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Short communication

Influence of carbon nanofiber content and sodium chloride solution on the stability of resistance and the following self-sensing performance of carbon nanofiber cement paste

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ABSTRACT

This paper aimed to study the influence of carbon nanofibers (CNFs) content and sodium chloride solution on the stability of the electrical resistance and the following self-sensing performance of CNFs cement paste. CNFs content ranged from 1.5% to 3.0% by the volume of cement. The electrical resistance and capacitive reactance of specimens were tested. AC voltage was applied to the dried or NaCl immersed specimens. While, DC voltage was supplied to dried specimens as contrastive group. Additionally, the piezoresistivity of dried samples was investigated. Results indicated that the capacitive reactance of drying specimens increased obviously with the increasing CNFs dosages. However, the capacitive reactance kept stably with the increasing CNFs content after the specimens were immersed in NaCl solution. While, the resistivity of the samples decreased obviously with the increasing CNFs content both in drying state and immersion in NaCl solution. The capacitive reactance was increased and the electrical resistivity was decreased after immersing in NaCl solution. The stability of electrical resistivity of drying specimens was decreased by increasing the dosages of CNFs. Meanwhile, the stability of electrical resistivity of specimens after disposed in NaCl solution first decreased then increased with the increasing CNFs content. The resistance of specimens determined by AC voltage was more stable than that tested by DC voltage. No obvious self-sensing performance was observed, when CNFs content was less than 2.5%. Additionally, CNFs cement paste presented the highest sensitivity of self-sensing performance when CNFs content was 2.5%.

1. Introduction

As a widely used construction building material, concrete has been produced and put into use for many years. In recent years, various kinds of functional concrete has been invented, such as self-sensing concrete, self-healing concrete, electromagnetic shielding concrete, thermal insulation concrete et al [1–4].

Intrinsic self-sensing concrete is proposed by Chung for more than 20 years [1]. This kind of concrete is manufactured by mixing some functional fillers like carbonic fillers and metal fillers in the matrix. The conductive fillers added in the concrete

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are effective to improve the conduction of composite. The conductivities of some functional materials are extremely significant for various functional applications such as health monitoring, electrothermal effect, cathodic protection and electromagnetic shielding performance [5–10].

Recently, nano functional cement-based materials are hot researching topics that attracted the interest of many researchers [11–15]. Kim et al [16–18] pointed out that carbon nanotubes (CNT) and nano carbon black (NCB) are both found to be able to modify the mechanical properties, durability and self-sensing properties of cement-based materials due to their excellent intrinsic properties and composite effects. In Han's papers [19,20], carbon nanotube/nano carbon black and graphene oxide composite fillers reinforced cement-based materials presented good piezoresistive performance when monotonic compressive loading and cyclic compressive loading were applied. Moreover, cement-based materials with carbon nanofibers (CNFs) can be self-sensing under different loading methods and different application environment [7,21].

Carbon nanofibers (CNFs) are excellent functional fibers. These fibers with their modified surfaces by oxidizer are easily dispersed in cement matrix [22]. Moreover, this kind of carbonic fibers shows excellent conductivity, tensile strength and toughness. Therefore, CNFs are effective to improve the conduction and increase the strength of CNFs cement-based composites [23]. CNFs cement-based materials with excellent conductivity and mechanical properties can show specific functional performance [24]. CNFs disperse more uniformly in cement matrix than carbon fibers (CFs) [22]. Besides, CNFs show fewer inner defects than CFs. When being compared with carbon nanotubes (CNTs), CNFs present advantageous chemical or physical interaction due to numerous exposed edge planes on their surfaces [23]. Additionally, CNFs are much cheaper than CNTs. Moreover, CNFs present perfect corrosion resistance compared to metal fillers [23]. Due to the above advantages, CNFs may have an excellent prospect of making special functional concrete [22,23].

Concrete is a kind of porous heterogeneous material, which means the water content of concrete varied with the ambient humidity environment. Therefore, the ionic migration conduction, electric phenomena and electric polarization may lead to the instability of electrical signals [25]. As reported in many papers, high frequency alternating current (AC), the addition of silica fume and external compressive loading were proved to diminish the electric polarization thus resulting in decreasing the instability of electrical signals [14]. However, little attention has been paid to the influence of CNFs content and the salt solution on the stability of electrical signals of CNFs cement paste.

The capacitive reactance, electrical resistance, electrical resistance-time curves and self-sensing performance of CNFs cement paste were determined in this research. Four CNFs dosages (1.5%, 2.0%, 2.5%, 3.0%) were selected in the experiment. Specimens were disposed in two environments (dried station and immersion in 3.5% NaCl solution for 4 days). Additionally, the self-sensing performance of CNFs cement paste was investigated in this research.

2. Experimental

2.1. Raw materials

The type of CNFs applied in this study was PR-19-XT-LHT-OX CNFs. It was produced by the Pyrograf Products, Inc. (United States) with the density of 2.1 g/cm^3. The average diameter and length of CNFs are 149 nm and 19 μm respectively. CNFs dispersed uniformly in cement-based materials by treating their surfaces with oxidizer. Ordinary Portland cement (Harbin Yatai Cement Co. Ltd., China) with the strength grade of 42.5 MPa was used as binder materials [26,27]. Polycarboxylate-based, high-range water-reducing agent (SP) was added to adjust the flowability of fresh cement-based materials to around 200 mm. This slump flow is very important to the dispersion of CNFs [22]. Prior studies [22,28] pointed out that the percolation CNFs concentration was 2.25 vol. % of cement. In this paper, two CNFs concentrations of 1.5% and 2.0% (bellow percolation threshold) were selected. Moreover, CNFs concentration of 2.5% (in the percolation zone) and CNFs concentration of 3.0% (close to the post percolation zone) were selected as well. Water-reducing agent was added by 0.3%, 0.6%, 0.8% and 1.0% for mixtures with CNFs contents of 1.5%, 2.0%, 2.5% and 3.0% respectively.

2.2. Mixing proportion and specimens preparation

The preparation of specimens making were carried out as follows:

Water-reducing agent, tap water and CNFs were put in a TDNJ-160A cement paste planetary mixer and mixed for 3 min at a velocity of 285 rmp for 2 min. After this procedure, cement was added and stirred at a speed of 140 rmp for 2 min firstly and then stirred at the speed of 285 rmp for the last 2 min.

The well-mixed fresh mixtures were poured into the oiled molds to form cuboid specimens. The size of the specimen was 20 mm × 20 mm × 25 mm. Finally, the fresh paste was compacted by artificial vibration after the mix was poured into the molds. The samples were sealed by plastic sheeting at room temperature for 2 days, and then they were demolded. After natural curing, all demolded specimens were cured at a standard fog room (95% RH, 20 ± 2°C) for another 26 days. 9 specimens were prepared for each group. After the standard curing, for each group, 3 specimens were dried in an oven of 60°C for 3 days, the remaining 3 specimens were immersed in 3.5% NaCl solution for 3 days.

2.3. Measurement

Capacitive reactance and electrical resistance were performed on TH2810D LCR digital electric bridge. Two-pole layout method was applied in the capacitive reactance and electrical resistance measurement. The TH2810D with AC voltage of 1 V and voltage frequency of 10 kHz was applied to determine the AC resistance.

Embedded electrodes (304 stainless steels meshes) with size of 2.5 cm × 1.8 cm and thickness of 0.8 mm were applied in the experiment. The space between two voltage poles was 2 cm. Additionally, 1 V DC voltage was provided to investigate the resistance-time curves of drying specimens.

A universal material testing machine (100 kN-loading capacity and displacement 0.5 mm/min-loading rate) was carried out for the compressive loading measurement (Fig. 1).

The loading rate of this experiment was 0.2 mm/min as shown. The piezoresistive measurement is shown in Fig. 2. The stress (σ) amplitude under monotonic loading was 10 MPa.

Each specimen should undergo preload of 0.2 kN to reduce the polarization effect before loading. The compressive strain of CNFs concrete was collected via two strain gauges. The strain gauges were stuck to the middle of two opposite sides of a specimen parallel to the stress axis. During the loading process, AC electrical resistance was simultaneously measured in the stress axis. The sampling rate of resistance, compressive loading and strain was about 2 times per second.

The fractional change in electrical resistance (*FCR*) can be given by:

$$FCR = \frac{R - R_0}{R_0} \tag{1}$$

Where R_0 is the initial resistance of the specimens before loading, R is the resistance during loading.

Fig. 1. Electrical resistance measurement.

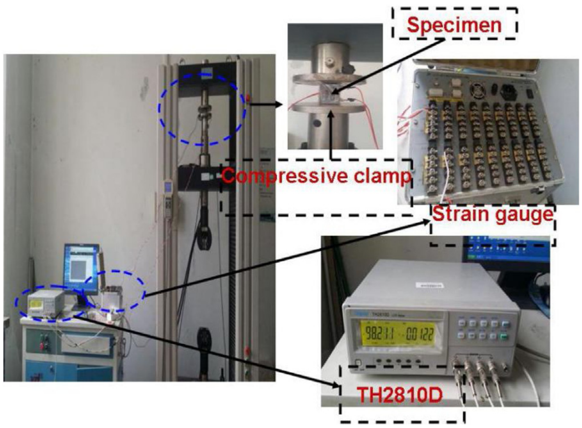

Fig. 2. The equipment for piezoresistivity measuring.

The gage factor (GF) was the fractional change on the resistance per strain unit. GF was calculated to assess the sensitivity of the self-sensing property. The GF is shown in Eq. (2) [29].

$$GF = \frac{FCR}{\varepsilon} \tag{2}$$

3. Results and discussions

3.1. Conductive performance

Figs. 3 and 4 show the capacitive reactance and electrical resistivity of drying CNFs cement paste and specimens after immersed in 3.5% NaCl solution as CNFs content ranged from 1.5% to 3.0%. When CNFs cement paste was in dried state, the capacitive reactance increased and the electrical resistivity decreased with the increasing CNFs dosages. However, when CNFs cement paste was in 3.5% NaCl solution, the capacitive reactance was kept at a value stably with the increasing CNFs dosage. Meanwhile, the electrical resistivity decreased obviously with the increasing CNFs contents. As CNFs cement paste was in dried state, electron conduction dominated the total conductive performance of CNFs cement paste. Additionally, the increased CNFs can provide many electric dipoles, leading to increasing the capacitive reactance of CNFs cement paste [30]. Therefore, the capacitive reactance of CNFs cement paste increased with the increasing CNFs content. While, the increasing dosages of CNFs can increase the amount of conductive particles. Consequently, the resistivity of dried specimens and the specimens immersing in 3.5% NaCl solution decreased with the increasing CNFs content.

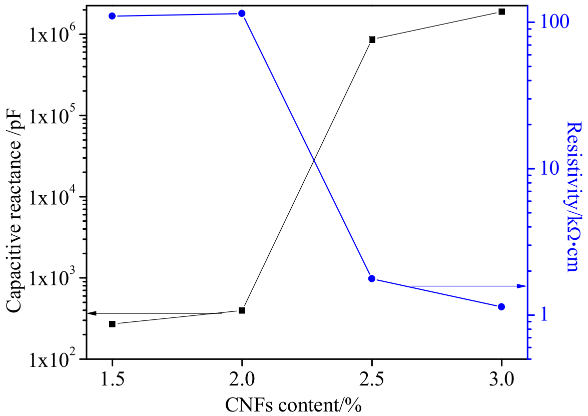

Fig. 3. Capacitive reactance and electrical resistance of drying CNFs cement paste.

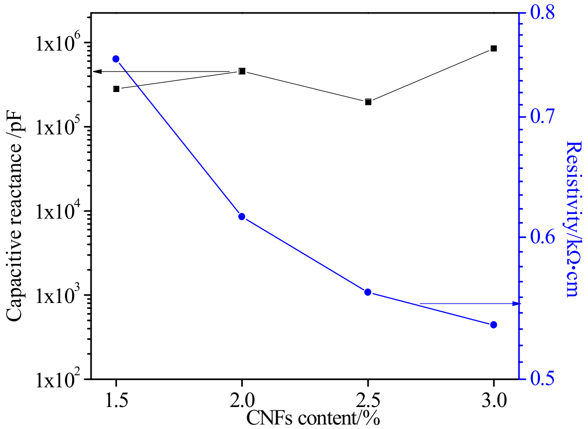

Fig. 4. Capacitive reactance and electrical resistance of CNFs cement paste immersing in 3.5% NaCl solution.

Additionally, when CNFs content was lower than 2.5%, the NaCl solution can increase the conductive free ions thus leading to more electric dipoles [30,31]. Therefore, the increased electric dipoles resulted in higher capacitive reactance when compared to the dried specimens. Moreover, due to the increased conductive free ions by NaCl solution, the electrical resistivity of specimens immersed in NaCl solution was lower than drying specimens. When CNFs content reached 2.5%, the capacitive reactance of specimens in the two states were almost the same.

3.2. Resistance evolution

Figs. 5 and 6 show the resistance evolution-time curves of drying CNFs cement paste and the specimens immersed in 3.5% NaCl solution for 4 days as CNFs content ranged from 1.5% to 3.0%. The maximum variation rate of resistance decreased from 3.0% to 0.015% when CNFs contents varied from 1.5% to 3.0%. The increasing CNFs dosages can increase the capacitive reactance of CNFs cement paste thus leading to higher reverse polarization electric field, therefore higher resistance variation may happen [30,31]. However, the conductivity of CNFs cement paste was improved by the increased CNFs content. Consequently, the free ions conduction was short circuited by strong electron conduction, so tunneling effect current dominated the conductivity of CNFs cement paste [31]. Therefore, the resistance kept stably with the increasing time.

As shown in Fig. 6 that the maximum variation rate of resistance of the specimens (immersed in NaCl solution) first increased and then decreased with the increasing CNFs content. The increased electric dipoles due to the increasing CNFs content might lead to the increased maximum variation rate of resistance [31]. However, higher electron conduction might lead to decreasing the variation rate of resistance by the short circuited ion conduction [32]. When CNFs content was 2.5%, the maximum variation rate of resistance of the specimens was the highest. Comparing to the dried specimens, the specimens immersed in NaCl solution performed higher variation rate of resistance, for the polarization effect was possibly increased by free conductive ions thus leading to the instability of electrical resistance [31]. Above all, the NaCl solution resulted in decreasing the stability of electrical resistance signals.

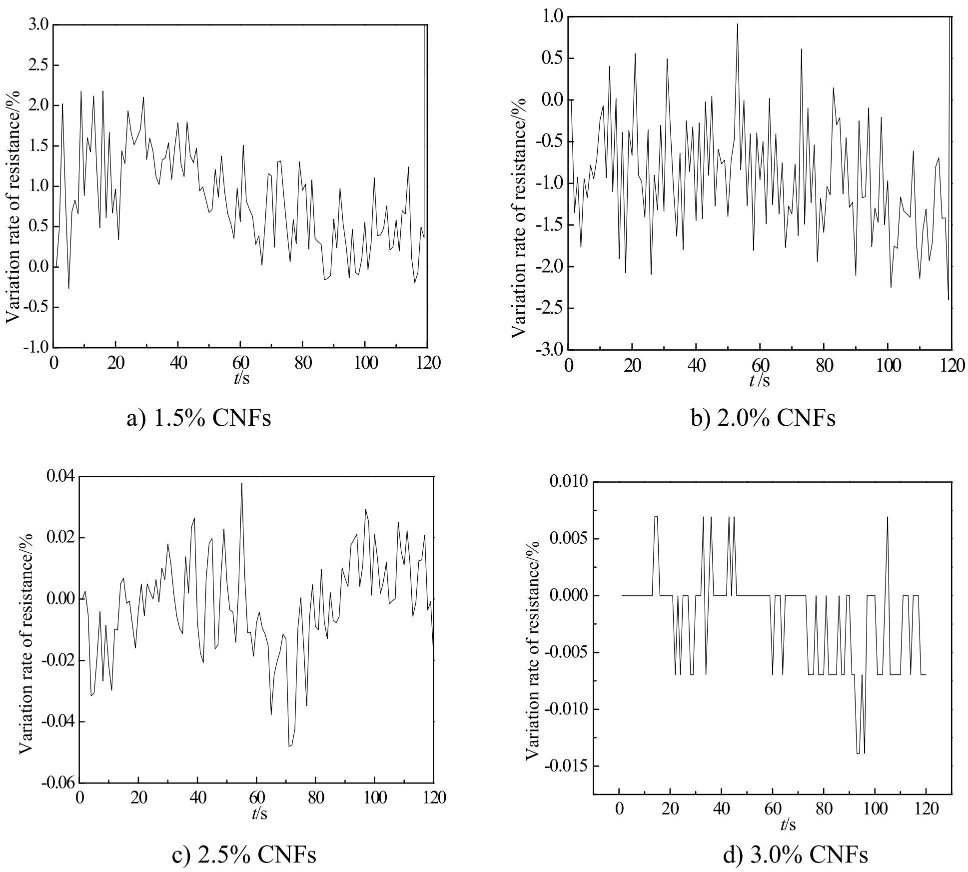

Fig. 5. Resistance-time curves of drying CNFs cement paste.

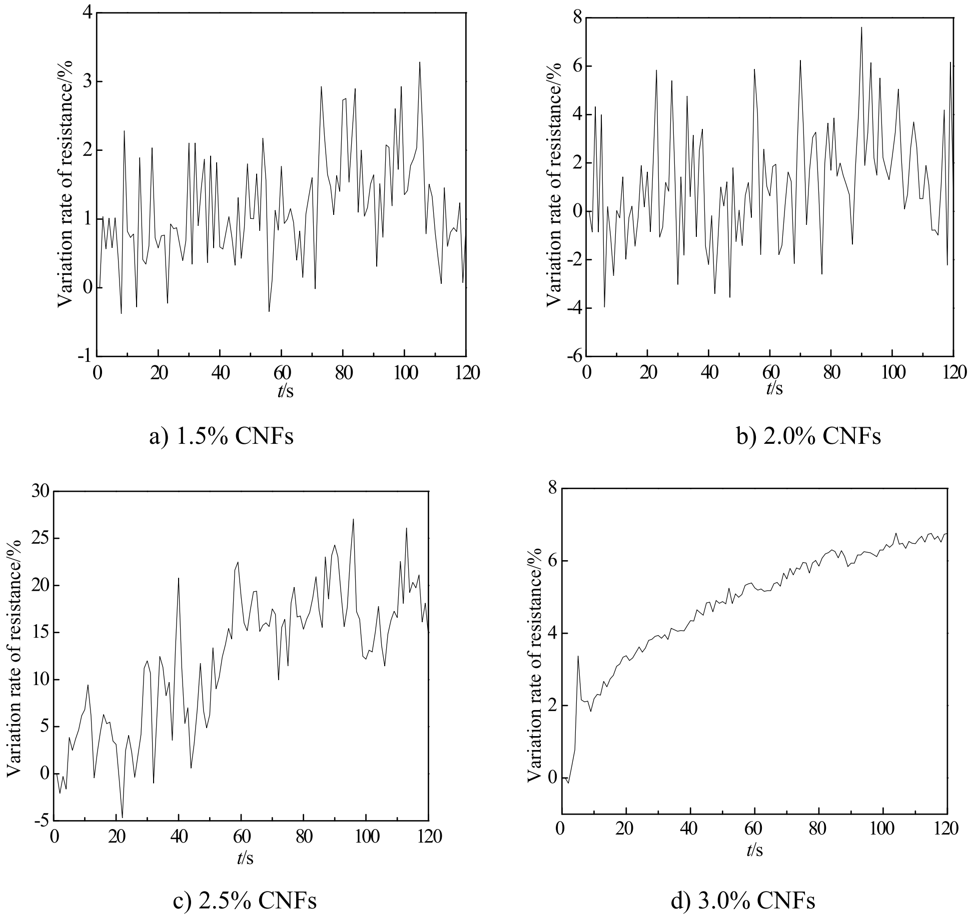

Fig. 6. Resistance-time curves of CNFs cement paste immersed in NaCl solution.

Fig. 7 shows the resistance evolution-time curves of drying CNFs cement paste determined by DC voltage. The resistance of the specimens increased obviously with the testing time when CNFs content were 1.5% and 2.0%. When CNFs content was 1.5% the variation of resistance of specimen was 160%. CNFs cement paste with 2.5% CNFs possessed the lowest variation rate of resistance. When compared to the drying specimens determined by AC voltage, resistance determined by DC voltage showed much higher variation rate of resistance. When AC current was used, the direction of voltage converted rapidly [12]. Therefore, the polarization was diminished by high frequency of AC voltage. Thus, the signals of AC resistance for specimens were more stable than that of the DC resistance.

3.3. The piezoresistive performance

From the researching results of Part 3.2, the electrical resistance of drying specimens was more stable than that of the specimens immersing in 3.5% NaCl solution. Resistance determined by AC voltage kept more stably with time than that tested by DC voltage. Therefore, drying specimens were selected to research the stress or strain self-sensing performance. AC voltage was applied to resistance determination.

Fig. 8 shows the stress self-sensing performance of drying specimens. When CNFs contents were 1.5% and 2.0% respectively, the electrical resistance behaved unsteadily for an axial compressive loading. This might be attributed to the excessive barriers between CNFs and the induced weak formation of tunneling current in cement paste that resulted in poor self-sensing performance [33]. However, when CNFs content were 2.5% and 3.0% respectively, obvious self-sensing performance was observed. While, when CNFs content was 2.5%, CNFs cement paste presented the most sensitive self-sensing performance. As CNFs content reached 2.5%, the tunneling effect played critical roles on the conductivity and piezoresistive properties [5,33]. Meanwhile, the contact resistivity between the CNF particles and cement decreased with the increasing loading [5]. When CNFs cement paste possessed 3.0% CNFs, only physical contact conduction of CNFs

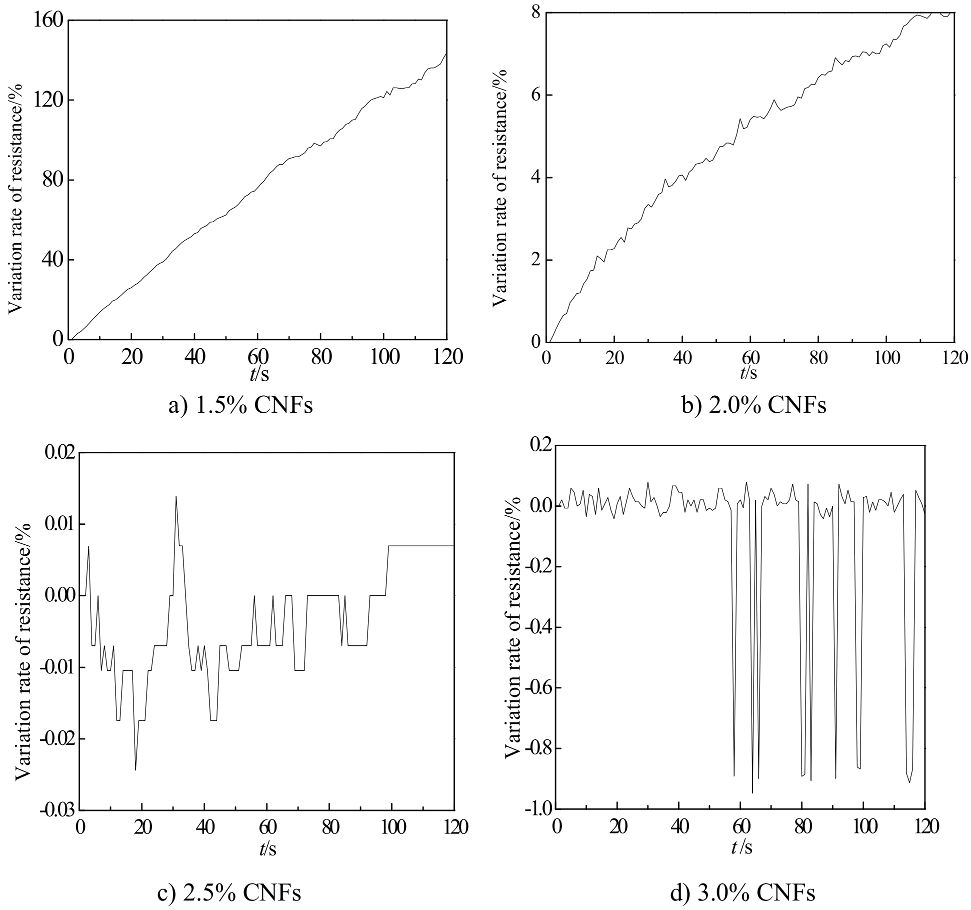

Fig. 7. Resistance-time curves of drying CNFs cement paste (tested by DC voltage).

dominated the conductivity and piezoresistive properties, therefore CNFs cement paste with 3.0% CNFs showed less self-sensing sensitivity than CNFs cement paste with 2.5% CNFs.

Fig. 9 illustrates the strain self-sensing curves of drying specimens with CNFs content of 2.5% and 3.0% respectively. The resistance of specimens decreased linearly with the increasing compressive strains. The GF of the specimens with 2.5% CNFs was 38.1, while the GF of the specimens with 3.0% CNFs was 15.4. Results further confirmed that the self-sensing performance of CNFs cement paste with 2.5% CNFs was more sensitive than that of specimens with 3.0% CNFs.

4. Conclusions

The following conclusions were obtained from the above experimental results.

1) The capacitive reactance of drying specimens increased obviously with the increasing CNFs dosages. While it kept stably with the increasing CNFs content after the specimens were immersed in the NaCl solution. The resistivity of specimens decreased obviously with the increasing CNFs content both in drying state and immersion in NaCl solution.
2) The capacitive reactance was increased and the electrical resistivity was decreased after immersing in NaCl solution. The stability of electrical resistivity of drying specimens was decreased by the increasing dosages of CNFs. Meanwhile, the stability of electrical resistivity of specimens after disposing in NaCl solution first decreased then increased with the increased CNFs content. The resistance signals of specimens determined by AC voltage was more stable than that tested by DC voltage.
3) No obvious self-sensing performance was observed, when CNFs content was less than 2.5%. Additionally, CNFs cement paste presented the highest sensitivity of self-sensing performance when CNFs content was 2.5%.

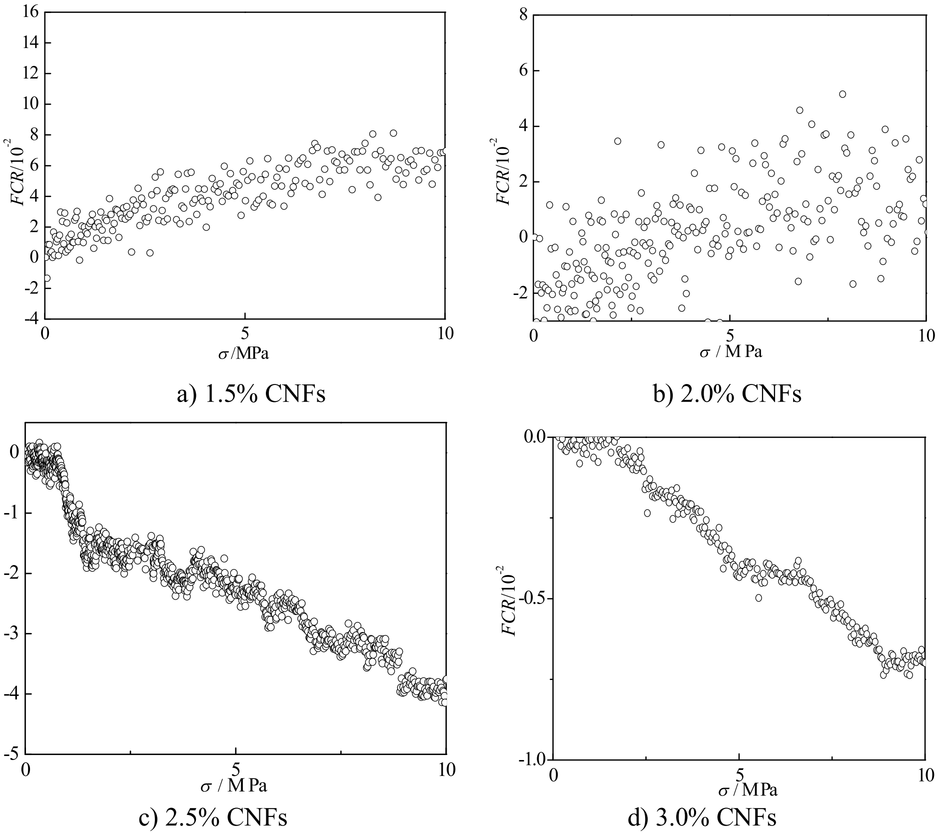

Fig. 8. Stress-sensing performance of drying specimens.

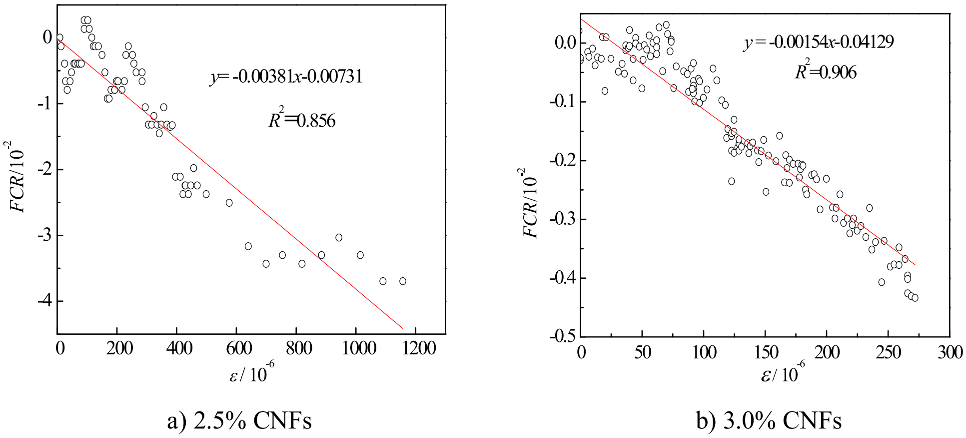

Fig. 9. Strain-sensing performance of drying specimens with 2.5% CNFs and 3.0% CNFs.

Conflicts of interest

The authors declare no conflict of interest.

Acknowledgements

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