The influence of AC and DC electrical resistance and piezoresistivity measurements of CNTs/cement composites

L. Coppola[1], A. Buoso[2] and F. Corazza[3]

ABSTRACT: In this paper data on electrical resistance on unloaded condition and pressure-sensitive behavior under different levels of compressive stress of cement paste specimens containing different percentages (0.1%, 0.25%, 0.50% and 1.0% vs. cement mass) of multi-walled carbon nanotubes are presented. AC and DC measurements of electrical characteristics of multi-walled carbon nanotube/cement composites unloaded or subjected to compressive stress were carried out by using two-probe configuration. Experimental results of DC test were affected by the electrode polarization. Therefore, DC method requires a pre-power time to let electrical resistance reach a stable value. On the contrary, the AC measurement can eliminate the effect of capacitor charging and discharging on the pressure-sensitive responses of MWNT/cement composites.

1 INTRODUCTION

Durability and health monitoring of concrete structures play an important role in civil engineering [Chen et al. 2011]. Actually, it's very important to study the possibility to build concrete structures able to evaluate their health. In particular, a smart-concrete has to be developed in order to guarantee a continuous monitoring of the stress level in structural elements with low costs.

Nanotechnology seems to offer some great opportunities for the development of new materials especially for construction engineering. In particular, the Carbon Nanotubes (CNTs) can be accounted as the most beneficial nano-reinforcement materials. CNTs have outstanding mechanical properties with a tensile strength of 63 GPa and Young's modulus of 1 TPa [Chen et al. 2011], in addition to high aspect ratio, small size and low density [Gopalakrishnan et al. 2011]. Regarding their electrical properties, carbon nanotubes have a very low resistance and, in addition, they can carry the highest current density of any known material, measured as high as 10^9 A/cm^2 [Khare and Bose 2005]. Consequently, the addition of carbon nanotubes to cementitious matrix should change dramatically electrical conductivity. The electrical conductivity of cement-based materials that is in a range from 10^6 to 10^9 Ω·cm, can be reduced incorporating conductive filler as CNTs [Pushparaj 2010]. Moreover carbon nanotubes can assign piezoresistivity to cement-based materials [Han et al. 2009], i.e. the electrical resistivity of cementitious composites reinforced with nanotubes changes with the stress conditions under static and dynamic loads to become a smart material, self-sensing [Azhari 2008]. In fact, CNTs present extraordinary piezoresistive properties: applying a load, the variation of electrical conductivity can reach 0.02 S/cm when change in compressive strain is 1.0% [Coppola et al. 2011].

The electrical and piezoresistive properties of CNTs cement composites depend on many factors: type and dosage of carbon nanotubes, quality of CNTs' dispersion, water content in the cement matrix, presence of aggregates, electrode type/set-up and the instruments used to evaluate electrical resistance and piezoresistivity of the nanocomposites.

[1] *Professor, University of Bergamo, Department of Engineering, luigi.coppola@unibg.it*
[2] *Assistant professor, University of Bergamo, Department of Engineering, alessandra.buoso@unibg.it*
[3] *CTG-Italcementi Group S.p.A, Bergamo, Italy*

This paper aims to study the influence of test instruments on electrical measurement using a two probe layout of cement pastes reinforced with CNTs.

2 MATERIALS AND EXPERIMENTAL WORK

2.1 Materials

An Ordinary Portland Cement (CE I 52.5 R) according to EN 197-1 provided by Italcementi Group S.p.A. was used in order to eliminate the influence of mineral addition (generally present in the standard cement available on the market) on electrical properties of cement paste. Chemical composition and principal physical properties of cement used are shown in Table 1.

Table 1. Specific surface area and chemical composition (% by mass) of the cement.

Loss On Ignition (L.O.I.) at 500°C	1.8
Specific surface area (m^2/kg)	392
SiO_2	20.6
Al_2O_3	4.0
Fe_2O_3	3.1
MgO	2.6
SO_3	3.1

Multi-Wall CNTs (MWNT) provided by Shenzhen NANO Tech. Port. Co. Ltd. (China) with average diameters in the range 10–30 nm were added to cement pastes. Their properties are given in Table 2.
Stainless steel gauzes with opening of 1.25x1.25 cm were used as embedded electrodes.

Table 2. Properties of multi-walled carbon nanotubes (CNTs).

External diameter [nm]	10 ÷ 30	Specific surface area [m²/g]	70 ÷ 90
Length[µm]	5 ÷ 15	Ash [%]	< 0.2
Purity [%]	> 95.0	Density [g/cm^3]	2.1
Amorphous carbon [%]	< 2.0	Electric Conductivity [S/cm]	$10^2 \div 10^{-4}$

2.2 Specimens preparation

The water/cement ratio was fixed at 0.60. In order to form a conductive network and investigate electrical properties, CNTs need to be fully dispersed in the cement matrix. In fact, CNTs tend to agglomerate and form nanotube clusters and bundles. In this research, Sodium Linear Alkyl Benzene Sulphonate – LAS (1.4×10^{-2} mol/l of concentration in water) was used [Coppola et al. 2011]. The surfactant was firstly mixed with water using a magnetic stirrer for 10 min. Then, MWNTs (0.1%-0.25%-0.5% and 1.0% by cement mass) were added into the aqueous solution and sonicated with an ultrasonicator for 2 hours to make a uniformly dispersed suspension. Then a mortar mixer was used to mix this suspension and the cement for 3 minutes. Finally a defoamer, tributyl phosphate, was added and mixed for another 3 minutes [Coppola et al. 2011].
Fresh cement composites were poured into steel molds (40x40x160 mm) immediately after the mixing. Two electrodes were embedded into the fresh cementitious mixtures at 4.0 cm apart.

Molds were stored at 20±2°C. All the specimens were demolded the day after the mixing, then marked, soaked into water at 20.0±1.0°C for 5 days, dried at a room temperature for 1 day and finally dried for 24 hours in oven at 30±2°C. Curing procedure was very important because it permits to reduce the water content in the matrix and, at the same time, to limit the development of shrinkage cracks. In fact, the water content in MWNT/cement composites is a key factor in influencing the piezoresistivity of composites. Generally speaking, the higher the water content the lower the resistivity and piezoresistivity of CNTs cement composites [Baoguo et al. 2010]. In the same way, also cracks in the specimens can influence the electrical measurement since they limit the current flow [Coppola et al. 2010].

2.3 Measurements

Electrical resistance was measured on unloaded specimens and then in the compressive stress direction perpendicular to electrodes under repeated compressive loading cycles. First the electrical resistance was measured by the two-probe set-up using a digital multimeter (*Keithley, model 2001*) on the unloaded specimen for 1500 s in order to study the time of polarization. Then, six repeated compressive load cycles with stress amplitude equal to 10% of compressive strength were applied. A time out of 120 seconds followed and finally specimens were subjected to a compressive stress corresponding to 50% of compressive strength. Similarly, AC-impedance (*Solartron SI 1280*) measurement method was used, varying the frequency between 1 and 20000 Hz on unloaded specimens. Then frequency was fixed at 20000 Hz during the load cycles. AC-impedance permits to evaluate the resistance and capacitance characteristics separately in order to estimate the influence of frequency on resistivity and piezoresistivity of CNTs reinforced cement pastes.

3 TEST RESULTS AND DISCUSSION

3.1 DC measurements

In DC measurement, the electrical resistance increases during the time, independently of carbon nanotubes dosage (Fig. 1). The electrical resistance increases rapidly at the beginning. Then it increases slowly and finally it becomes stable. The resistance of composites includes the resistance of the electrode (R_e), that of carbon nanotubes cement paste (R_c) and the interface resistance between electrodes and composites (R_{int}). Since R_e is small enough to be negligible, the resistance measured by the direct-current two-probe method mainly represents R_c and R_{int}.

According to the conductive model of CNT/cement composites proposed by Shi and Chen [1998] (Fig. 2), the interface electrodes/composite should be modeled as a resistance and a capacitance in parallel. Therefore, during the DC measurement, the capacitor will be charged, generating an opposite current compared with that generated by the multimeter.

The capacitor charging varies during the time: initially faster and then more slowly. Hence, the polarization can occur in cement-based composites with carbon nanotubes during DC measurement. As a consequence of this an apparent electrical resistance (R_a) was measured during the test. This apparent resistance is equal to the ratio between voltage (V) across the multimeter and the difference between the charging current of capacitor ($I_c(t)$) and current in the circuit within multimeter (I) [Han et al. 2012 b]:

$$R_a = V / [I - I_c(t)].$$

The variations of the electrical resistance with time for piezoresistive cement-based composites with CNTs under loading are illustrated in Fig. 3.

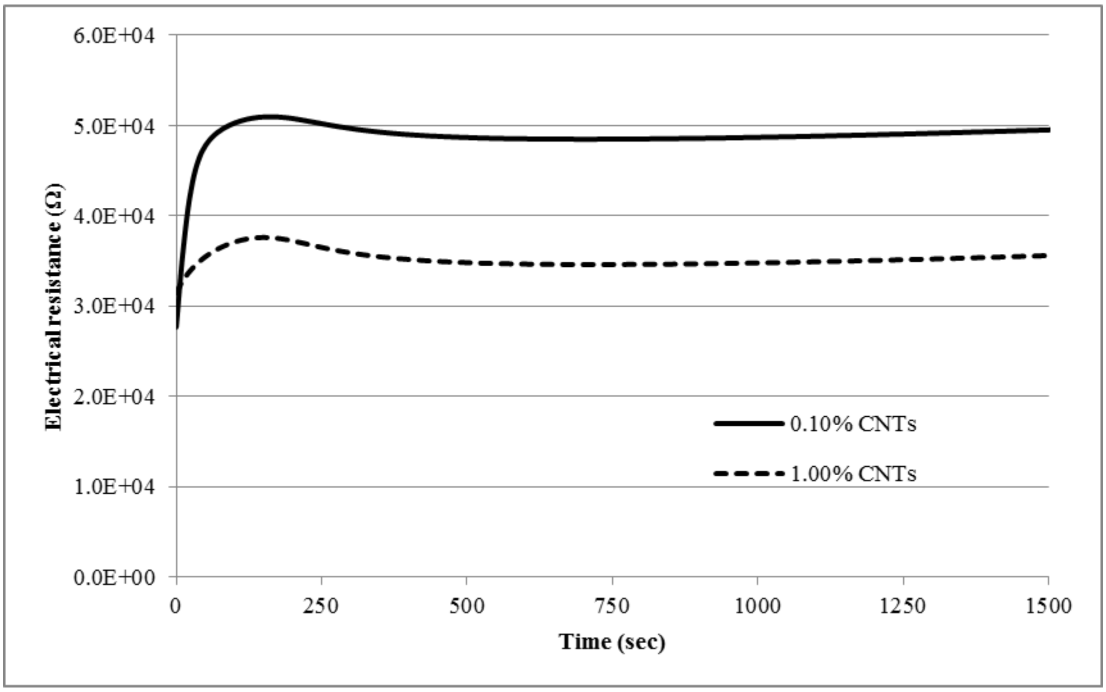

Fig. 1 Variation of measured electrical resistance with time.

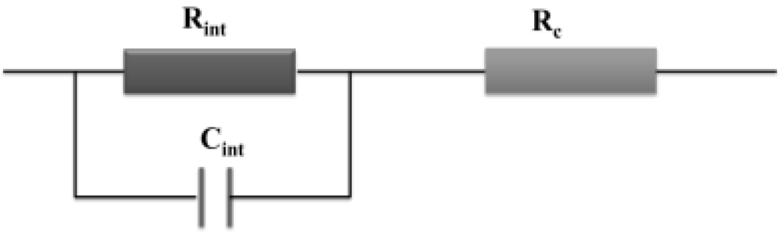

Fig. 2 Conductive model of CNT/cement composites [Shi and Chen 1998].

In this case the load was applied before the capacitor was charged. Therefore, the test was strongly influenced by the polarization effect, independently of CNTs dosage. The resistance measured at initial time (0 s) doesn't represent the actual value, since it is strongly affected by the polarization effect. After 1500 s, when the polarization of electrodes is stable, the resistance measured is representative of the electrical properties of the composite. In such a situation, the higher the CNTs dosage, the lower the electrical resistance, as expected.

The resistance of CNTs cement paste decreases upon loading and increases upon unloading in every load cycle but its original value changes in each loading and unloading cycle due to the polarization. The variation of electrical resistance due to the capacitor charging is approximately linear. Consequently, the linear increase in measured electrical resistance can be eliminated in order to obtain the piezoresistive response of the CNTs cement composites [Han et al. 2012 b].

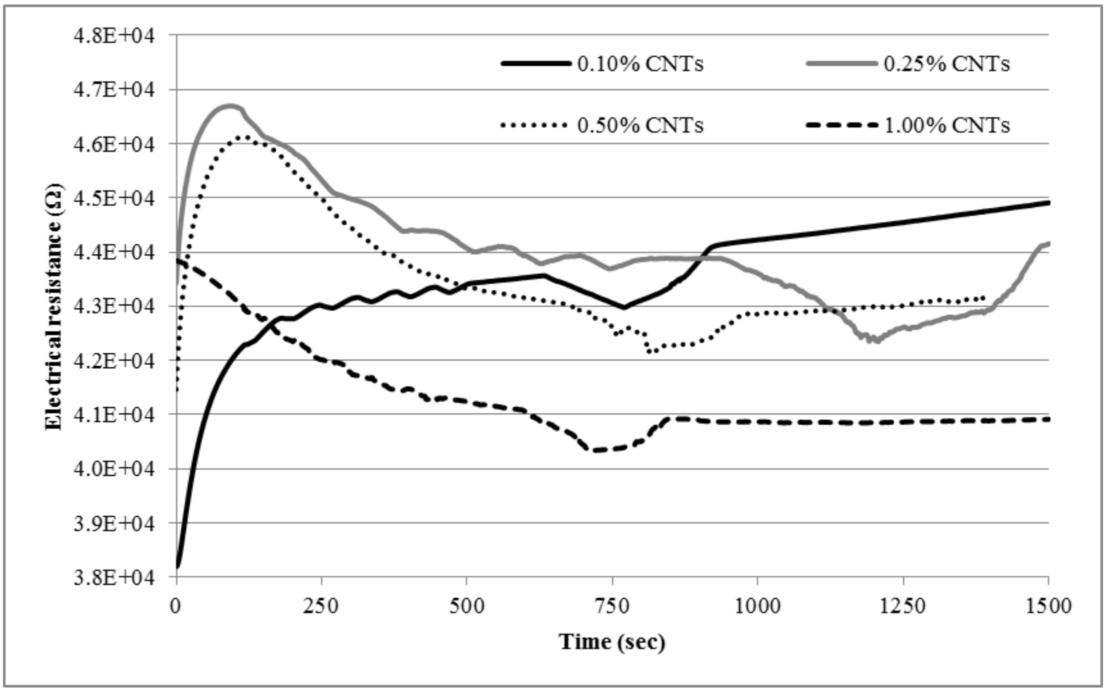

Fig. 3 Variation of electrical resistance with time for loaded specimen.

Fig. 4 and Fig. 5 show the electrical resistance variation during the load cycles.
The electrical resistance remarkably changed for the cement pastes containing 0.25% of CNTs.

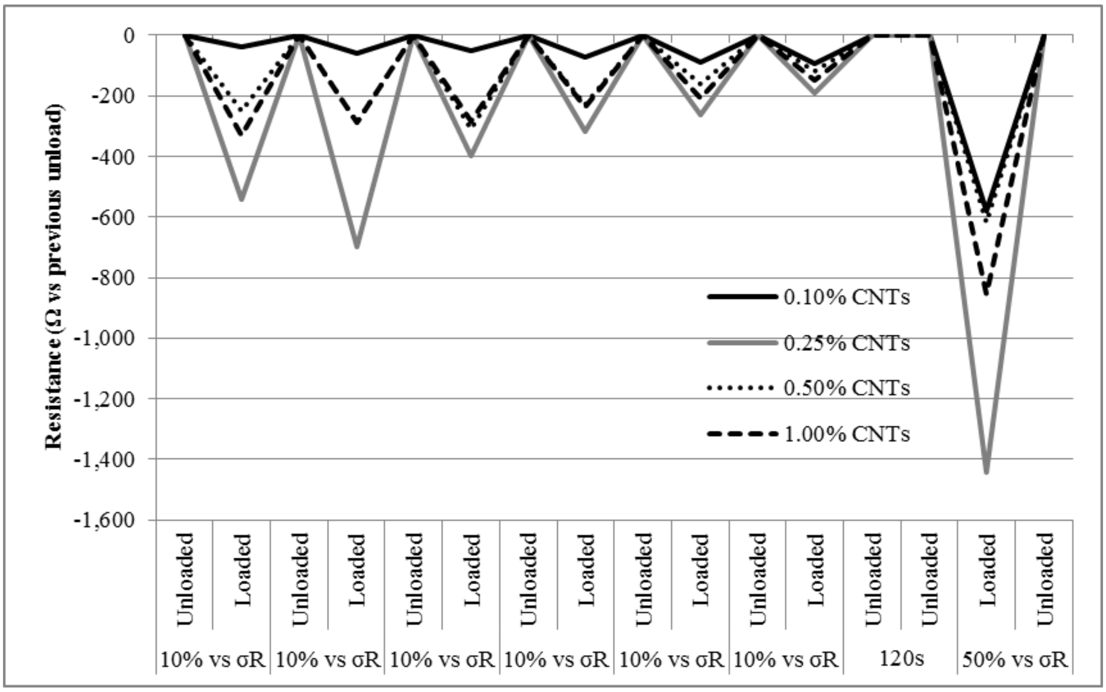

Fig. 4 Cement paste electrical resistance change (Ω) under load cycles.

Results highlight that evident pressure-sensitivity is achievable using a CNTs dosage equal to 0.25%. Increasing the dosage of CNTs over this value the stress sensitivity behavior is less evident because the difference in the number of contact points between the unloaded and loaded condition is lower. However, independently of the stress level applied, a critical percentage exists and above this value further fiber addition will not produce any significant variation in conductivity [Coppola et al. 2011].

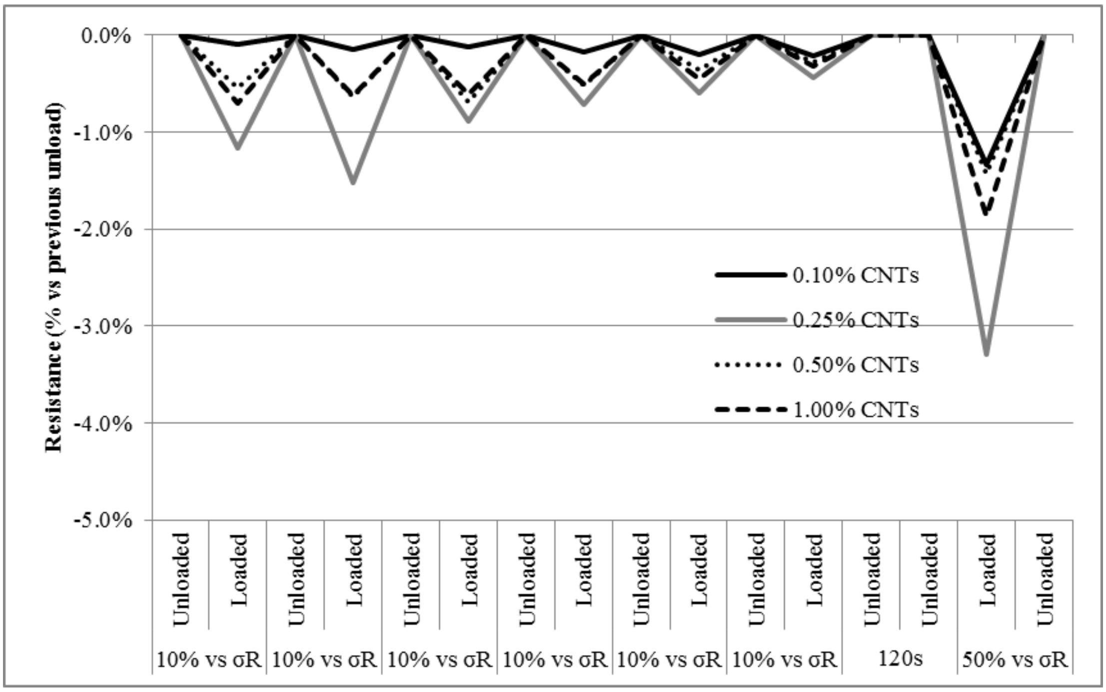

Fig. 5 Percentage variation of electrical resistance under load cycles of CNTs/cement paste.

3.2 AC measurements

In order to separate electrical resistivity and capacitance of MWNT/cement composites, impedance measurements were carried out varying the frequency on unloaded condition.

Fig. 6 and

Fig. **7** show the resistance and the capacitance (reactance) of cement pastes with different CNTs dosage as a function of frequency, respectively. As the reactance is the opposition to AC in a circuit due to the capacitor, the resistance and capacitance characteristics of MWNT/cement composites can be studied separately.

It can be seen from Fig. 6 that the electrical resistance decreases with the increase of frequency, independently of the CNTs dosage. Similarly, the higher the frequency, the lower the capacitance (

Fig. **7**). Therefore the decrease of capacitance is about 3 times than that of electrical resistance. These results confirm the hypothesis that MWNT/cement composites have both resistance and capacitance characteristics.

Furthermore, the capacitance can be eliminated or minimized increasing the test frequency, independently of CNTs percentage. Therefore, increasing the frequency, the polarization effect due to the capacitor charging can be radically reduced and, consequently, also its influence on piezoresistive response. For these reasons, an high frequency (20000 Hz) was chosen to evaluate the piezoresistivity of CNTs composites.

The impedance modulus vs. time under load cycles is illustrated in

Fig. **8**. Without a pre-power time, the impedance does not increase linearly during the time because the polarization effect doesn't influence the measurement at high frequency. The impedance decreases applying a compressive load and returns to the initial value on unload condition, independently of CNTs dosage.

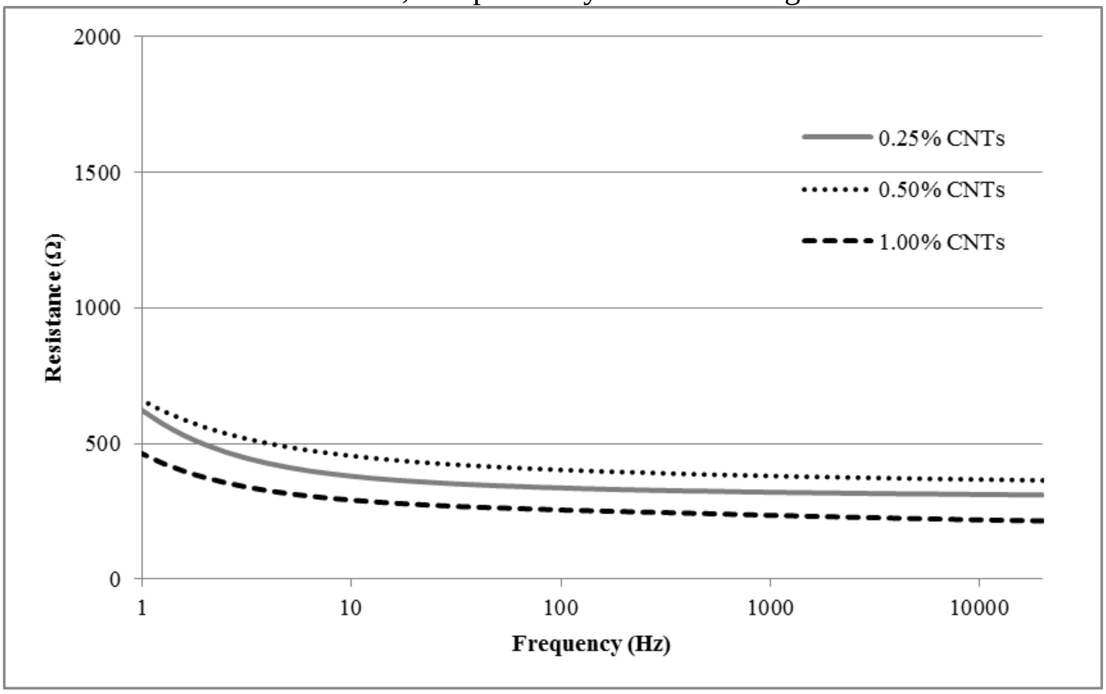

Fig. 6 Electrical resistivity of MWNT/cement pastes with different CNT concentrations as a function of frequency.

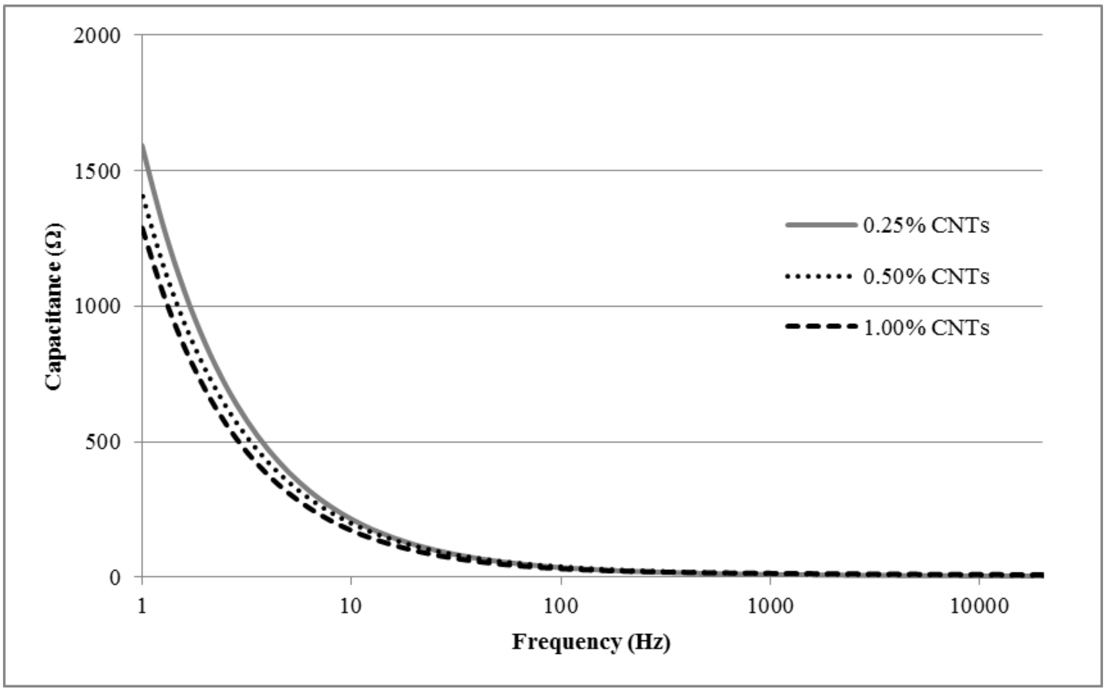

Fig. 7 Capacitance of MWNT/cement pastes with different CNT concentrations as a function of frequency.

Fig. 9 and

Fig. **10** show the impedance modulus variation at 20000 Hz during the load cycles. Similarly to DC results, the impedance modulus changes under load cycle.
Under the same load cycles, the numerical variation of impedance is lower than that of electrical resistance measured by DC (about 100 times). In fact, during the AC test, the true electrical resistance was measured because the capacitance was reduced and the contribute of capacitor was eliminated.

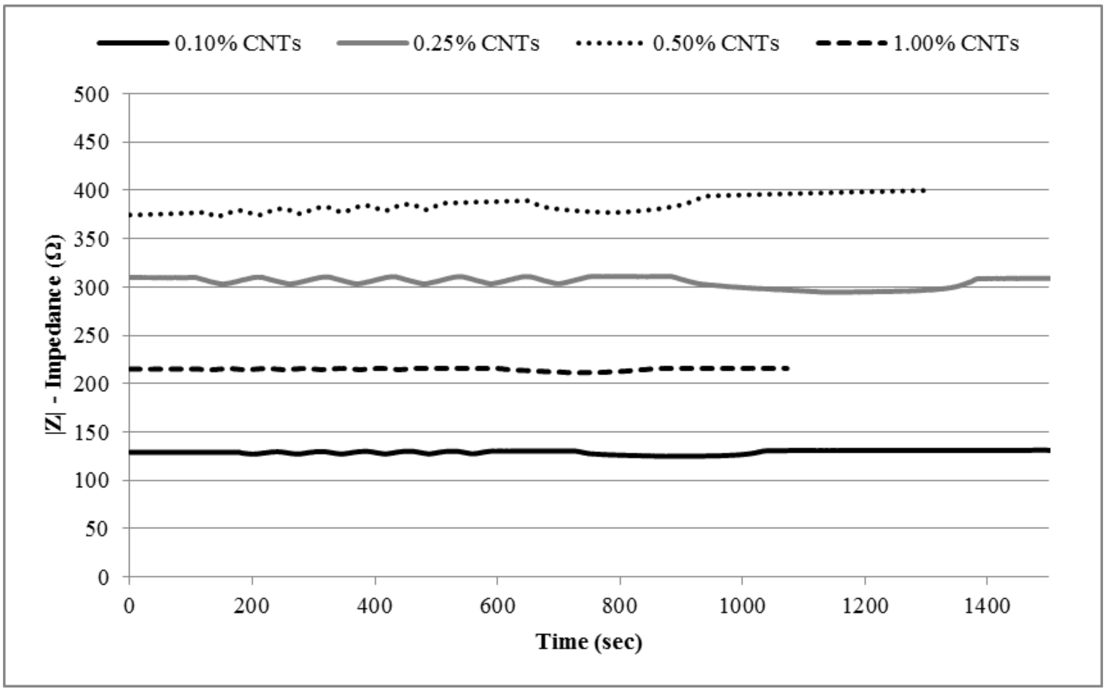

Fig. 8 Variation of impedance modulus with time during load cycles.

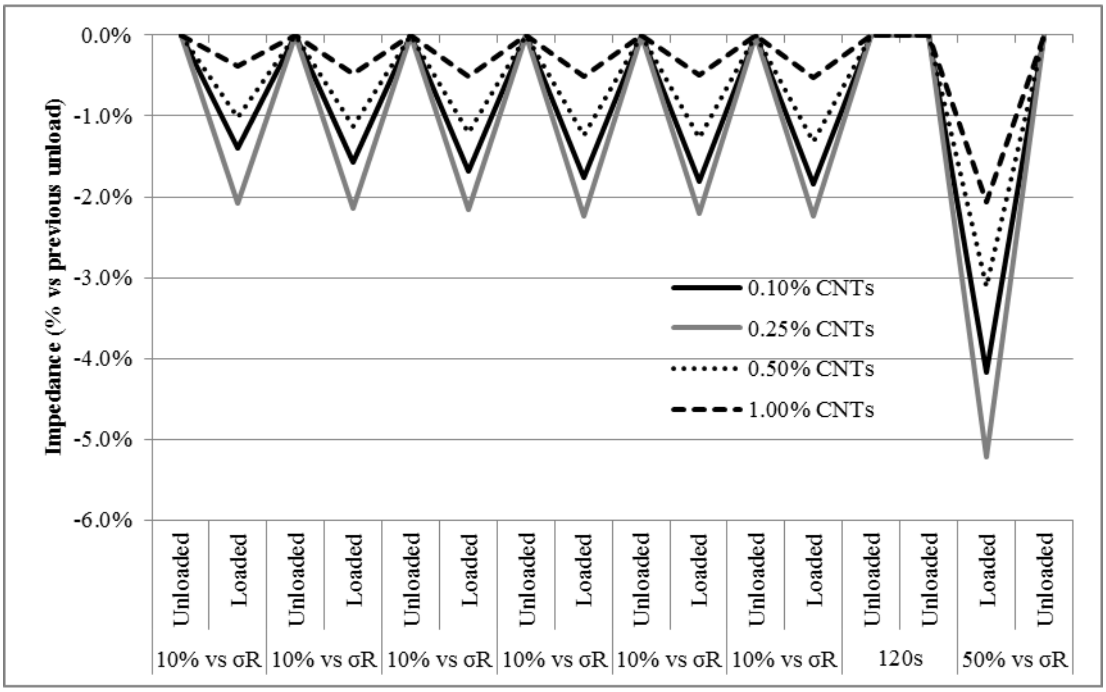

Fig. 9 Cement paste impedance modulus change (Ω) under load cycles.

Therefore, in terms of percentage variation (

Fig. **10**), the values are very similar and the order of magnitude is the same for both DC and AC measurement. Therefore, increasing the CNTs dosage from 0.10% to 0.25%, the piezoresistivity increases, but if the dosage exceeds this value, the pressure-sensitivity decreases. As stated in the "percolation" theory, the magnitude of the electrical conductivity increases with the CNTs content, but a critical value exists to maximize piezoresistivity properties.

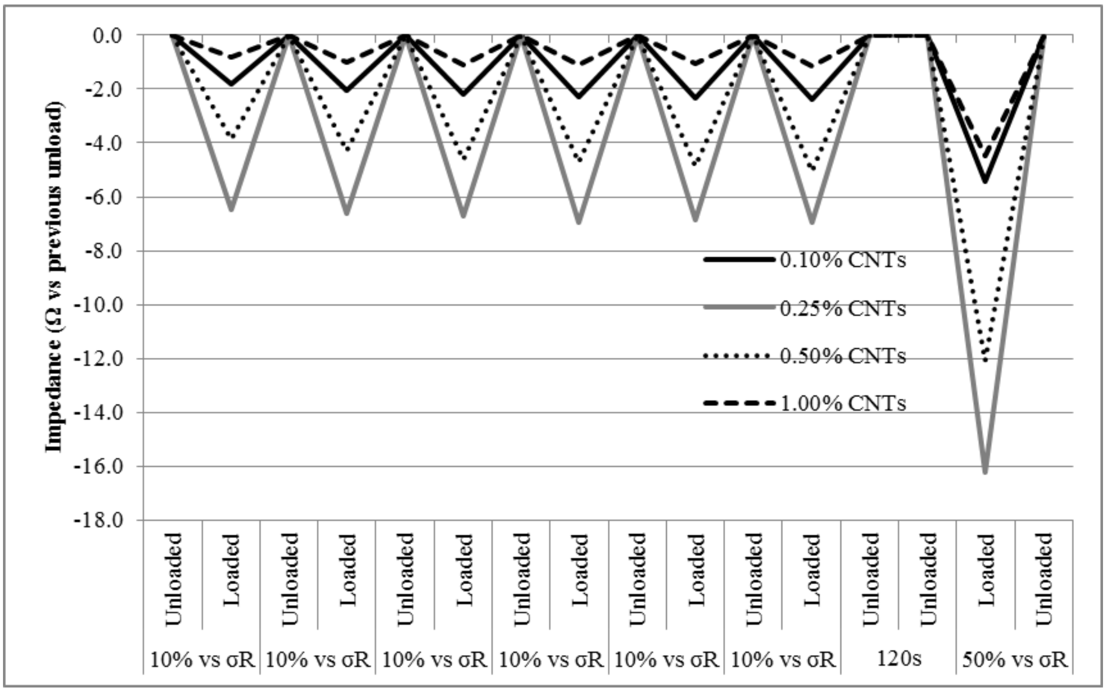

Fig. 10 Percentage variation of impedance modulus under load cycles of CNTs/cement paste.

In fact, if the dosage is too high, the carbon nanotubes are in contact with each other on unloaded condition, so the load application doesn't change the electrical resistivity. Moreover, independently of the CNTs percentage, the higher the stress applied the lower the electrical resistance of the composite materials. Data seem to indicate good piezoresistivity when CNTs are added to the cement matrix, independently of the percentage of CNTs used, even if a low dosage (0.25%) is more sensitive to the variation of the stress applied. Finally, we can observe that the AC results are not influenced by polarization effect. So it's possible to study the piezoresistive behavior without eliminating the linear electrical capacity in the electrical resistance.

4 CONCLUSIONS

The influence of test instruments on electrical properties of CNTs/cement composites using a two probe layout was studied. The DC test results are strongly influenced by the polarization effect. Having MWNT/cement composites both resistance and capacitance characteristics, during the DC measurement, the capacitor will be charged and an opposite current is generated.

The piezoresistivity of the CNTs cement paste can be evaluated by eliminating the linear electrical capacity part in the measured electrical resistance or waiting for a pre-power time in order to let resistance reach its linear stage.
The AC measurement method at high frequency gives results about pressure-sensitivity of composites that can be directly analyzed without considering the polarization. Indeed, the capacitor charging and discharging are minimized and the piezoresistivity behavior of the CNTs composites is more evident. Good piezoresistive properties are achieved when CNTs are added to the cement matrix. In particular, using a low dosage (0.25%), the composite is more sensitive to the variation of the stress applied with respect to the specimens with higher dosage (1.0%). Probably this percentage of CNTs (1.0%) exceeds the percolation threshold value. Finally, the electrical property variation depends linearly on stress level: the higher the load applied, the lower the electrical resistance measured.

ACKNOWLEDGMENT

Authors thank the financial support from the Italcementi Group S.p.A. (Bergamo, Italy).

REFERENCES

Azhari F. (2008). "Cement-based sensors for structural health monitoring", Civil Engineering Thesis, University of British Columbia, Vancouver, Canada, ubc_2009_spring_azhari_faezeh.pdf.

Chen S.J., Collins F.G., Macleod A.J.N., Pan Z., Duan W.H. and Wang C.M. (2011). "Carbon nanotube–cement composites: A retrospect", *The IES Journal Part A: Civil & Structural Engineering*, 4(4), 254-265.

Coppola L., Borgarello E., Buoso A., Corazza F., Crippa E. (2010). "Experimental Study on the Properties of Cement Composites with Carbon Nanotubes for Monitoring the Stress Conditions of the Reinforced Concrete Structures", *Proc. 1st Workshop "The new boundaries of structural concrete"*, Ed. by A. Grimaldi, G. Plizzari, R. Realfonzo, Edizioni Cues, Fisciano (SA), Italy, 317-324.

Coppola L., Buoso A., Corazza F. (2011). "Electrical Properties of Carbon Nanotubes Cement Composites for Monitoring Stress Conditions in Concrete Structures", *Applied Mechanics and Materials*, 82, 118-123.

Gopalakrishnan K., Birgisson B., Taylor P. and Attoh-Okine N. (2011). *Nano-technology in Civil Infrastructure - A Paradigm Shift*, Springer-Verlag, Berlin, Germany.

Han B.G., Han B.Z., Yu X. (2009). "Experimental study on the contribution of the quantum tunnelling effect to the improvement of the conductivity and piezoresistivity of a nickel powder-filled cement-based composite", *Smart Materials and Structures*, 18, 065007.

Han B., Yu X., Ou J. (2010). "Effect of water content on the piezoresistivity of MWNT/cement composites", *J. Mater. Sci.*, 45(14), 3714–3719.

Han B., Qiao G., Jiang H. (2012a). "Piezoresistive response extraction for smart cement-based composites/sensors", *Journal of Wuhan University of Technology - Mater. Sci. Ed.*, 27 (4), 754-757.

Han B., Zhang K., Yu X., Kwon E., Ou J. (2012b). "Electrical characteristics and pressure-sensitive response measurements of carboxyl MWNT/cement composites", *Cement and Concrete Composites*, 34(6), 794–800.

Khare R., Bose S. (2005). "Carbon Nanotube Based Composites- A Review", *Journal of Minerals & Materials Characterization & Engineering*, 4(1), 31–46.

Pushparaj V.L., Nalamasu O., Manoocher Birang M. (2010). "Carbon nanotube-based load cells", Patent No. US 7,971,489 B2.

Shi M.L. Chen Z.Y. (1998). "Study of AC impedance on the porous structure of hardened cement paste", *J. Build. Mater.*, (1), 30–35.