Testing methods of various materials for development of cement composites with low electrical resistance

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Abstract. Our entire planet is filled by communication routes, and as a result of the evolving information technologies, their numbers will continue to grow in the future. Demand for their reliability and hence the importance of protecting related technologies from all kinds of interference is increasing as well. Therefore, it is necessary to develop new materials in order to protect these routes against negative influences of the environment such as the atmospheric discharge. The main aim of the research is to develop and verify the properties of the cement composite that can be applied in systems of protection of building structures against lightning strike and overvoltage. The first step in the development of this material was the selection of suitable feedstocks, which by their presence in the newly developed material will increase its electrical conductivity respectively reduce its electric impedance. For this purpose, a spectrum of potential raw materials with a high content of metals and organic carbon was chosen. By means of a suitably selected set of laboratory methods which consisted of determination of specific surface, impedance and total organic carbon content (TOC), materials with the most suitable properties were selected and their parameters determined also in a cement matrix. In order to realize this goal specimens with each conducive material as filler were created with incorporated copper electrodes. Impedance has been significantly reduced compared to the reference samples. The lowest values in the tens of ohms were obtained from samples containing carbon grit 0.5–4.0. This fact proves that the tested fillers can be used in order to produce electrically conductive cement composites.

1. Introduction

In the vast majority of industries, environmental awareness has recently taken place as a result of changing waste management regulations. By 2020, the recycling rate should have increased to 50%. In 2024, an amendment to the Act, passed in 2014, will come into force, banning the storage of municipal and recyclable waste. Therefore, it is not only necessary to reduce the production of unnecessarily generated waste, but also to invent recovery for waste substances generated as by-products of some production and energy processes. Search for applications for waste products and the use of secondary raw materials is an even more important task now than ever. [1]

The current trend is the development of modern composite materials, the aim of which is to expand the number of functions that the materials can simultaneously perform. The appropriately chosen secondary raw materials could play an important role in the development of electrically conductive composites, which could not only significantly shift the area of pre-stress protection of buildings against...
lightning and overvoltage, but also its production should mean lower environmental burden and economic demands. [2]

Lightning and surge protection systems for buildings can be extended by use of the special materials mentioned above. Even a completely new functioning lightning and surge protection system based exclusively on the use of advanced composite materials can be developed. The system could not only be more functional in terms of lightning discharge, but also economically and environmentally acceptable. [3]

The aim of the research described in this paper is to develop new silicate composites capable of conducting electrical current to such extent that it will be possible to apply them in lightning protection or overvoltage protection systems due to the use of suitable electrically conductive fillers mainly from secondary sources. The subject of this article is the study of raw materials with the potential of the above mentioned parameters.

Resistivity of metals is in the values of 10⁻⁶ ohm·cm⁻¹ (silver, copper, aluminium, steel). The conductive composite material is prepared by admixing fine conductive particles into the cement matrix. It has been found that the conductivity of the composite increases sharply when a certain filler concentration value is reached, at which moment each particle in the matrix contacts at least two other adjacent particles, thereby forming a three-dimensional network in the matrix. This critical value is called the percolation threshold and is often expressed in the literature as the volume fraction of filler in the matrix. By increasing the filler concentration further above the critical limit, the resistivity does not decrease in proportion to the filler addition. [4]

As a possible filler for increasing the electrical conductivity of silicate building materials has been tested various materials, such as carbon fibres and steel shavings. [1] In other research graphite powder, steel powder and aluminium chip or steel fibres and graphites were tested in order to increase the electrical conductivity of concrete. [2, 3]

The percolation threshold also depends on the shape of the filler particles. An important aspect is the aspect ratio. Fibres or flakes with a large length to diameter (thickness) ratio have a much lower percolation threshold (less than 6 to 8 vol. %). The electrical conductivity can be reduced by an oxide layer covering some metals such as copper or aluminium. [5]

The addition of conductive or semiconductive particles to the non-conducting matrix affects the electrical properties in proportion to the amount, proximity and shape of the particles. The following three situations may occur with the additive particles:

- The particles do not touch – the particles are isolated from each other, the conductivity of the mixture changes only slightly or not at all. The composite material remains an insulator / non-conductor, but its dielectric properties vary significantly.
- Particles are very close to each other – electrons can jump the gaps between particles and allow the passage of electric current. The possibility of electron jump across the gap under a given (electrical) voltage increases exponentially with decreasing gap width between particles.
- Particles are touching – under these conditions the composite conducts electrical current through a network of conductive filler particles. The conductivity mechanism of the filler is applied here. Metal filler composites exhibit band conductivity. The band and flashover conductivity can be distinguished according to the AC or DC current behavior of the composite.

2. Materials and methods
The initial step in solving the issue was selection of a potentially appropriate raw material base. It contains both a binder component (Portland cement CEM I 42.5) and filler components. The filler components were expected to increase the electrical conductivity of the resulting mixtures. Therefore, it is important to conduct analysis and tests to determine the basic properties of the fillers under consideration.

Among the potentially suitable electrically conductive fillers were selected three types of carbon grit (UD N 0-2, UD N 0.5-4.0 and UD S 0.4-4.0) pictured in figure 1, solid salts and solutions containing heavy metals (PSK), Cooling Belt Dusts (OCP), Zirconium Waste Tablets (ZrO₂), Wood Pellet Pyrolysis
Waste (OPD) and as potentially suitable additives soot CHEZACARB and Carbon Black (CABOT) pictured in figure 2.

Figure 1. Three types of carbon grits (left to right: S 0.4–4.0; N 0–2; N 0.5–4.0).

Figure 2. Other types of potentially suitable fillers and additives (a – PSK, b – OCP, c – ZrO₂, d – OPD, e – CHEZACARB, f – CABOT).

In order to determine the required parameters and to choose the most suitable raw materials, a spectrum of laboratory methods was developed consisting of the determination of electrical conductivity (or rather impedance), specific surface area and total organic carbon content (TOC method).

In order to determine the electrical impedance, the sample was firstly loaded in the TRYSTOM press with a force of 10 kN (16 MPa). Impedance spectroscopy was measured for each pressure in the frequency range 1 MHz – 0.1 Hz and for potential values of 1, 10, 50 and 100 mV. The impedance value is read at 1 kHz. The thickness of the sample is calculated by first measuring the distance of the plates of the press with inserted measuring piston without the measured material, and then measuring the distance of the plates of the press with inserted measuring piston in which the measured material is already placed. From the difference of these distances, the thickness of the sample is
determined, and the specific conductivity of the material is calculated from the measured impedance values. [6] The realization of testing method is pictured in figure 3.

Figure 3. Procedure of impedance determination of individual raw materials.

The specific surface of the raw materials was determined using an AccuPyc II 1340 helium pycnometer. It is a very accurate method of measuring by varying the volume of helium (or other gas). [7]

The method for determining the total organic carbon content was based on the thermal and catalytic oxidation of organically bound carbon to CO₂, which was analytically determined, most often by analysis in the infrared region. [8]

![Diagram of placement of copper electrodes in the sample.](image)

Figure 4. Diagram of placement of copper electrodes in the sample.

![Test samples with four selected fillers](image)

Figure 5. Test samples with four selected fillers (a – UD S 0.4–4.0; b – UD N 0-2; c – UD N 0.5–4.0; d – OCP).

3. Results and discussion

From the obtained results it is evident that the fillers PSK, ZrO₂ and OPD exhibited insufficient impedance values and will not be considered in the further research. Filler OCP and all three types
of carbon grit reached impedance values lower than 0.5 Ω and therefore their properties in cement matrix were further tested. For each type of filler, three beams of 40 × 40 × 160 mm were built with built-in electrodes as shown in figure 4. The composition of the mixture was 30% Portland CEM I 42.5 and 70% of the individual filler. Three test specimens (figure 5) were prepared from each material and their impedance determined. Both types of soot tested also appear to be perspective for further research. Table 1 shows the results of laboratory tests.

**Table 1. Results of analysis of tested fillers.**

| Filler     | Specific surface [cm²/g] | Impedance [Ω] (1 kHz, 10 kN) | TOC [%] |
|------------|--------------------------|-------------------------------|---------|
| UD S 0.4–4.0 | 230                      | 0.002                         | 97.12   |
| UD N 0–2   | 520                      | 0.31                          | 98.10   |
| UD N 0.5–4.0 | 220                      | 0.009                         | 98.21   |
| PSK        | 770                      | 12000000                      | 0.81    |
| OCP        | 2560                     | 0.38                          | 1.41    |
| ZrO₂       | immeasurable             | 11000000                      | 0.0033  |
| OPD        | 740                      | 280.0                         | 61.37   |
| CABOT      | immeasurable             | 0.003                         | 99.20   |
| CHEZACARB  | immeasurable             | 0.022                         | 98.76   |

During the measurements, the influence of the AC current frequency and the effect of the magnitude of the measuring voltage were monitored so that the magnitude of the measuring voltage and current is not on the limits of measurability. The impedance spectroscopy graph proved that at 1 kHz the impedance stabilized and could be considered steady. At this frequency, the real and imaginary components of the impedance have already stabilized. The measurement was carried out using an Agilent E4980 RLC meter (figure 6).

**Figure 6. Impedance measurement by device Agilent LCR E4980A.**

The resulting impedance values of the individual mixtures after drying the bodies to constant weight and stabilizing the obtained values are given in table 2 below.
Table 2. Results of impedance determination of test specimens.

| Mixture     | Impedance [Ω] |
|-------------|---------------|
| UD S 0.4–4.0| 140.8         |
| UD N 0–2    | 9·10⁶         |
| UD N 0.5–4.0| 31.9          |
| OCP         | 272.3·10³     |

4. Conclusion
In the development of new silicate composites capable of conducting electric current, a spectrum of materials has been assembled, mainly from secondary sources, which should help this goal. The materials were chosen on the basis of the high proportions of metals or organic carbon in their structure. Their parameters were determined by laboratory methods and four fillers with the best parameters were chosen for further testing. Suitable fillers were selected mainly on the basis of their electrical impedance values. The impedance values of the selected materials were then verified also in the cement matrix. The final results show that the resistivity, respectively electrical impedance, has been reduced to very low values, thus proving that by usage of the tested fillers (especially UD S 0.4–4.0 and UD N 0.5–4.0) it is possible to produce electrically conductive cement composites.

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