PAPER • OPEN ACCESS

Impedance spectroscopy measurement of metakaolin-based alkali-activated building materials

To cite this article: I Kusak *et al* 2021 *IOP Conf. Ser.: Mater. Sci. Eng.* **1039** 012020

IOP Conf. Series: Materials Science and Engineering 1039 (2021) 012020 doi:10.1088/1757-899X/1039/1/012020

Impedance spectroscopy measurement of metakaolin-based alkali-activated building materials

I Kusak[1,2], M Lunak[1], C Mizerova[2] and P Rovnanik[2]

[1] Institute of Physics, Faculty of Civil Engineering, Brno University of Technology, Veveri 95, 602 00 Brno, Czech Republic
[2] Institute of Chemistry, Faculty of Civil Engineering, Brno University of Technology, Veveri 95, 602 00 Brno, Czech Republic

Email: kusak.i@fce.vutbr.cz

Abstract. Cement-containing as well as cement-free building materials are regarded as dielectrics. Therefore, electrically conducting admixtures are to be added to them in order to increase their electrical conductivity. Steel or carbon fibres, metal powder, graphite, carbon soot or carbon nanotubes are commonly used for this purpose. The conductivity increase offers new application options, such as sensor property materials, self-heated materials, or electromagnetic smog shielding materials. The specimens of the mixes to be studied were subjected to an electrical analysis carried out within the frequency range from 100 MHz to 3 GHz by means of an ZNC vector analyser and an SPEAG-made DAK-12 coaxial probe and, furthermore, a dedicated automatically measuring device operating within the frequency range from 40 Hz to 1 MHz. The frequency spectra of interest were measured on various copolymer specimens differing from each other by the content of graphite and carbon nanotubes. Higher content of these admixtures increases the electrical conductivity and the building materials thus become easier to measure by means of electromagnetic measuring methods.

1. Introduction

The development and the study of cement-containing as well as cement-free composites featuring increased electrical conductivity can be noticed, above all, during the recent two decades. The research focuses mainly on the behaviour of materials in electric fields, both DC and variable frequency AC ones, and also on the determination of the material properties which are closely related to the electrical conductivity change [1–3]. Water glass, NaOH and Na_2CO_3 is most frequently used as alkali activator. As far as their mechanical properties are concerned, the alkali-activated materials are comparable with the PC (Portland cement), particularly in the cases where the water glass is used as activator. These materials also feature better endurance, better resistance against aggressive environment, better frost resistance and lower amount of hydration heat released. Among their most important drawbacks there are the high autogenous as well as dry-up-related shrinkage, which is particularly characteristic for activators in the form of water-glass. If NaOH and Na_2CO_3 are used, their shrinkage is similar to that of PC [4].

Our results show that the application of carbon nanotubes in materials results in improving their strength, elasticity and a general durability [5] The nanotubes feature a low density (1.3-1.4 $g \cdot cm^{-3}$ depending on the nanotube type), a high thermal conductivity (1 750 to 5 800 $W \cdot m^{-1} K^{-1}$) and – thanks to delocalized bonds along the entire carbon layer – 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 fibers [5, 6]. The research results also show that high length-to-diameter-ratio fibrous fillers can change the concrete detachable capabilities at considerably lower concentrations than the particulate ones. However, attention is to be paid to the dispersion of fibrous fillers in comparison with the particulate ones, as the fibrous fillers are more difficult to disperse and easier to damage during the manufacture process [7].

2. Experiment setup

Following materials were used to prepare the graphite-admixture (MKG: metakaolin-graphite) test specimens: Mefisto K05 metakaolin, PMM 11 graphite powder, sodium water glass ($M_S = Na_2O/SiO_2 = 1.6$), PG1-3 normalized quartz sand, Triton X-100 ion-free detergent (2% solution), Lukosan S defoaming additive (1% solution) and water. First, PMM 11 graphite powder, Triton X-100 and a part of the water amount were added to the water glass. This mix was stirred in a mixer for three minutes. Subsequently, metakaolin (Mefisto K05), the remaining amount of water and 3 filler gradings (PG1-3 sand) were added. Finally, Lukosan S defoamer was added. From each of eight mixes with different graphite content, a set of three bodies of dimensions 40 × 40 × 160 mm each was made. Once the specimens were demoulded, they were wrapped in a foil and deposited in the laboratory for a period of 28 days. Subsequently, the specimens were dried up at a temperature of 105°C until their constant mass was reached. The measurement results are compared with those obtained on reference formula, graphite-powder-free specimens.

Following materials were used to prepare the test specimens with carbon nanotubes added (MKCNT: metakaolin-carbon nanotubes): Mefisto K05 metakaolin, carbon nanotubes (CNTs), Graphistrength CW2-45 (1% solution), sodium water glass ($M_S = Na_2O/SiO_2 = 1.6$), PG1-3 normalized quartz sand and water.

Table 1. Composition of graphite-added mixes (MKG).

	REF	G2	G4	G5	G6	G8	G10	G12	G15
Metakaolin (g)	350	350	350	350	350	350	350	350	350
Sodium silicate (g)	350	350	350	350	350	350	350	350	350
Graphite powder (g)	-	7	14	17.5	21	28	35	42	52.5
Sand (g)	1 050	1 050	1 050	1 050	1 050	1 050	1 050	1 050	1 050
Triton 2 % (ml)	-	7	14	17.5	21	28	35	42	52.5
Lukosan S 1 % (ml)	-	3	3	3	3	3	6	6	6
Water (g)	120	130	137	146	164	181	196	216	242

Table 2. Composition of carbon-nanotube added mixes (MKCNT).

	REF	CNT0.05	CNT0.10	CNT0.15	CNT0.20
Metakaolin (g)	350	350	350	350	350
Sodium silicate (g)	350	350	350	350	350
Sand (g)	1 050	1 050	1 050	1 050	1 050
CNTs solution 1 % (g)	-	17.5	35	52.5	70
Water (g)	120	102.5	85	67.5	50

First, a CNT suspension (1% CNT solution) and water were added to the water glass. This mix was stirred in a mixer for three minutes. Subsequently, metakaolin and 3 filler gradings (PG1-3 sand) were added to it. From each of the four mixes with different graphite content, a set of three bodies of dimensions 40 × 40 × 160 mm each was made. Once the specimens had been demoulded, they were wrapped in a foil and deposited in the laboratory for a period of 28 days. Subsequently, the specimens were dried up at a temperature of 105°C until their constant mass was reached. The measurement results are compared with those obtained from a reference formula specimen, which is CNT-free.

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

The prepared samples were characterized by impedance spectroscopy in the range of 40 Hz to 1 MHz using an Agilent 33220A sinusoidal signal generator and an Agilent 54645A dual-channel oscilloscope. The output voltage of the signal generator was 5.5 V. The input values of the electrical capacitance and the resistance of the oscilloscope were 13 pF and 1 MΩ, respectively. These instruments were assembled for fully automated measurement. In order to perform impedance analysis, the prismatic specimens were placed between parallel brass plate electrodes (30 × 100 mm) so that the distance between the electrodes was 40 mm (figure 1.) [7].

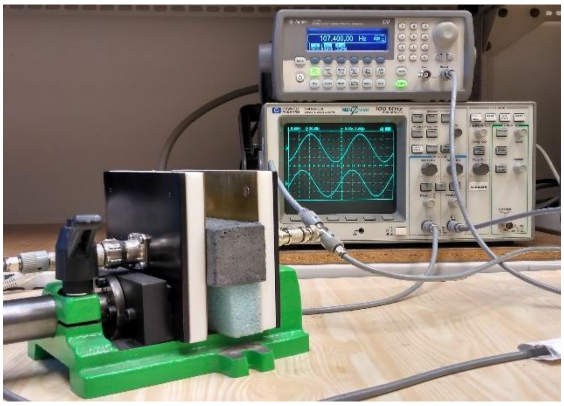

Figure 1. Experiment arrangement.

For higher range of frequencies, 100 MHz up to 3 GHz, R&S ZNC vector analyzer with DAK 12 coaxial probe manufactured by Speag was used. In this frequency spectrum the electrical conductivity and relative permittivity as a function of frequency have been measured.

3. Results

The Speag touch probe supplemented high-frequency analyzer has determined the specimen permittivity real components in the frequency range of 500 MHz to 3 GHz. For the reference specimens, the permittivity values begin at the value of about 2.3 at the lowest frequencies. When the frequency increases, they rise up to 2.8. Due to the CNT addition (figure 3), the permittivity levels grow up, whereas the curves for 0.05 and 0.1 additions intertwine with each other. The highest permittivity values, almost 3.5, were reached on specimens containing 0.2 CNT.

The specimens to which only graphite powder was added show elevated permittivity values, too (figure 2), reaching as much as 4.8. The lower permittivity values of carbon nanotube-added specimens are apparently due to the intertwined structure of the nanotube incorporation in the matrix, while the amount of isolated particles accountable for polarization effects is lower. The graphite powder containing specimens appear to contain more metakaolin-isolated particles, showing a polarization capability in the frequency range from 500 MHz to 3 GHz.

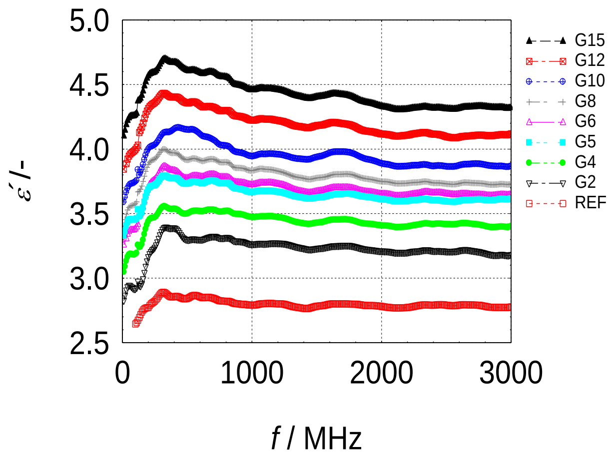

Figure 2. Permittivity real components for graphite-added specimens, as measured by means of Speag probe.

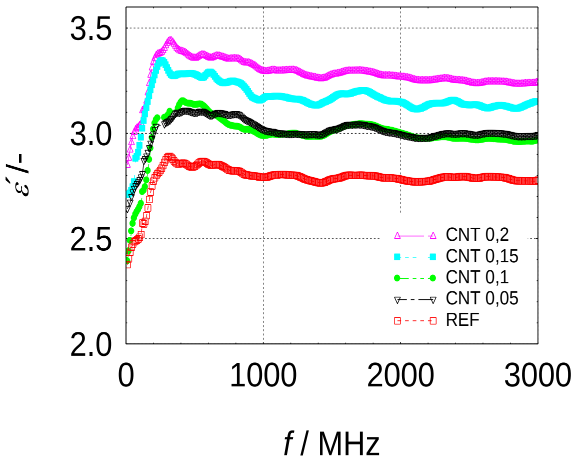

Figure 3. Permittivity real components for CNT-added specimens, as measured by means of Speag probe.

Different trends in the electric capacitance curves obtained by the impedance spectroscopy methods are observed in the lower frequency range from 40 Hz to 1 MHz. The capacitance of graphite-added specimens (figure 4) goes down, when the graphite amount grows up throughout almost the entire frequency range. The curves intertwine from G8 to G15, however, from 100 kHz upwards, the capacitance rises with the addition of G12, G15. The measurements results obtained in this frequency range (100 kHz to 1 MHz) are affected by a higher measurement error. Therefore, we do not attach relevance to them for the time being.

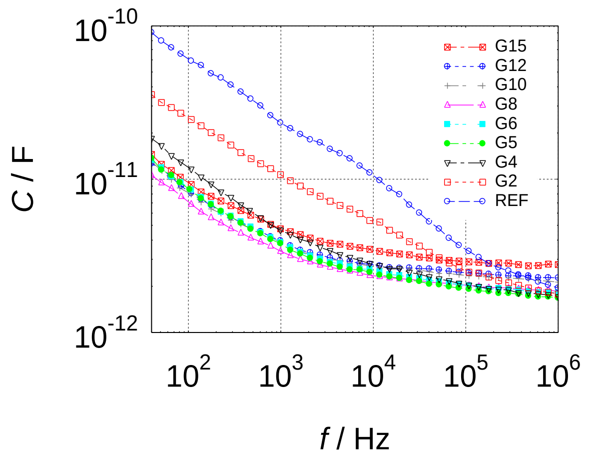

Figure 4. Capacitance of graphite-added specimens as measured by impedance spectroscopy method.

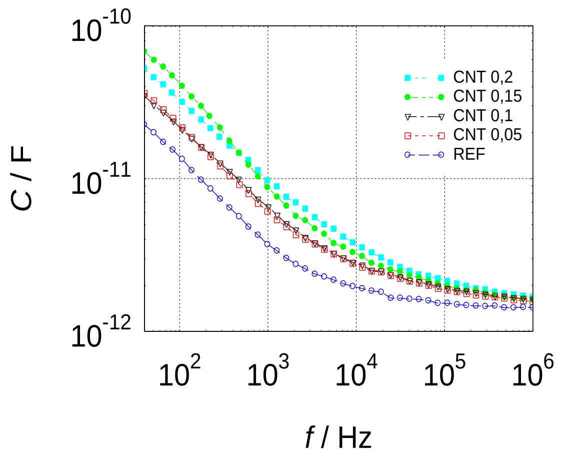

Figure 5. Capacitance of CNT-added specimens as measured by impedance spectroscopy method.

As expected for the carbon-nanotube-added specimens (figure 5), the capacitance grows up with increasing the amount of the nano-material in the specimen.

The unexpected capacitance fall shown by graphite-added specimens is explained by drying up the specimens containing metakaolin, which, as such, is predominantly composed of aluminium and silicon oxides. Due to the drying, conducting paths between carbon particles as well as possible conducting paths for ions in the matrix have disappeared. Absence of water thwarts the polarization in the low frequency range for the specimens used.

The electrical resistance of graphite-added specimens, as determined by means of the impedance spectroscopy method (figure 6), ranged from 100 MΩ at the lowest frequencies up to 10 kΩ in the 1 MHz region. The resistance spectra of graphite-added specimens grow up with the graphite content from 40 Hz to 10 kHz. At higher frequencies, the spectra intertwine, but the subsequent spectrum part is affected by a considerable measurement error. Prior to the measurements, the specimens were dried up. Together with the metakaolin, the graphite prevents the specimens from fast re-moistening. The specimens show a high DC resistance outwardly. For CNT specimens, the trend is reversed. Carbon nanotubes make the specimen electric resistance decrease (figure 7), the respective values being of the same order as those of the spectra of figure 6. The CNT strings create conducting paths in the metakaolin matrix, however, to a lesser extent. Compared to the resistance values for cement paste [7], the values of resistance were lower. It is not appropriate to compare the results of this article with [7], our recipes and results are new and original.

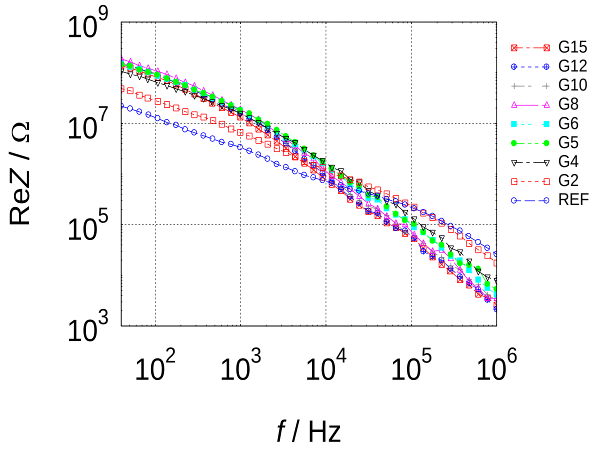

Figure 6. Impedance real component of graphite-added specimens as measured by impedance spectroscopy method.

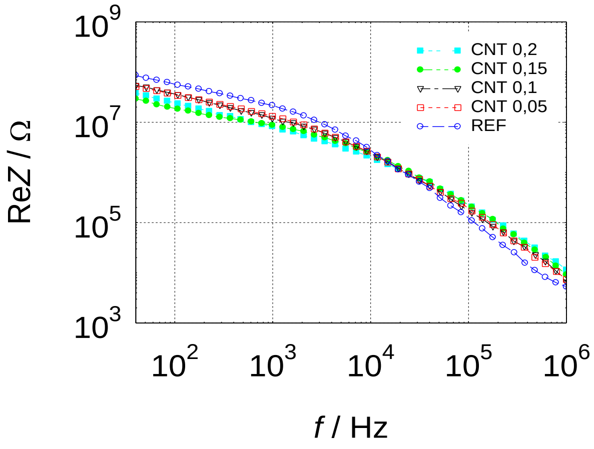

Figure 7. Impedance real component of CNT-added specimens as measured by impedance spectroscopy method.

4. Conclusion

The present paper deals with the change of electric parameters of metakaolin-based alkali-activated mixes. Graphite and carbon nanotubes were added to the different mixes. The electric conductivity of the materials in question is improved, which makes them easier to measure by electromagnetic-principle-based methods.

The metakaolin-based specimens have been measured by means of the impedance spectroscopy method in the low-frequency region and by means of a vector analyzer with a touch probe in the high frequency region. The graphite-added and CNT-added specimens featured a high electric resistance, corresponding to the specimen drying up and, in spite of several-day-storage in laboratory environment, a negligible wetting, which would improve the measurability of electrical quantities.

Pronounced changes in the spectra have been found out when the coaxial probe was used in the frequency region from 0.5 GHz to 3 GHz. The composition of metakaolin specimens and the matrix low moisture make it difficult to measure the conductivity of relatively big size specimens. Capacitance measurements using short electrode distances appear to be more convenient.

Acknowledgments

This paper has been worked out under the project GAČR No. 19-11516S supported by Czech Science Foundation.

References

[1] Han B, Ding S and Yu X 2015 *A review, Measurement* **59** pp 110–128
[2] Hou Z, Li Z and Wang J 2007 J *Wuhan Uni. Technol.-Mater. Sci. Ed.* **22** pp 346–349
[3] Guan H, Liu S, Duan Y and Cheng J 2006 *Cem. Concr. Compos.* **28** pp 468–474
[4] Fernandez-Jimenez A 1999 *Cement Concrete Res.* **29** p 1313
[5] Saafi M, Andrew K, Mcghon D, Taylor S, Rahman M, Yang S, Zhou X and Tang P L 2013 *Construction and Building Materials* **49** pp 46–55
[6] Ding Y, Chen Z, Han Z, Zhang Y and Pacheco-Torgal F 2013 *Constr. Build. Mater.* **43** p 233
[7] Rovnanik P, Kusak I, Bayer P, Schmid P and Fiala L 2019 *Cement and Concrete Research* **118 No. 1** pp 84–91
[8] Cabeza M, Merino P, Miranda A, Novoa X R and Sanchez I 2002 *Cement and Concrete Research* **32** pp 881–891
[9] Li GY, Wang P M and Zhao X H 2007 *Cem. Concr. Compos*. **29** pp 377–382
[10] Kusak I, Lunak M and Schauer P 2013 *Appl. Mech. Mater*. **248** p 370