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Electrical properties of alkali-activated slag composite with combined graphite/CNT filler

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Abstract. Alkali-activated industrial by-products such as blast furnace slag are known to possess properties which are comparable to or even better than those observed for ordinary Portland cement. The combination of alkali-activated slag matrix with conductive filler introduces new functionalities which are commonly known for self-sensing or self-heating concrete. The present paper discusses the effect of the mixture of two different conductive fillers, graphite powder and carbon nanotubes (CNTs), on the electrical properties of alkali-activated slag mortars. Prepared samples were also tested for their mechanical properties and microstructure was investigated by means of mercury intrusion porosimetry and scanning electron microscopy. The percolation threshold for the resistance was reached for the mixture containing 0.1% CNTs and 8% graphite powder.

1. Introduction

Electrically conducting cement-based composite materials have been extensively studied during the last two decades [1, 2]. The studies are generally engaged in materials behaviour in various electric fields (DC, AC with various frequency) and determine a variety of material properties that are dependent on the change of the electrical resistivity. Aluminosilicate materials are considered good electrical insulators with the resistivity up to 10^9 $\Omega\cdot$m achieved for dry concrete [3]. In order to improve the electrical conductivity of these materials a conductive filler must be added to the basic mixture. Common conducting admixture are steel fibres or carbon fibres, graphite powder, steel slag, carbon nanotubes, carbon nanofibers, carbon black, or nickel powder [4–6]. Decrease in the electrical resistivity of the concrete results in new application possibilities such as development of self-sensing and self-heating composites, security composites eliminating electrical signal throughput or composites used for determining the weight of moving objects [7].

Alkali-activated slag (AAS) used in current study is a clinker-free material which is considered an alternative to ordinary Portland cement concrete. This material is composed of granulated blast furnace slag and alkaline activator, which is usually alkaline hydroxide, carbonate or the most preferably silicate [1]. Alkali-activated slag is appreciated for its superior properties such as higher corrosion resistance against acid or sulphate attack [2, 8–10] and also higher resistance to elevated temperatures [11–14].

The electrical properties of AAS with different conductive admixtures were reported by Kusák et al. [15, 16]. Graphite as well as carbon nanonubes (CNTs) prove to have positive effect on the electrical conductivity of AAS-based material. CNTs appeared very effective because addition of just

0.2% reduced the resistivity by almost 50%. On the other hand, CNTs are still quite expensive material and larger amounts of CNTs in building materials bring about severe technological drawbacks, such as worsened workability of fresh mixes, increased water demand and strength deterioration [17, 18]. In case of graphite, decrease of the resistivity by 50% was reached with 2% of graphite powder; however, its addition has a negative effect on the compressive strength and fracture toughness of AAS composite [19].

The present study aims to assess the synergic effect of CNTs and graphite powder on the electrical properties of alkali-activated slag mortars. The addition of CNTs may improve the electrical conductivity of the composite because it may form a continuous conduction net and interconnect the graphite particles via conductive bridges. Addition of CNTs also reduces cracking of the matrix during drying shrinkage and can diminish the negative effect of graphite on the fracture properties of AAS-based materials because CNTs are proved to improve fracture toughness and fracture energy [18]. The electrical properties were determined in the way of the specific conductivity, resistance and capacitance as a function of AC frequency and dosage of conductive admixtures. Together with these measurements the mechanical properties and microstructure were also investigated.

2. Experimental part

2.1. Materials
The basic reference material was composed of finely ground granulated blast furnace slag supplied by Kotouč, s.r.o (CZ) and solid sodium silicate SUSIL MP 2.0 produced by Vodní sklo, a.s. (CZ). The chemical composition of the slag and sodium silicate is presented in Table 1. Specific surface area of the slag determined by Blaine method was 383 $m^2 \cdot kg^{-1}$ and the average grain size obtained by laser granulometry was d_{50} = 15.5 µm and d_{90} = 38.3 µm, indicating that 50% or 90%, repectively, of all grains is smaller than a given value.

Graphite and carbon nanotubes were used as conductive admixture. Graphite PMM 11 was supplied by Kooh-i-noor (CZ) as a powder containing more than 99.5% of carbon with the average grain size d_{50} = 10.9 µm and d_{90} = 20.9 µm. Multi-walled carbon nanotubes Graphistrength CW 2-45 (Arkema, France) were supplied in the form of small pellets. Since CNTs are commonly not water-soluble, the received CNTs already contained 55% of carboxymethyl cellulose as a dispersing agent. Carbon nanotubes were used in the form of 1% aqueous dispersion. In order to prepare the dispersion, the procedure prescribed by the producer was followed. CNT pellets were dissolved in hot water and dispersed bundles of CNTs were further disintegrated by mechanical homogenizer (3 h at 14000 rpm). Quartz sand with a maximum grain size of 2.5 mm was used as aggregate.

Table 1. Chemical composition of granulated blast furnace slag and SUSIL MP 2.0 (%)

	SiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	CaO	MgO	K$_2$O	Na$_2$O	MnO	SO$_3$
Slag	39.75	6.61	0.46	39.03	10.45	0.63	0.38	0.37	0.71
SUSIL	25.03						12.98		

2.2. Preparation of samples
The reference mixture (Ref) was prepared by mixing 450 g of slag, 90 g of sodium silicate SUSIL, 1350 g of quartz sand and 200 ml of water. At first, sodium silicate activator was suspended and partially dissolved in water. Then, slag and quartz aggregate was added and the mixture was stirred in a planetary mixer for about 5 min to prepare a homogenous mortar. The same amount of basic components was used also for the preparation of composites with conductive admixtures. The amount of CNTs was 0.1% with respect to the mass of the slag, as it contributes to the best improvement of mechanical properties [18], and the dosage of graphite varied between 2 to 10 %. Since CNTs were used in the form of aqueous dispersion and graphite powder reduced the workability, the amount of additional mixing water was adjusted to achieve workability of reference mixture. The composition of

the mixtures is presented in Table 2. Graphite powder was mixed with CNTs and part of additional mixing water to prepare homogenous suspension. Then, sodium silicate, slag and quartz aggregate together with the rest of mixing water were added in the successive steps and the mixing procedure followed the one given for the reference mixture. Prepared fresh mortars were cast into $40 \times 40 \times 160$ mm prismatic moulds and left to set. The hardened specimens were immersed in water for 27 days. In order to avoid the influence of moisture on the measurement of electrical parameters, all specimens were dried at 105 °C to a constant weight before testing.

Table 2. Composition of AAS mixtures

	Slag (g)	SUSIL (g)	Sand (g)	1% CNTs (g)	Graphite (g)	Water (ml)
CG2					9	165
CG4					18	165
CG6	450	90	1350	45	27	180
CG8					36	200
CG10					45	220

2.3. Testing procedures

Prepared test samples were characterized by impedance spectroscopy using sinusoidal signal generator Agilent 33220A and dual-channel oscilloscope Agilent 54645A [20]. Output voltage of the signal generator was 5.5 V. Input values of electrical capacitance and resistance of oscilloscope were 13 pF and 1 MΩ, respectively. These instruments were assembled under the proposed scheme for fully automated measurement. The samples were measured in the use of the frequency spectrum of 40 Hz to 1 MHz. In order to perform impedance analysis, the specimens were placed between brass electrodes (30×100 mm) (Figure 1). Electrical parameters were also analysed in higher frequency range from 100 MHz to 3 GHz using the vector analyser ZNC (Rohde & Schwarz) and coaxial probe DAK-12 (SPEAG).
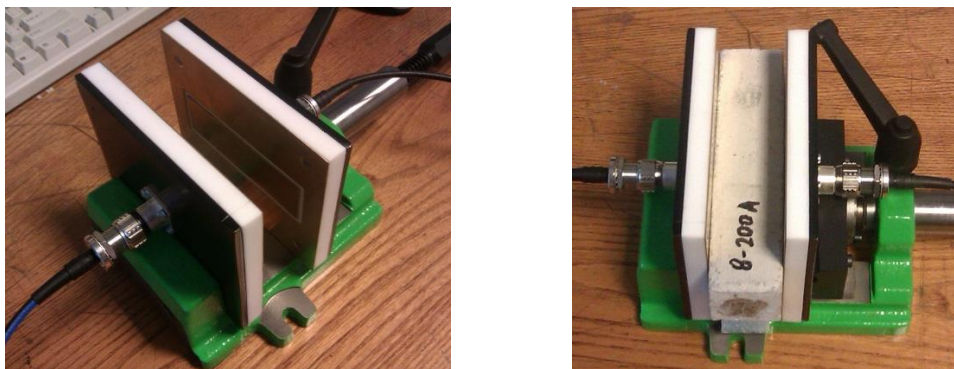
Figure 1. Experimental setup for the measurement of the electrical parameters with Agilent appliance

The specimens were also tested for their residual mechanical properties. Flexural strengths were determined using a standard three-point-bending test and compressive strengths were measured on the far edge of each of the two residual pieces obtained from the flexural test according to the EN 196-1 standard.

Pore distribution was evaluated by means of mercury intrusion porosimetry analysis, which was conducted on samples using a Micromeritics Poresizer 9300 porosimeter that can generate a maximum

pressure of 207 MPa and can evaluate a theoretical pore diameter of 0.006 μm. Micrographs of the alkali activated slag mortars were taken on a TESCAN MIRA3 XMU scanning electron microscope in SE mode. The experiments were carried out on dry samples that were sputtered with gold.

## 3. Results and discussion

3.1. Electrical properties
Electrical properties of alkali-activated slag composite with graphite and CNTs were determined in two different frequency ranges of AC source. At lower frequencies between 40 Hz and 1 MHz, electrical resistance (R) and capacitance (C) was analysed. At higher frequencies between 10 MHz and 3 GHz, specific conductivity was measured. Electrical resistance was assessed as real part of impedance and capacitance was calculated from the capacitive reactance (X_C) according to equation (1) where f is a frequency of AC source.

$$C = \frac{1}{2\pi f \cdot X_C} \tag{1}$$

The resistance of the reference sample at 40 Hz is more than four times higher than the resistance of composites with conductive fillers (Figure 2a). However, as the frequency increased its resistance considerably decreased, and for frequencies higher than 100 kHz the differences between all mixtures almost disappeared. The effect of graphite dosage is not so important in further reduction of resistance because the difference of resistance between samples CG2 and CG10 is 5.5× smaller than between reference sample and CG2.

Since differences in resistance at frequencies higher than 1 MHz are too small, specific conductivity was used instead to describe the electrical properties of AAS composites. Specific conductivity of AAS composites versus frequency is depicted in figure 2b where each point was obtained as an average value from 15 independent measurements. The specific conductivity almost linearly rises with increasing AC frequency. It is also obvious that at extremely high frequencies the amount of graphite markedly influenced the specific conductivity. Such increase in specific conductivity is tightly connected with a decrease in polarization effect which in turn leads to an increase of the eddy current [21, 22].

The assessment of percolation threshold was performed at three different AC frequencies (50 Hz, 1 kHz and 10 kHz). Figure 3 shows the dependence of resistance on the amount of graphite admixture. The combination of just 0.1% of CNTs and 2% of graphite decreased the resistance of AAS composite by almost 80%. The percolation threshold can be considered a minimum amount of conductive filler forming 3D network with predominating contacting conduction. Therefore, the effect of further addition of conductive filler on the improvement of electrical properties is diminished. Regardless of the AC frequency the percolation threshold was reached with CG8 mixture because CG10 sample showed no improvement of resistance.

(a)   (b)
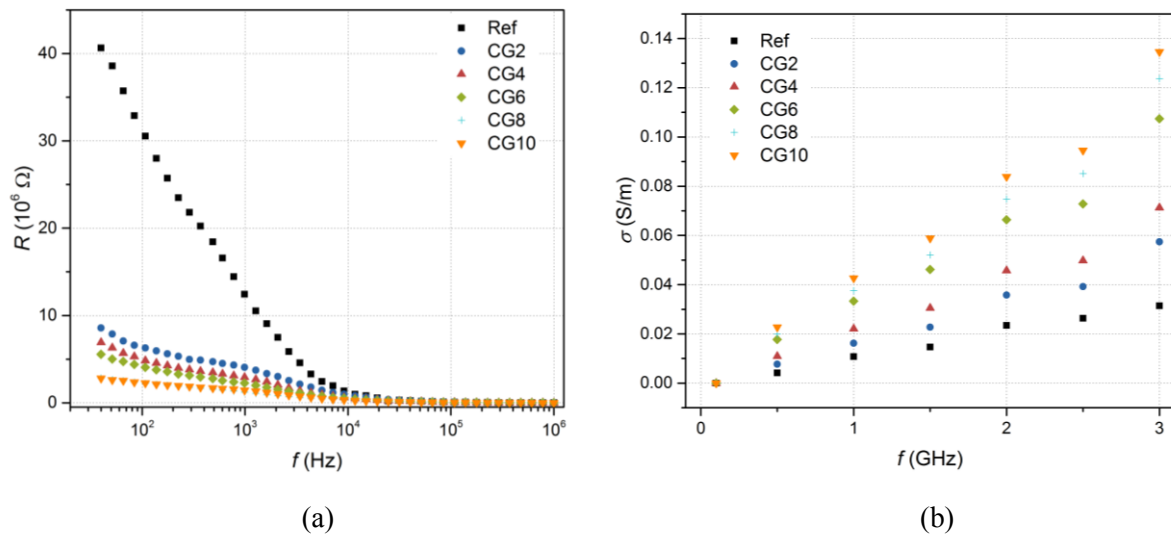
Figure 2. Electrical properties of AAS composites with CNTs and graphite powder: a) resistance in the frequency range of 40 Hz – 1 MHz; b) specific conductivity in the frequency range of 0.01–3 GHz
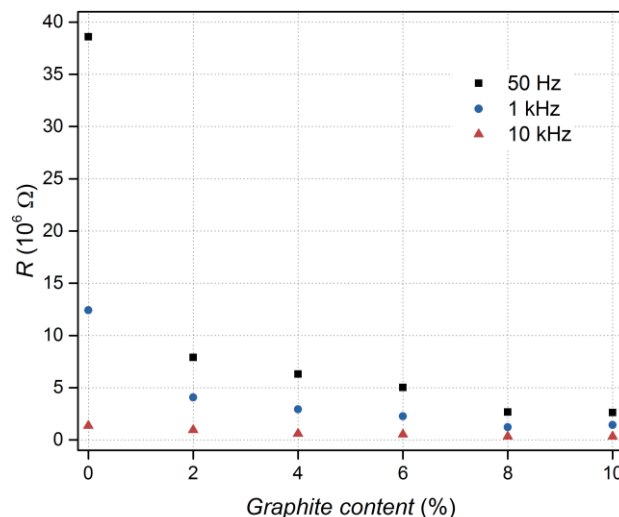
Figure 3. Resistance vs. graphite content measured at 50 Hz, 1 kHz and 10 kHz

Electrical capacitance of tested samples was calculated from measured data and is presented as a function of AC frequency in figure 4a. The capacitance rises with increasing amount of graphite but decreases with frequency. Figure 4b shows the dependence of capacitance on graphite content for different AC frequencies. It is obvious that the increase in capacitance is more remarkable for very low frequency but at higher frequencies the differences between various composite mixtures diminished. In other words, the capacitance is less sensitive to the amount of conductive admixture at higher frequencies. However, similarly to the resistance values there was no difference in capacitance of mixture CG8 and CG10, which is related to the percolation threshold reached with CG8 mixture. The increase in capacitance with increasing amount of conductive admixture is caused by the ability of graphite and CNTs to absorb electrical charge, either as a free charge carrier or by the formation of dipole elements. It is assumed that only isolated graphite particles contribute to the capacitance. At the percolation threshold when the connectivity throughout the specimen is established, no further

addition of graphite particle can increase the capacitance because they are discharged via conduction routes. Therefore, large excess of graphite should result in a decrease in capacitance once again.

(a)   (b)
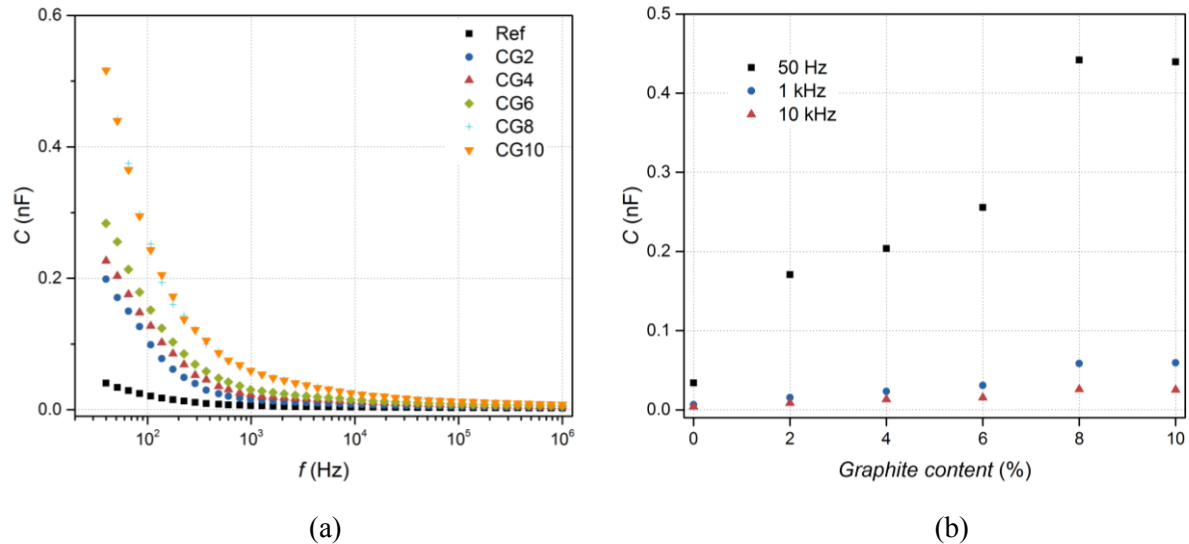
Figure 4. Capacitance of AAS composites with CNTs and graphite powder: a) as a function of frequency of 40 Hz – 1 MHz

*3.2. Mechanical properties and microstructure*

Compressive and flexural strengths of alkali-activated slag composite with CNTs and various amount of graphite powder are presented in figure 5. The compressive strength of the reference AAS mortar was 51 MPa. Although according to the previous results, CNTs at the dosage of 0.1% improve the mechanical properties of AAS [18], addition of graphite caused considerable strength deterioration which can be attributed to increasing water-to-slag ratio and rather soft structure of graphite. This has quite long and weak bonds between parallel carbon layers which are prone to slippage causing the destruction of the sandwich structure when the stress is applied. The results show almost linear decrease in strength with the lowest value of 25 MPa achieved for the mixture CG10 which is 49% of the reference strength. The corresponding flexural strengths were not affected so much and only slight decrease by 1.3 MPa was observed between reference sample and CG10 mixture.
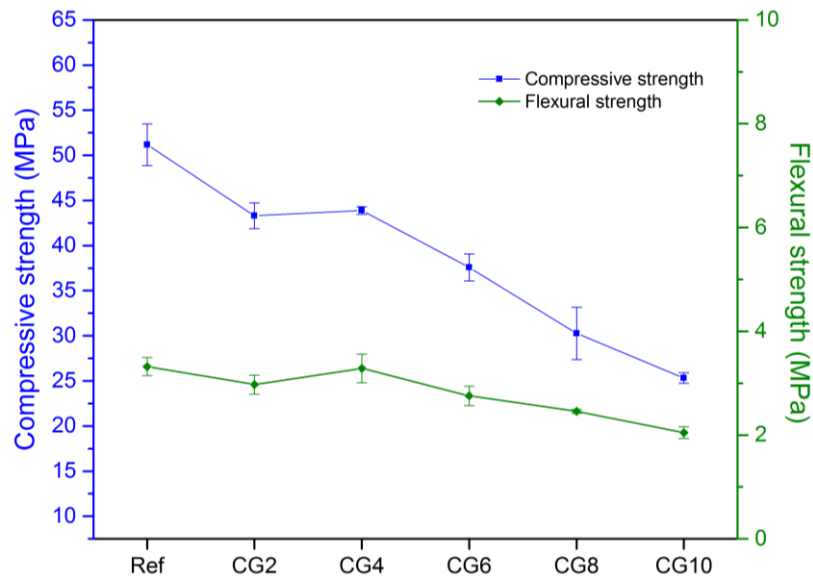
Figure 5. Compressive and flexural strengths of alkali-activated slag composite with CNTs and various amount of graphite powder

Pore system was analysed by means of mercury intrusion porosimetry. Figure 6 shows the cumulative pore volume curves of tested AAS composites. Most of the porosity belongs to large capillary pores ($> 1\ \mu m$) and secondly to the gel pores, which is common for AAS binders. It is obvious that with increasing amount of graphite the porosity increased as well. This can be attributed to two phenomena: increasing amount of mixing water which is necessary to maintain the same workability of all mixes and partial delamination of graphite flakes. The increase in volume of large pores is also responsible for the strength deterioration of the mixtures with higher graphite content.

Morphology of AAS matrix with graphite particles and CNTs presented of figure 7 shows that graphite is not very well bonded to AAS matrix because of its nonpolar character. Therefore, it can be quite easily pulled out from the matrix during the fracture. Carbon nanotubes can be observed at higher magnification (Figure 7b). These are quite well dispersed in the matrix having direct contacts with graphite; thus, enable local contacting conductivity throughout the bulk material.
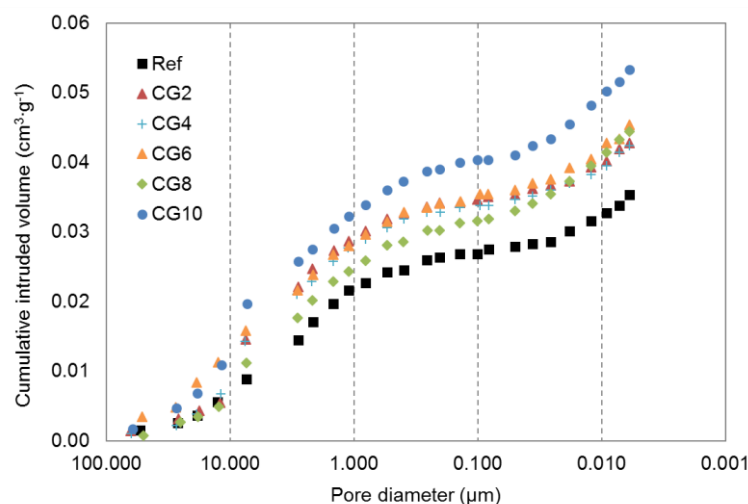
Figure 6. Cumulative pore volume curves of AAS composite with CNTs and various amount of

graphite powder
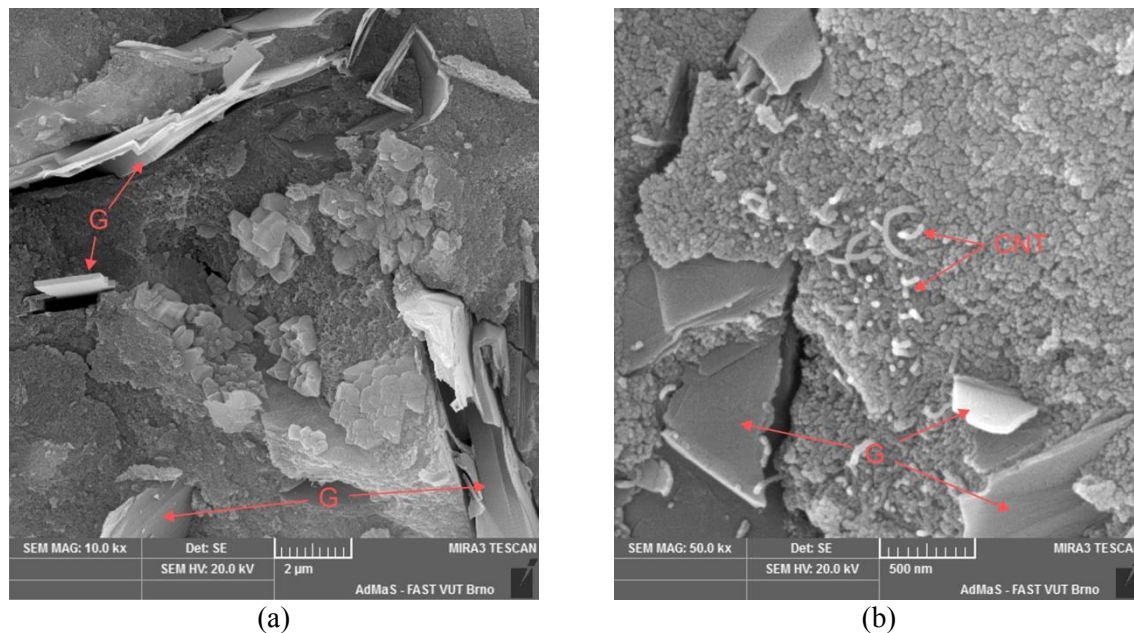
Figure 7. SEM micrographs of CG10 mixture at magnification: a) 10 000×; b) 50 000× – showing graphite (G) and carbon nanotubes (CNT) particles

4. Conclusions

This paper presents an investigation of electrical properties of AAS composite with mixed graphite/CNT conductive filler. Electrical resistance decreased with increasing amount of graphite powder as well as increasing frequency of AC source. Mixture of just 0.1% of CNTs and 2% of graphite can reduce the resistivity by 80% at 50 Hz and by 67% at 1 kHz, respectively. According to the results from the measurement of electrical resistance the percolation threshold was achieved for the mixture containing 8% of graphite filler because with larger amount of graphite no further improvement was reached. Contrary to the resistance, electrical capacitance increased with addition of conductive filler because both graphite and CNTs are capable of charge absorption. However, at the percolation threshold the capacitance reached its maximum because the established conduction routes enable discharging of non-isolated particles.

The addition of graphite to AAS mortars led to the deterioration in compressive strength, which can be attributed mainly to increased demand of mixing water and consequently to increased porosity of AAS composite. However, only minor influence on flexural strength was observed mainly due to the reinforcing effect of CNTs.

This study is a part of a complex project devoted to an enhancement of electrical properties of AAS composites and the results can be used in designing new sorts of materials having self-sensing properties. Since the best sensing properties can be achieved below percolation threshold, the maximum amount of conductive graphite filler which is still suitable for the application in self-sensing alkali-activated slag materials is 6%.

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