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On the effect of addition of carbon nanotubes on the electric conductivity of alkali-activated slag mortars

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Abstract This paper presents basic electric properties of laboratory prepared alkali-activated composite materials on the basis of finely ground granular high furnace slag to which various quantities of carbon nanotubes (CNT) have been added. Impedance spectroscopy in the frequency range from 40 Hz to 1 MHz was used to measure the specimens. Electric resistivity ρ versus frequency and electric resistivity ρ versus CNT content relationships were examined on our specimens. R&S ZNC vector analyser with DAK-12 coaxial probe (made by Speag) was used to carry out the measurements at higher frequencies (from 100 MHz to 3 GHz). Electric conductivity σ as a function of the frequency and as a function of the specimen CNT content was studied in this frequency range. Up-to-date instruments and a unique approach have evidently been employed to carry out non-destructive measurement of mortar materials.

1. Introduction

In the structure of the mortars under investigation there are air gaps, which influence the resulting properties both directly and indirectly. In a porous environment, the carbon nanotubes can behave as micro-binders, which will create a thicker and less porous structure [1]. The air gaps are reduced in number or become totally extinct in the composite material. In this way, the mix becomes more homogeneous. A cardinal effect on the physical and mechanical properties (their improvement) is evident. A change in electric parameters of the nano-composite (geopolymer), for example, the electric capacitance without and with carbon nanotubes is clearly observable. These results may contribute a lot to the further research and development of alkali-activated systems with a focus on their practical application in the building industry.

The measurements, which have been carried out to date, show that the application of carbon nanotubes in materials results in improving their strength, elasticity and a general durability [2]. The nanotubes show a low density (1.3 to 1.4 g·cm⁻³ depending the nanotube type), a high thermal conductivity (1 750 to 5 800 W·m⁻¹ K⁻¹) and – thanks to delocalized bonds along the entire carbon layer – an excellent electrical conductivity. Carbon nanotubes are considered to be a potential replacement of the composite reinforcement, their mechanical, electric and thermal properties exceeding those of the traditional fibres [2].

Alkali-activated materials, or, geopolymers, make a specific group of inorganic cement-free materials. They arise in a reaction of latently hydraulic substances or pozzolans (granulated slag, fly ash, meta-kaolins) with a suitable activator. Solutions of soluble compounds of alkali metals, above all, sodium and potassium, namely, carbonates, hydroxides and silicates, can be used as activators. This activation gives rise to hydraulic binders which - after water is added to them - can be used to



form composite compounds featuring excellent applicability [3]. Alkali-activated materials can serve as an alternative of classical building materials, in particular, the cement concrete, but – thanks to their other features - they can also be employed in a number of other branches (such as the renovation of historic objects, etc). However, their potentiality is being exploited on a small scale in the building industry, even though the research of alkali-activated materials has been going on since the sixties of the last century [4,5].

An indisputable advantage of the alkali-activated materials consists in their economical and environmental features. These materials can substantially increase the value of secondary raw materials which show latent hydraulic or pozzolanic activity, first of all, the large-volume by-products of metallurgy and power engineering. The preparation of alkali-activated binders and composites takes place at common or slightly elevated temperatures. It requires neither previous firing of the semi-products to a high temperature (which is the case, e.g. of the portland clinker), nor high-temperature sintering, thus reducing the generation of CO₂ by combustion processes and limestone decomposition. Another benefit of the alkali-activated materials consists in the possibility of apply a wide choice of non-standard binders, which are not commonly used in the concrete technology.

This paper presents basic electric properties of laboratory prepared alkali-activated composite materials on the basis of finely ground granular high furnace slag to which various quantities of carbon nanotubes have been added.

2. Experiment setup

Several brands of the input raw material have been used to prepare the specimens. Alkali-activated finely ground granular blast-furnace slag is used to act as a binding agent. The activation was carried out using a water glass solution the silicate module of which was adjusted to $M_s = 2.0$ by means of 50 % sodium hydroxide. Both standard testing sand, which is used to prepare test cement specimens, and carbon nanotubes in various amounts were used as a binding agent. The composition of partial mixes is summarized in Table 2.

Three test bodies of dimensions 40 x 40 x 160 mm from each of the mixes were manufactured. The results obtained from each test body are compared with those of the reference specimen.

Table 1. Chemical composition of granular blast-furnace slag (%)

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	K ₂ O	Na ₂ O	MnO	SO ₃
39.75	6.61	0.46	39.03	10.45	0.63	0.38	0.37	0.71

Table 2. Mixture composition

Mixture	Slag [g]	Water glass [g]	Sand [g]	CNT [g]	Water [ml]
REF				0	185
0.1 % CNT				4.5	185
0.2 % CNT				9	185
0.3 % CNT	450	90	1350	13.5	185
0.5 % CNT				18	185
1.0 % CNT				22.5	185
1.5 % CNT				27	185
2.0 % CNT				31.5	185
2.5 % CNT				36	185

Thus prepared test bodies are shown in Fig. 1, their composition is in Table 2. They were characterized by means of the impedance spectroscopy method. Agilent 33220A sine waveform generator and Agilent 54645A double-channel storage oscilloscope were used. The specimens were measured in the frequency range from 40 Hz to 1 MHz. Electric resistivity ρ versus frequency and electric resistivity ρ versus CNT content relationships were studied on our specimens. To carry out the impedance analysis, the specimens were placed between brass electrodes of an area of 30×100 mm. To measure at higher frequencies (from 100 MHz to 3 GHz), R&S ZNC vector analyser with DAK-12 coaxial probe (made by Speag) was used. Electric conductivity σ as a function of the frequency and as a function of the specimen CNT content was studied in this frequency range.

Residual mechanical properties of the specimens were studied, too. To determine the bending forces, a standardized 3-point test was employed. The compressive strength was measured at remote edges of each of the bending test remaining specimens according to of EN 196-1 standard, "Cement testing methods".

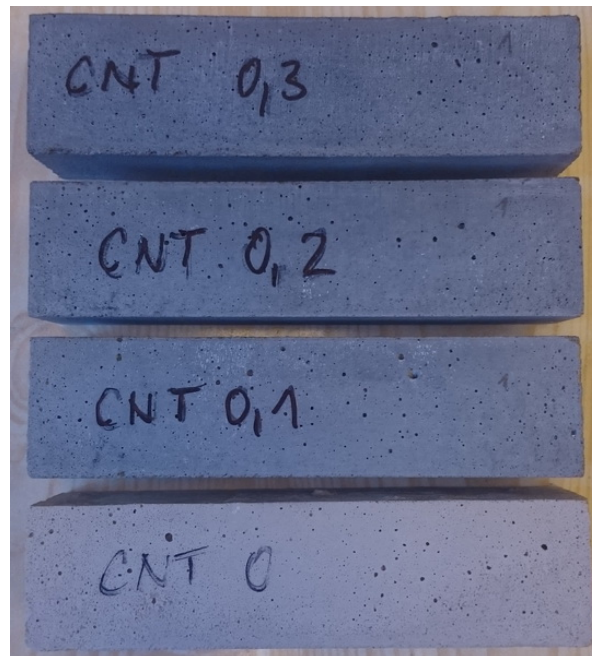


Figure 1. Specimens with respective CNT additions of 0 %, 0.1 %, 0.2 % and 0.3 %. The specimen dimensions: 40 x 40 x 160 mm.

3. Results

The electric resistivity ρ of AAS composites with CNT ranging from 0 to 2.5 % was measured at the frequencies from 40 Hz to 1 MHz (Fig. 2). The maximum values of the electric resistivity were found to be $3.3 \times 10^8 \Omega \cdot \text{cm}$ at a frequency of 40 Hz. These values of the electric resistivity pertain to specimens to which 0, 0.1 and 0.2 % of CNT were added and are in very close proximity of each other. The electric resistivity values are decreasing in the same way for all specimens and are converging to tens of $\text{k}\Omega \cdot \text{cm}$ at the frequencies above 10 kHz. At higher frequencies, the electric resistivity values show a sloping down trend. They almost coincide at frequencies above 10 kHz for all CNT admixture percentage values (0 through 2.5 %).

The carbon nanotubes create conducting paths in the specimens. Consequently, the electric resistivity of higher CNT concentration specimens is reduced, as is illustrated in the diagram of Fig. 2. The electric resistivity curves of specimens with CNT 0 to 1 % are mingling throughout the spectre. A more significant decrease is taking place for the specimens with CNT 1.5 %. At a frequency of 100

Hz, the electric resistivity difference between the CNT 1 and CNT 1.5 % specimens is $1.37 \times 10^8 \Omega \cdot \text{cm}$ approximately.

The electric resistivity decrease with the CNT concentration will most probably stop at substantially higher CNT concentrations. In this case, however, we encounter problems when mixing fine CNT's into the geopolymer fresh mixture, as the nanotubes are clustering and, consequently, are not distributed uniformly at the specimen faces, to which conducting plate electrodes are attached. The nanotubes might get broken into fragments in consequence of blending, which also aggravates the higher CNT concentration problems.

Generally speaking, the electric resistivity differences are very low at CNT concentrations of 0.1 through 1 %. More pronounced electric parameter variations take place at a CNT concentration of 1.5 % and more. Different raw material mixing procedures as well as different calendar dates of mixing contribute also to the differences in the readings. Our objective therefore consists in comparing the trends in the different batches rather than the batches with graphite admixtures against those with CNT.

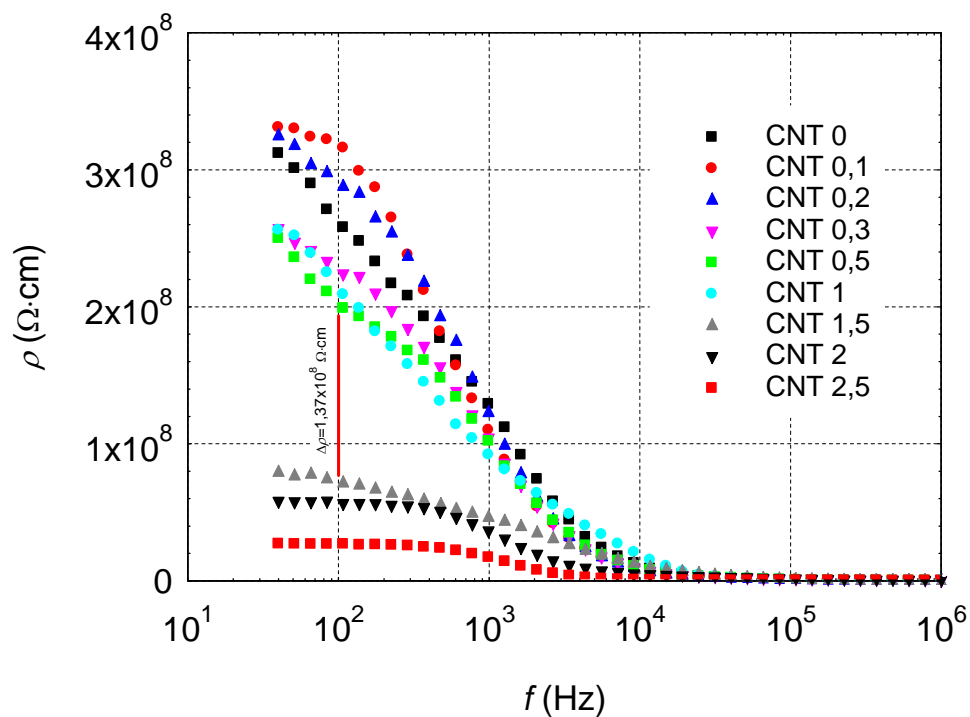


Figure 2. Electric resistivity of AAS composites with 0 through 2.5 % of CNT in the frequency range from 40 Hz to 1 MHz (the frequency is plotted in log scale).

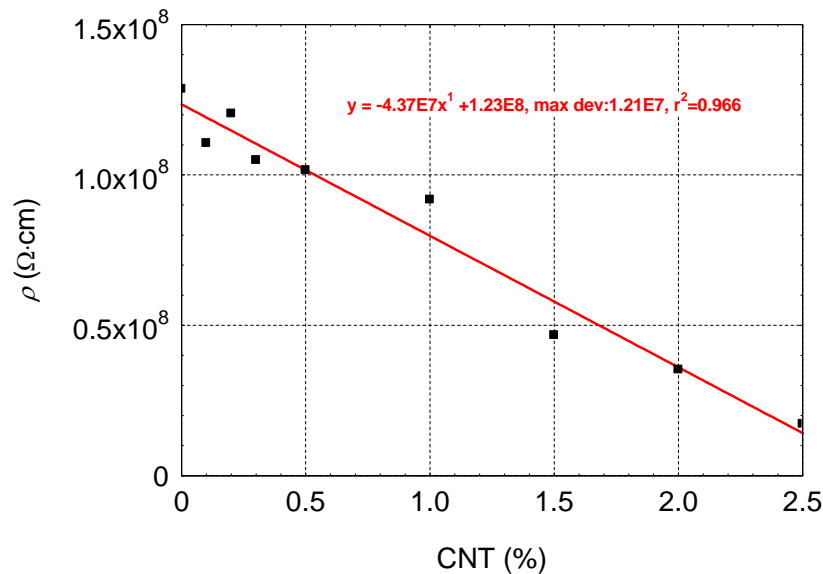


Figure 3. Variation of the electric resistivity of the composite AAS as a function of the CNT content at a reference frequency of 1 kHz.

Electric properties of AAS composites with added CNT were investigated at higher frequencies, too. Specifically, in the frequency range from 10 to 3000 MHz, where R&S ZNC vector analyser with DAK-12 coaxial probe made by Speag was used. An electric conductivity of AAS composites versus frequency plot is shown in Fig. 4. The electric conductivity initially increases with the alternating electric field frequency between 10 – 2 000 MHz. A maximum is observed to occur at a frequency of 2 GHz for all mixtures with different CNT contents as well as the reference mixture (with no CNT added). Therefore, location of the peak is constant at the above mentioned frequency, showing no shift with the frequency. Subsequently, the electric conductivity decreases.

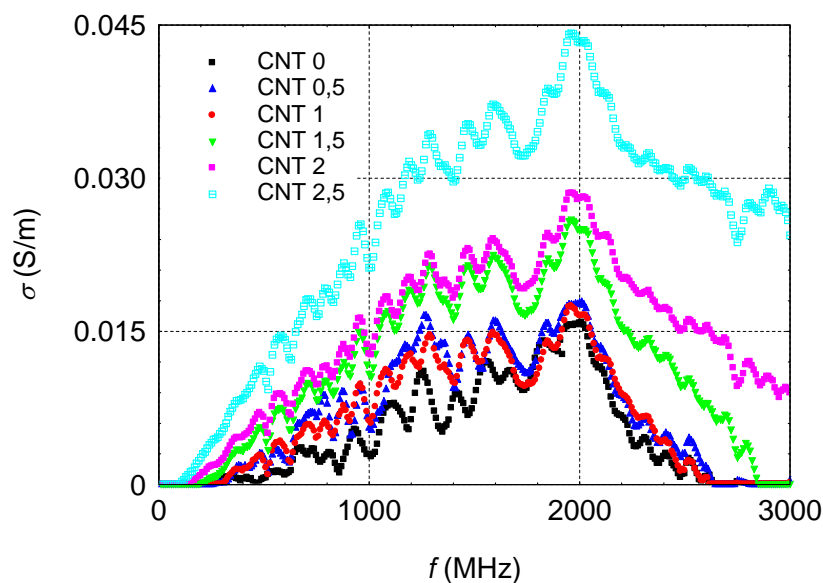


Figure 4. Electric resistivity of AAS composites with 0 through 2.5 % of CNT in the frequency range from 40 Hz to 3000 MHz.

The shapes of all curves with CNT 0 through 1 % are very similar, the differences in values being very low. A considerable change in the electric conductivity takes place at CNT 1.5 %. It is therefore in accordance with the electric resistivity. The largest differences in the electric conductivity occur at a frequency of 2 GHz, at which the above mentioned maximum is observed. For example, at a the frequency of 2 GHz, the specimen with CNT 0 % reaches the electric conductivity of 0.0156 S/m; for CNT 0.5 %, a value of 0.0175 S/m; for CNT 1 %, a value of 0.0170 S/m; for CNT 1.5 %, a value of 0.0252 S/m; for CNT 2 %, a value of 0.0281 S/m; for CNT 2.5 %, a value of 0.0433 S/m are obtained. For example, an addition of CNT 2.5 % resulted in an increase of the electric conductivity at 2.5 GHz by 0.0277 S/m against the reference specimen (CNT 0 %).

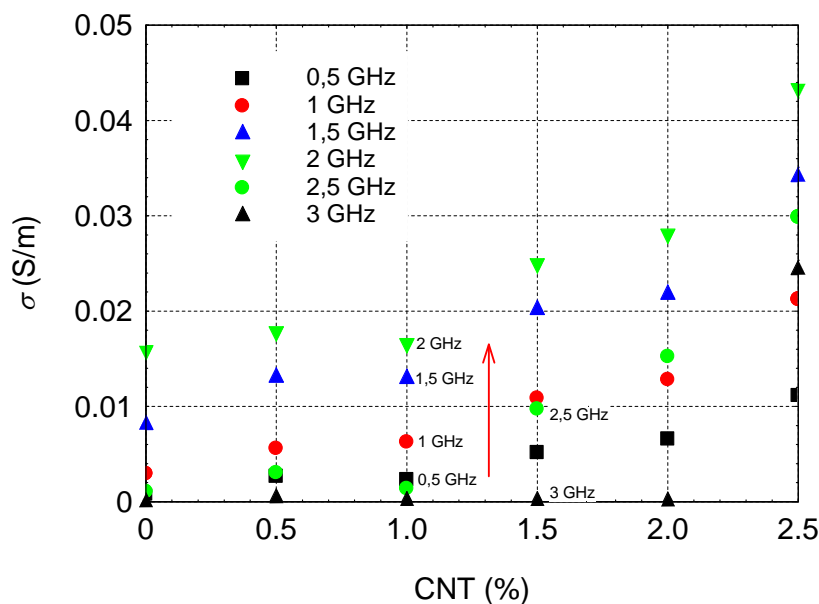


Figure 5. Electric conductivity of an AAS composite versus the addition of CNT ranging from 0 to 2.5 % (at selected frequencies of the electric field).

The diagram of Fig. 5 shows a plot of the electric conductivity versus CNT content as the material addition. A growth of the electric conductivity is observed when the CNT content is increased. At the same time, a growth of the electric conductivity can be observed when the alternating electric field frequency is increased. This corresponds to the selected frequencies of 0.5 GHz, 1 GHz, 1.5 GHz and 2 GHz. Therefore, when the frequency is increased up to 2 GHz, the electric conductivity grows up for all amounts of the CNT addition. However, at higher frequencies, i.e., 2 GHz and 2.5 GHz, the electric conductivity is observed to decrease. This can be documented by the local maximum at a frequency of 2 GHz, see Fig. 4. The growth of the electric conductivity with the frequency is due to the polarization current, which arises from the orientation oscillation movement of the dipoles. The total electric conductivity is therefore equal to the sum of the DC conductivity and the dipole polarization conductivity [6,7]. The reason for which the electric conductivity dropped at 2 GHz, will be the object of a further research.

4. Mechanical properties

Table 3 lists the compressive strength values for composites with various quantities of CNT filler. The compressive strength of an AAS composite without any CNT added equalled 58.6 MPa. Addition of CNT caused this strength to decrease dramatically. This can be accounted for the growing water to slag ratio and, also, for complications which arise on mixing the suspension with increasing CNT

content. A strength increase occurred for and addition of 0.5 % CNT, namely to 51.3 MPa. A noticeable decrease took place afterwards. The compressive strength of the specimens with CNT 2.5 % is reaching about one half of the value of the specimens with CNT 0 % and 0.5 %. Our results show that only 45 % of the reference force are sufficient for the CNT 2.5 % specimens.

Table 3. Compressive strengths of AAS composites with 0 to 2.5 % of CNT added, together with the root-mean-square deviations.

Mixture	f_c [MPa]	Root-mean-square deviation
REF (0 % CNT)	58.6	3.2
0.1 % CNT	46.8	3.3
0.2 % CNT	48.4	5.6
0.3 % CNT	44.1	1.6
0.5 % CNT	51.3	2.0
1.0 % CNT	47.4	1.3
1.5 % CNT	45.0	1.1
2.0 % CNT	27.0	1.2
2.5 % CNT	26.2	1.8

The bending strength (Table 4) shows a similar trend. The highest bending strength value, 7.01 MPa, is reached by a CNT 0.3 % specimen. A radical reduction of the bending strength results from increasing the CNT content. Only 52 % of the reference force are sufficient for the CNT 2.5 % specimens.

Table 4. Compressive strengths of AAS composites with 0 to 2.5 % of CNT added, together with the root-mean-square deviations.

Mixture	f [MPa]	Root-mean-square deviation
REF (0 % CNT)	6.92	0.55
0.1 % CNT	6.19	0.91
0.2 % CNT	6.96	0.15
0.3 % CNT	7.01	0.25
0.5 % CNT	4.84	0.25
1.0 % CNT	4.69	0.20
1.5 % CNT	5.06	0.13
2.0 % CNT	3.74	0.18
2.5 % CNT	3.63	0.03

5. Conclusion

The present paper deals with the change of electric parameters of alkali-activated slag mortars to which carbon nanotubes have been added. This CNT admixture improves the electric conductivity of the materials in question, making them easier to measure by electromagnetic-principle-based methods. A suitable CNT admixture was described from the viewpoint of both its amount and the most effective increase of the electrical conductivity. Another quantity to study was the electric resistivity and its frequency dependence. The measurements were carried out in two frequency ranges, namely 40 Hz to 1 MHz and 10 MHz to 3 GHz, by means of two measuring systems. The specimens have subsequently been subjected to mechanical testing (compressive strength and bending strength).

Acknowledgments

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Corrigendum: On the effect of addition of carbon nanotubes on the electric conductivity of alkali-activated slag mortars

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Acknowledgments at the end of the article should be replaced by the following text (page 8):

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