AC electrical properties of geopolymers with carbon black admixture

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Abstract. Geopolymers as competitors to the cement-based construction materials are intensively studied in the present. Their competitiveness mainly arises from their high strength, favourable development of hydration heat at early age, good chemical resistance and thermal stability. Further qualitative improvement of functional properties can be achieved by adding electrically conductive admixtures. In an appropriate amount (called percolation threshold), mechanical properties remain reasonable and electrical properties become sufficient to ensure evolution of heat by acting of an external power source (self-heating), to detect material damage (self-sensing) or to harvest thermoelectric energy (energy harvesting). In this paper three geopolymers with different dosages of carbon black (CB) admixture (0 wt. %, 4 wt. %, 10 wt. %) were studied by means of LCR bridge AC measurements. It was observed significant difference in electrical behavior of the studied geopolymers. 0 wt. % geopolymer exhibited highly capacitive character, 4 wt. % geopolymer was slightly shifted to resistive behavior and 10 wt. % geopolymer behaved like resistor even to high frequencies with reasonable resistance which indicates its possible self-heating ability.

1. Introduction
Geopolymers are inorganic materials based on various aluminosilicate-rich precursors that in order to gain sufficient mechanical properties need to be activated by alkalis. Strength can be comparable or even higher than of the cement-based materials when an appropriate precursor and activator is used. Together with good behaviour at high temperatures [1], good durability characteristics [2], and the fact that precursors are very often of waste nature [3], such materials can be considered as good competitors to the cement-based materials with lower impact to environment [3].

The type of precursor determines material structure that is formed during hydration and influences material properties of the formed geopolymer. In high-calcium systems (blast-furnace slag), typically C-A-S-H structures are formed [4], whereas in low-calcium systems (fly-ash, metakaolin, clay), N-A-S-H type gels appears [5]. However, both, C-A-S-H and N-A-S-H type geopolymers are typical electrical insulators which is a limiting factor for their utilization in smart applications in building industry. Such deficiency can be solved by addition of electrically conductive admixtures (ECA), such as steel fibres (SF), carbon fibres (CF), carbon black (CB), nickel powder (NP) or graphite powder (GP), that in appropriate amount ensures self-heating [6], self-sensing [7] or energy harvesting ability [8] of the enhanced composites.
Research presented in this paper was focused on determination of AC electrical properties of geopolymers based on high-calcium granulated blast-furnace slag electrically enhanced by CB. Such ECA consisting of aggregated spherical particles with high surface area was used in three different dosages in order to prepare composites with different electrical properties. AC electrical properties were determined in the frequency range of 10 Hz – 300 kHz and acquired functional properties were compared in terms of the materials applicability in sophisticated applications.

2. Experimental
The studied geopolymers were based on high-calcium precursor, alkali activator, filler and ECA. Precursor was represented by granulated blast-furnace slag with fineness of 380 m² kg⁻¹, SMŠ 380 (Kotouč Štramberk Ltd.) which is an industrial by-product of iron production with high calcium content (39.8 %). Alkali activation was carried out using water glass (sodium silicate solution, molar ratio Na₂O/SiO₂ = 2.07). Filler was represented by three normalized CEN fractions of quartz sand (fine aggregates: PG1, PG2, PG3) produced by Filtrační písky, Ltd. complying with ČSN EN 196-1. The reference samples were prepared for comparison of materials properties with the electrically enhanced ones. Enhancement of electrical properties of samples was secured by 5 % and 15 % CB suspension CS CABOT VULCAN 7H in amount of 4 wt. % and 10 wt. %.

VULCAN 7H is manufactured by thermal cracking of a heavy aromatic feedstock in a hot flame. Oil is a typical feedstock that is injected into a hot flame zone in oil furnace where present hydrocarbons are cracked to carbon and hydrogen by means of quenching the flame by water. It is mainly used in tires production and industrial rubber product applications, but for its to high surface area and reasonable high electrical conductivity, it can be effectively used for optimization of electrical properties of polymers [9] and inorganic building materials [10].

Consistence of the fresh mixtures was tested in terms of ČSN EN 1015-3 standard (Determination of Consistence of Fresh Mortar by flow table) and kept at the same, reasonable level to attain good workability of the mixtures. Water-slag ratio of the mixtures with the consistence (average base diameter equal to 160 mm) was equal to 0.44 (CB 0 wt. %), 0.65 (CB 4 wt. %) and 0.88 (10 wt. %). Composition of the studied materials is presented in Table 1.

| Component [g] / Mixture | 0 wt. % CB | 4 wt. % CB | 10 wt. % CB |
|-------------------------|------------|------------|-------------|
| Slag                    | 1170       | 1170       | 1170        |
| Water glass             | 234        | 234        | 234         |
| Sand                    | 3 × 1170   | 3 × 1170   | 3 × 1170    |
| Water                   | 520        | 759.2      | 1027        |
| Carbon black            | 0          | 46.8       | 117         |

The bulk density was determined on samples with dimensions (50 × 50 × 50) mm³ by gravimetric method.

AC electrical properties represented by the absolute value of impedance |Z| [Ω], the phase angle \( \theta \) [°], the resistance \( R \) [Ω] and the reactance \( X \) [Ω], were experimentally determined on samples with dimensions (50 × 50 × 50) mm³ (Figure 1a) by LCR bridge GW Instek LCR-6300. Such device provides precise measurements of AC electrical properties in the frequency range of 10 Hz – 300 kHz. Two opposite lateral sides of the samples were first painted by conductive carbon paint and pasted by copper tapes in order to gain good contact of the samples with measuring device (Figure 1b). Measurements were carried out at voltage level 1V at wide frequency range: 10 Hz, 50 Hz, 60 Hz,
100 Hz, 120 Hz, 1 kHz, 2 kHz, 10 kHz, 20 kHz, 40 kHz, 50 kHz, 100 kHz, 200 kHz, 250 kHz and 300 kHz, respectively.

Figure 1. a) Measuring LCR bridge b) Samples for measurements of electrical properties.

3. Results and discussion

The bulk density of the studied geopolymers were equal to 2278 kg·m\(^{-3}\) (0 wt. % CB), 2070 kg·m\(^{-3}\) (4 wt. % CB) and 2004 kg·m\(^{-3}\) (10 wt. % CB), respectively. Decrease in the bulk density with an increasing amount of CB admixture was due to an increase in porosity influenced by increase of the water-slag ratio.

In Figure 2 and Figure 3, the absolute value of impedance and the phase angle dependence on the frequency are presented. It was observed considerable decrease of the absolute value of impedance on increasing amount of CB admixture. Comparing the absolute value of impedance of 0 wt. % CB and 10 wt. % CB, the difference was more than three orders of magnitude for low frequencies and about two orders of magnitude for high frequencies. In case of 0 wt. % CB and 4 wt. % CB, the absolute value of impedance decreased about two and one order of magnitude, respectively, with increasing frequency. 10 wt. % CB did not exhibit any significant change. Concerning the phase angle on the frequency dependence, it was nearly constant for 10 wt. % CB in the whole frequency spectrum with the values close to the zero value which exhibit resistive character of such material. Both, 0 wt. % CB and 4 wt. % CB exhibited increasing capacitive behavior with increasing frequency (\(\approx 90^\circ\) - ideal capacitor, \(0^\circ\) - ideal resistor).
In Figure 4 and Figure 5, the resistance and the reactance dependence on the frequency are presented. Results were significantly lower for 10 wt. % CB in comparison with the other two geopolymers. The resistance was almost constant for 10 wt. % CB, whereas for 0 wt. % CB and 4 wt. % CB it was significantly frequency dependent. Reactance which is not participating in heat evolution was in the range from the fourth to the sixth order of magnitude for 0 wt. % CB and 4 wt. % CB which was significantly higher compared to the 10 wt. % CB (first or second order of magnitude). Reactance of all the geopolymers were frequency dependent.
Figure 4. Dependence of the resistance on the frequency.

Figure 5. Dependence of the reactance on the frequency.

4. Conclusions
The paper is focused on experimental determination of AC electrical properties of three geopolymers with different dosages of CB admixture (0 wt. %, 4 wt. %, 10 wt. %). Measurements were carried out in frequency range 10 Hz – 300 kHz by LCR bridge GW Instek LCR-6300.
It was observed distinctly capacitive character of the geopolymer without CB admixture, slight transition to the resistive behavior of the geopolymer with 4 wt. % of CB admixture and distinctly resistive character of the geopolymer with 10 wt. % of CB admixture. Capacitive character and high resistance of the reference geopolymer does not allow to evolve heat using the external power source. In case of geopolymer with 4 wt. % of CB admixture, the resistance is slightly lower compared to the reference material but still pretty high which is not a favor assumption for evolution of heat. Geopolymer with 10 wt. % of CB admixture is due to its resistive character and reasonably high resistance promising candidate for self-heating applications.

With respect to the presented results, future observations will be devoted to further electrical analysis of geopolymers with various electrically conductive admixtures together with comparison of their self-heating ability under DC and AC electric field load.

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