2.1 g/cm$^3$ supplied by the Pyrograf Products, Inc. were used in this research. The surface of CNFs was treated with oxidizer by producers for easily dispersing in cement matrix. This type of CNFs shows the average diameter of 149 nm and the average length of 19 μm. Ordinary Portland cement was used as cementitious material in this research. The strength grade of the cement is 42.5 MPa in accordance with Chinese standard GB175-2007 (2007). River sand was used as fine aggregate with a fineness modulus of 2.82. The flowability of fresh cement mortar was adjusted by adding a polycarboxylate-based, high-range water-reducing agent (SP), which has a solid content of 40% and water reduction of around 30%.

### 2.2. Mixing proportion and specimens preparation

Previous studies presented that the damage self-monitoring performance was very weak for cement mortars when the dosage of CNFs was lower than 2.25% of cement volume (Wang et al., 2017; Molero et al., 2012; Setzer et al., 2001; Wang et al., 2013). This can be attributed to the large distance between CNFs that caused electrons difficult to transit. Consequently, tunneling current in cement mortar was hard to form (Wang et al., 2017; Ding et al., 2015; Ding et al., 2013) and CNFs mortar could not present self-sensing property. Therefore, the CNFs content was selected as 2.25 vol% of cement volume in this study. To obtain a suitable flowability (around 180 mm) which is very important to the dispersion of CNFs (Wang et al., 2017), the water-reducing agent was added by 1.0%, 1.5%, 2.5% and 3.0% for mixtures with w/c ratios of 0.5, 0.45, 0.4 and 0.35 respectively. The mixtures with different water-cement ratios were labelled as w/c-0.35, w/c-0.4, w/c-0.45 and w/c-0.5 respectively. For all mixtures, the mass ratio of sand to cement was kept at 2.5. The mixing proportion of CNFs mortar is shown in Table 1.

**Table 1**
Mixing proportion of cement mortar.

| No. | Cement | Water | CNFs (vol% of cement) | SP (wt% of cement) | Sand |
|---|---|---|---|---|---|
| w/c-0.35 | 1 | 0.35 | 2.25 | 1.0 | 2.5 |
| w/c-0.4 | 1 | 0.4 | 2.25 | 1.5 | 2.5 |
| w/c-0.45 | 1 | 0.45 | 2.25 | 2.5 | 2.5 |
| w/c-0.5 | 1 | 0.5 | 2.25 | 3.0 | 2.5 |

The water-reducing agent was mixed uniformly in water and then CNFs were added for a 3 min high speed stirring operation to obtain a homogeneous solution. A Hobart A200C (I.T.W. Inc., Chicago, America) planetary mixer was used to prepare fresh mortars with the same procedure. Firstly, the weighed cement was added into the prepared solution containing CNFs for 3 min mixing at a low speed of 140 ± 5 rpm. Secondly, the sand was added for another 3 min mixing at a high speed of about 285 ± 10 rpm until the homogeneous fresh mortar mixtures were obtained. Due to the dispersing effect of water-reducing agent and a suitable rheological performance of fresh mixture, CNFs reached a good dispersion in mortar samples that was confirmed by the low variability coefficient of resistivity (lower than 0.05) in every group of specimens (Wang et al., 2017).

Prismatic specimens with size of 35 × 35 × 55 mm were prepared immediately after the mortar mixing procedure was completed. A concrete vibrating table was used to facilitate the compaction and decrease the air bubbles in specimens. The specimens in molds were sealed by plastic sheets for 2 days storage at room temperature and then were demolded. The demolded specimens were cured in a fog room with temperature of 20 °C and relative humidity of above 95% for another 22 days.

In this study, six freeze-thaw exposure conditions were designed for mortar specimens as illustrated in Table 2. Specimens were immersed in tap water, 1.5% NaCl solution and 3.0% NaCl solution for 4 days respectively and then exposed to freeze-thaw cycles in these solutions with temperature of −10 °C ∼ 10 °C and −20 °C ∼ 20 °C respectively. On the other hand, load-unload cycles from 0% to 30% of the ultimate compressive strength were applied to selected samples for researching the coupling effect of cyclic loading and freeze-thaw damage. The freeze-thaw test was carried out in accordance with Chinese Standard GB/T 50082-2009 (2009). Every specimen was placed in a rubber tube in the rapid freeze-thaw testing machine. The rubber tubes were filled with different medium (0, 1.5% and 3.0% NaCl solution) and were covered by plastic sheets to avoid water evaporation.

### 2.3. Measurement methods

Electrical resistivity measurement was performed on 3 specimens for each group by using the embedded two-pole layout method with an AC voltage of 1 V and frequency of 10 kHz. AC electrical resistance was determined along the longitudinal axis direction of prsim. The electrodes were perpendicular to the longitudinal axis of specimen and the

**Table 2**
Freeze-thaw conditions.

| No. | Cyclic stress level accounting for axial compressive strength | NaCl concentration |
|---|---|---|
| M1 | 0 | 0 |
| M2 | 30% | 0 |
| M3 | 0 | 1.5% |
| M4 | 30% | 1.5% |
| M5 | 0 | 3% |
| M6 | 30% | 3% |