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TRACKING OF CONCRETE HARDENING BY MEANS OF IMPEDANCE SPECTROSCOPY

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Abstract

Concrete setting and hardening designate the concrete grade. The impedance spectroscopy method, as one of the non-destructive testing method group, was used to characterize concrete specimens and track the changes in the concrete spectrum. Variances in the tan δ (f) and Im Z(f) or Re Z(f) of the specimens under investigation have been observed. The specimen quality has been described by means of the loss type prevailing in the material. The results of this study are expected to provide information about the correlation between the n-factor and the concrete setting time.

Key words: *impedance spectroscopy, dielectric losses, loss factor, conductivity losses, polarization losses, porosity*

1. INTRODUCTION

The impedance spectroscopy is a non-destructive testing method employing the impedance characteristic frequency dependence to analyzing the properties of the material in question. The experiment set-up designed to study the system under investigation includes: a metal-material-metal network, which is relevant for identifying the application limits of the impedance spectroscopy method. The method cannot be applied to thick-layer low-conductivity materials. Reinforced concrete products may serve as an example. The principle of the mentioned method consists is studying the dielectric losses versus frequency plots. The dielectric losses of composite materials and plastics can assume values which are many times as high as those of most material commonly used in the building industry.

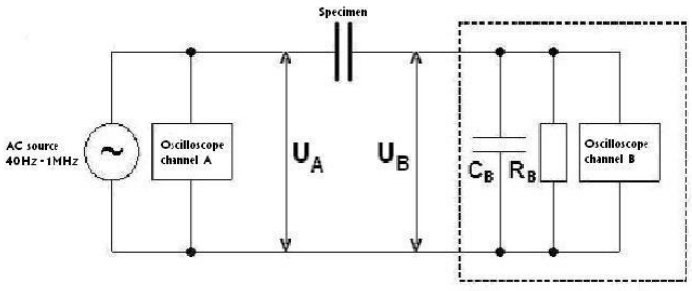


Fig. 1. Measuring set-up and one of specimens. [1].

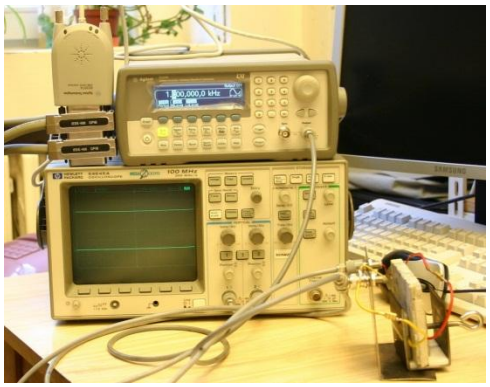


Fig. 2. Circuit diagram of the measuring set-up: AC power supply, specimen under test, double-channel oscilloscope [1].

Analysis of impedance spectra of inhomogeneous materials is a part of the impedance spectroscopy which is still waiting for its development. At present, one is not able to determine unambiguously the individual material component contributions to the total electric conductivity and polarization at various frequencies of the exciting field. Materials having higher electric resistance values (over 500 kΩ) can be regarded – under certain simplifying assumptions – as dielectrics. A theory of dielectric polarization was formulated by Debye [7,8] for homogeneous materials. However, experiments carried out on real materials and the respective conclusions did not show to be in agreement with the fundamentals theories. K S Cole and R H Cole and, also, Fuoss and Kirkwood, started from the Debye's theory to derive models of a dielectric which appear to fit experiment results and conclusions [7] more closely. The behavior of a dielectric in an AC electric field is best described in terms of the complex relative permittivity. Debye has derived a formula for the complex relative permittivity, ε^*, of weakly polar liquid dielectrics, as follows:

$$\varepsilon^*(j\omega) = \varepsilon_\infty + \frac{\varepsilon_s - \varepsilon_\infty}{1 + j\omega\tau}. \quad (1)$$

Here τ is the relaxation time, independent of the time, however dependent on the temperature, ε_s - static permittivity (frequency → 0 Hz), ε_∞ - optical permittivity (frequency → ∞ Hz), angular frequency $\omega=2\pi f$, f - frequency of the exciting electric field [7, 8].

Following equation holds for the loss factor tan δ:

$$tg\delta = \frac{\varepsilon''(\omega)}{\varepsilon'(\omega)} = -\frac{(\varepsilon_S - \varepsilon_\infty)\omega\tau}{\varepsilon_S + \varepsilon_\infty\omega^2\tau^2}. \quad (2)$$

There are several different relaxation times in a real dielectric. Their distribution is described by a distribution function. Exact determination of a suitable distribution function being difficult, an approximation by a properly selected analytical function is usually carried out. According to Cole's, the complex relative permittivity can be expressed as follows [7]:

$$\varepsilon^*(j\omega) = \varepsilon_\infty + \frac{\varepsilon_S - \varepsilon_\infty}{1 + (j\omega\tau_1)^{1-\alpha}}. \quad (3)$$

Here, τ_1 is the most probable relaxation time, around which the particular relaxation times are distributed according to a distribution function $f(\tau)$, where α is a distribution parameter ($0<\alpha<1$).

J R Macdonald [8] made a reference to the formal equivalence between the complex relative permittivity as described by equations (1), (3), and the formulas for a complex impedance Z. Formulas for the real and imaginary components of the complex relative permittivity have been derived and, based on the above mentioned equivalence, equations for the components of the complex specific impedance have been obtained. Using an appropriate software package, parameters of the two model types have been searched for the material under investigation. The degree of correlation between the model and experiment properties is expressed by means of Pearson's correlation coefficient r [7].

The frequency dependence of the quantities studied by the impedance spectroscopy method is determined from the relative voltage (U_B/U_A) and the phase shift ($\Delta\varphi$) between the double-channel oscilloscope A and B-channels (Fig. 2).

An external electric field gives rise to dielectric losses in the specimen in consequence of three different effects:

Dipole polarization relaxation: It occurs in polar materials. Being accompanied by energy losses in a dielectric, it is temperature and frequency dependent. The set-up time: 10^{-12} to 10^{-8} s in low-molecular compounds, being a great many orders of magnitude higher in macromolecular compounds.

Ion polarization relaxation: It occurs in non-dense ion-packing ion solids (inorganic glasses, ceramics). Being accompanied by energy losses in a dielectric, it is temperature and frequency dependent. The set-up time: 10^{-13} to 10^{-8} s.

Electric conductivity: Losses arise in both DC and AC conductivity processes, giving rise to the electric field losses and their conversion into Joulean heat. The physical nature of the losses consists in free-charge-carrier scattering by oscillating particles constituting the solid structure.

The relaxation polarization is a phenomenon which is characterized by slow response, by contrast to the elastic polarization, in which the recovery is almost instantaneous. Let polar particles of different kind exist in a dielectric being only loosely bound to their neighbours. These particles will simultaneously perform oscillations and chaotic displacements with respect to their environment. If an external electric field is applied, these thermal movements will be gradually aligned with the direction of this electric field. In this way, there arises a non-symmetric distribution of electric charges, thus giving rise to a dipole moment. Both the polarization growth and decrease (after the external electric field is switched off) are proceeding slowly. The relaxation polarization is temperature dependent, being always accompanied by dielectric losses and dielectric heating. Thermal ionic polarization and thermal dielectric (dipole) polarization are the main types in this category.

2. MATERIAL TO BE MEASURED

For the impedance spectroscopy measurements, our concrete specimens of dimensions 100 mm x 100 mm x 400 mm (Fig. 3) have been split so as to reduce their thickness to 10 mm, i.e., 100 mm x 100 mm x 10 mm.

The specimen composition follows from the formula, see table 1:

Table 1. Concrete component percentage

C 30/37 XF4, S4, surface NH		
	kg/m^3	%
CEM I 42,5R	320	14,45
Slug 420	100	4,52
Water	210	9,48
Spolostan 7L	4	0,18
Chrysoair	0,15	0,01
Halámky D5 0/4	800	36,13
Rejta 4/8	280	12,65
Rejta 8/16	500	22,58

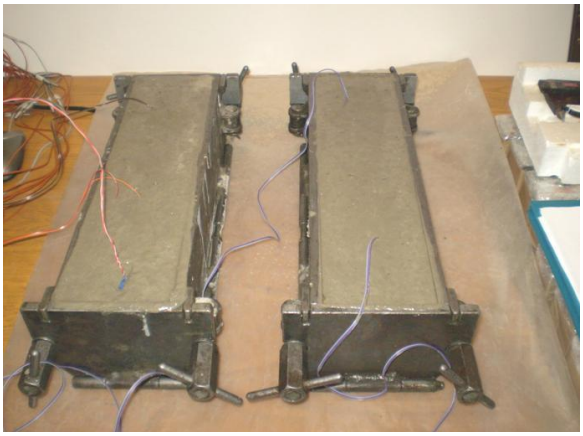


Fig. 3 Two concrete specimens intended for the temperature measurement, immediately after having been poured into the beams.

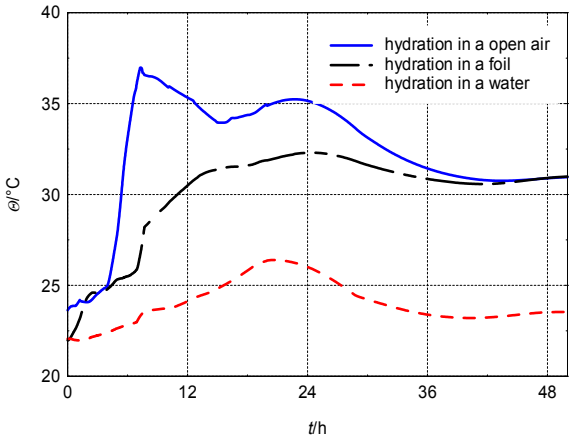


Fig. 4. Monitoring the temperature inside the concrete specimens during the concrete setting process.

3. EXPERIMENTAL SET UP

The experiments, described below, was making by using sinus signal generator Agilent 33220A and Agilent 54645A oscilloscope (Fig. 1):

Experiment 1: The experiment was designed so as to provide distinguishable impedance spectra of self-setting concrete during the setting process.

Experiment 2: The concrete samples were characterized after 15 days. The samples were saved at the different environment (water, air, plastic foil).

The *specimens* under investigation were inserted between two electrodes (which were pressed against the specimens using a screw fixture) and subsequently subjected to the impedance analysis.

The loss factor frequency dependence was obtained by using specific software for measurement instruments control. So the frequency dependent of imaginary part of specific impedance versus real part of specific impedance was obtained. The specific impedance values were calculated of experimental values. Of created and calculated models was determined the coefficients values, which are expressed on the Table 2.

4. MEASUREMENT RESULTS

Experiment 1:

The porosity or the porosity degree is related to the impedance imaginary component Im (Z) versus the impedance real component Re (Z) plot. In this plot, we can determine the angle made by the abscissa (line connecting the arc starting point with the arc centre with the impedance real axis (see Fig. 5 - the angle made by the straight line with the real axis). Putting the mentioned angle Θ into the formula, we can calculate the value of the n-factor, characterizing the specimen porosity degree:

$$n = 1 - (2\theta / \pi) \tag{4}$$

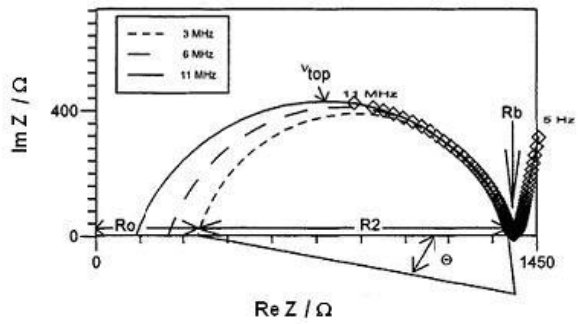


Fig. 5. Illustration of an impedance imaginary component Im(Z) versus the impedance real component Re(Z) plot. [8].

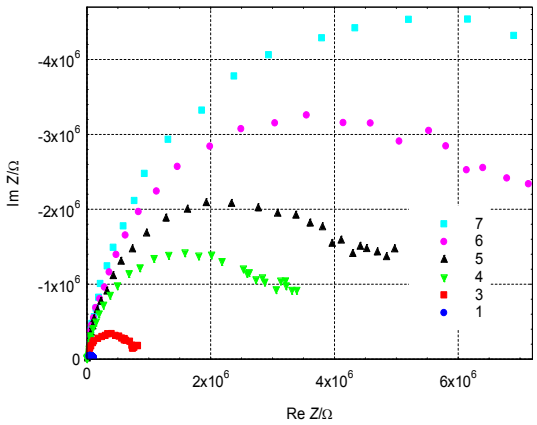


Fig. 6. Impedance imaginary component Im(Z) versus the impedance real component Re(Z) plot.

The table 2 shows n-factors for different hydration stages calculated from the impedance imaginary and real parts:

Table 2. Calculated values of the n-factor in the course of concrete hydration. The concrete was fabricated on 29.03.2011

Measurement date	Setting period (days)	*n*
30.3.2011	1	0,618
2.4.2011	3	0,899
3.4.2011	4	0,908
4.4.2011	5	0,930
5.4.2011	6	0,932
6.4.2011	7	0,933

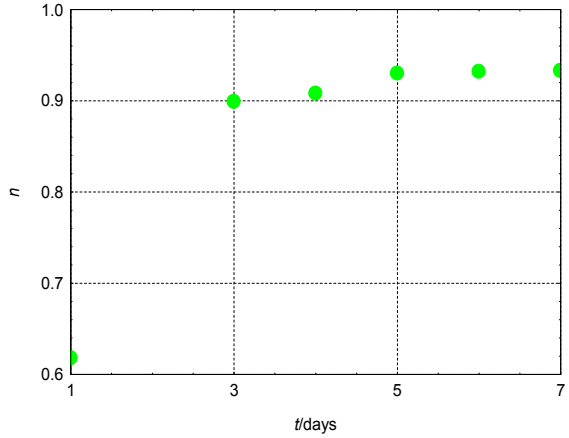


Fig. 7. The n-factor versus time of hydratation dependent.

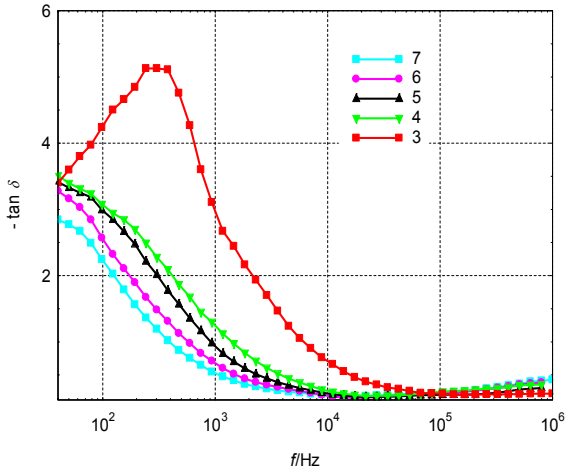


Fig. 8. Loss factor versus frequency plot for a concrete specimen (the frequency being plotted in log scale).

It is clearly seen that the n-factor grows with the hydration time. It remains almost unchanged at the end of the 1-week cycle. The initial lines used in the n-factor calculations are shown in Fig. 6.

The drawback of this characteristic tracking method (Fig. 6) consists in the need for equal-thickness specimens being cut from the original specimen. From this point of view, the loss factor (tan δ) versus frequency (f) plot is more convenient (in Fig. 6, the frequency is plotted in a logarithmic scale for lucidity). The loss factor, as a parameter, is a pure material constant. It is related neither to the specimen size, nor to its dimensions [4].

In Figure 6, the curve gradation corresponds to a one-day time interval between the measurements. The values of the curve obtained after the first hydration day (30.03.2010) are by several orders of magnitude lower as compared with the other ones, so that this curve is difficult to identify in the diagram.

Fig. 8 diagram shows clearly the predominance of conductivity losses in the material (the loss factor tan δ decreasing with the frequency) throughout all concrete hydration stages. The longer the hydration time was, the lower the loss factor values were measured (almost throughout the whole frequency spectrum). For example, the sixth day minus the first day hydration tan δ value is about 2.5 for the frequency of 1 kHz. It means that the material electric conductivity decreased during the hydration process. One might assume that the lower the material conductivity (which in turn is due to newly formed capillary pores) the lower loss factors at given frequencies, however, the loss factor value depends on the material permittivity, too. It follows from the Im Z(Re Z) phasor diagram, that when the impedance real part is going down, the impedance imaginary part is decreasing as well. This is in a good agreement with the growing loss factor. The predominance of the polarization losses (growing trend of tan δ) was observed after the first hydration day only at frequencies below about 500 Hz. When the water content grows, the material loss factor grows as well. In general, polarization mechanisms can be used to characterize the material water content, elasticity variations, defect occurrence etc.

Experiment 2:

Fig. 9 shows experimental frequency spectra of the loss factor tan δ for the indicated range of frequencies f. The loss factor reaches maximum values at the lowest frequencies of the exciting electric field being applied.

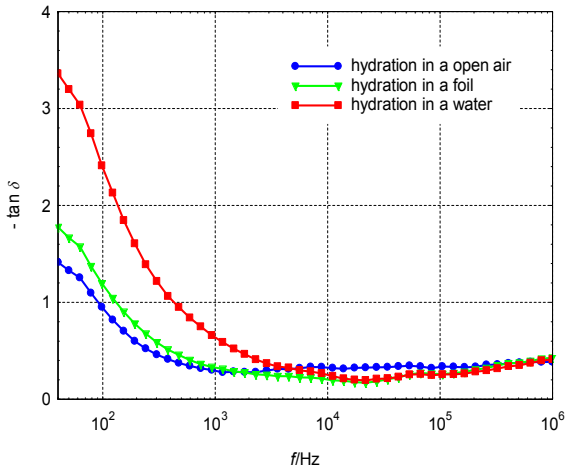


Fig. 9. The dielectric loss factor spectra versus frequency after 15 days of hydration at different environmental.

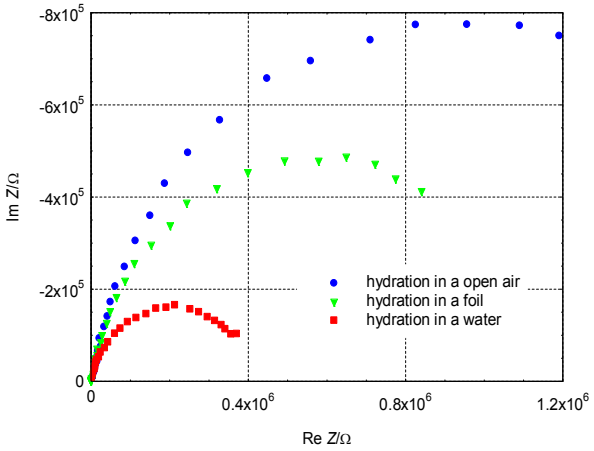


Fig. 10. The specific impedance values of concrete hydratation at different environmental.

It is seen that the concrete specimens whose hydration took place in water feature a higher loss factor than those hydrated in a foil or in the open air up to a frequency of about 4 kHz, where the spectra are nearing each other. Higher values of the loss factor (Fig 9) in the spectrum low-frequency region give evidence of the relaxation processes to influence the resulting tan δ spectrum in the low-frequency region more strongly than in the higher-frequency region. It can be presumed that a local extreme of the loss factor tan δ is lying in the low-frequency region (outside the frequency range used) for the concrete specimens under investigation. For the local extreme in question, the reciprocal value of the frequency equals the most probable relaxation time of the material in the defined frequency range (for the current specimen condition, i.e., composition, hydration degree, water content). From the spectrum

differences, we may infer the most probable relaxation time to be higher for the open-air-hydrating specimen. The most probable relaxation time of the foil-ageing specimen appears to be closest to the most probable relaxation time of the specimen in question, the relaxation time distribution being similar to that of the open-air-hydrating specimen. From 4 kHz upwards, all loss factor curves show fluctuations, however, a trend is clearly apparent. The specimen that has hydrated in the open air shows different lass factor values than the other specimens in the frequency interval from 9 kHz to 100 kHz. All spectra show a slight loss factor increase in the high frequency region. This can be explained by either the presence of water in the aggregates or in the specific aggregate kind (Halámky stone quarry – 0/4 fraction – kind of granite). The second hypothesis is in a better agreement with the conclusions concerning the characterization of the kinds of granite in dry and wet condition by means of the impedance spectroscopy method [5]. The specific impedance spectra as measured on the material under investigation are in a good agreement with the theory of a semi-circle (Cole's, MacDonald) [7,8], whose centre has been shifted downwards below the horizontal axis (see illustrative Fig. 5).

The lowest specific impedance values have been observed throughout the exciting electric signal spectrum (the frequency is growing from the right-hand-side of the diagram to the left-hand-side, Fig. 10) for a specimen that had aged in water. At the time of the experiment, the conductivity of the specimen was higher, but the specific impedance imaginary component to the real component ratio exceeded the same ratio for other specimens. This is in a good agreement with the loss factor behavior described above. The specific impedance curves (Fig. 10) reach maximum values at different frequencies. The specimen that hydrated in the open-air peaks at 50 Hz to 60 Hz, the curve in the middle peaks at 80 Hz to 120 Hz, the last curve, at about 250 Hz.

Table 3. The model parameters values, obtain of dielectric loss factor spectra by using different hydratation environment, ε_∞ - optical permittivity ($f\to\infty$), ε_s - static permittivity ($f=0$), τ - relaxation time, α - distribution parameter, r - Pearsons correlation coefficient, N - number of spectra points.

	Hydratation environment		
Parameter / environment	**water**	**plastic foil**	**air**
ε_∞	72,3	91,6	99,8
ε_s	$5{,}3\cdot10^5$	$3{,}6\cdot10^4$	$1{,}3\cdot10^4$
τ [s]	6,4	0,964	0,473
α	0,114	0,176	0,268
r	0,9924	0,9621	0,8837
N	46	46	46

From the loss factor spectra, complex relative permittivity values for limiting values of the exciting frequency, the most probable relaxation time τ and the distribution parameter α have been obtained. The dynamic permittivity of specimen having hydrated in various environments shows a rising trend, whereas the static permittivity values tend to decrease. The most probable relaxation time confirms the estimates resulting from the analysis of the loss factor spectra. The distribution parameter α increases if the water content in the concrete hydration environment decreases. The correlation coefficient has lowest values for the open-air-ageing concrete loss factor spectra.

5. CONCLUSIONS

The impedance spectroscopy method was employed to characterize the concrete hydration process stages.

The resulting change in the frequency characteristics fits the assumption that the respective physical property changes are reflected in the impedance loss factor. Dielectric losses have been described. The characteristic reproducibility was good within narrow time intervals.

For open-air hydration, a relation between the porosity (its degree) and the shape of Im Z (impedance imaginary component) versus Re Z (impedance real component) plot has been confirmed to exist. The characteristics proved to be reproducible within narrow time intervals.

The impedance spectroscopy method has been used to characterize concrete ageing in various environments. This was confirmed by the spectrum model, which was able to identify these values. Approximation and best-fit-search of the loss factor spectrum for the concrete specimen that hardened in the open air proved to be difficult and less accurate, which is due to the low value of Pearson's correlation coefficient.

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