Changes in the immitance spectra of the cement paste in the initial period of hardening

V A Zhuravlev¹, D O Ugodenko¹, A V Zhuravlev¹, V I Suslyaev¹, I A Prischepa², Yu S Sarkisov², N P Gorlenko², A I Kudyakov²

¹ Department of Radiophysics, National Research Tomsk State University, 36 Lenin Ave., Tomsk, Russia
² Department of Physics, Chemistry and Theoretical Mechanics, Tomsk State University of Architecture and Building, 2 Solyanaya sq., Tomsk, Russia

Abstract. The paper analyzes changes in the impedance and admittance spectra of the cement slurry during hardening. The spectra were measured in the frequency range from 20 Hz to 2 MHz on a precision RLC meter Agilent E4890A using a homemade capacitor measuring cell. The studies in order to establish the optimal equivalent electrical circuits describing the transformation of the electrophysical properties of the cement slurry and interface phenomena in the near-electrode layer of the measuring cell from the time of hardening were carried out. The sensitivity of the parameters of equivalent circuits to different stages of cement slurry hardening has been established.

1. Introduction
Currently, a number of well-developed modern physical, physicochemical and chemical methods are widely used to determine the quality, structure and properties of various building materials. The use of impedance spectroscopy and dielectrometry methods along with them makes it possible to evaluate additionally a number of important characteristics of water-containing building materials, such as water-cement mixtures, mortars and concretes [1, 2].

The methods of the impedance spectroscopy and dielectrometry are very sensitive to the molecular mobility of water molecules in various states and ionic complexes dissolved in it. In turn, the structural state of water largely determines the most important properties of artificial stone, including mechanical strength [3]. Therefore, scanning the impedance characteristics of water-containing building materials in continuous time mode is of considerable interest. It can provide important information about the processes occurring both in the initial period of the hydration interaction of cement with water, and at the subsequent stages of setting and hardening of this complex dispersed system [4, 5].

The aim of this work is to study changes in the immittance spectra (impedance and admittance) of cement paste samples in an electrochemical measuring cell during the twenty-four hours, as well as to compile and analyze equivalent electrical circuits describing these changes.

2. Samples for research and method of measuring immittance spectra
Experimental studies were carried out on the samples of cement paste of normal density (ND = 26%) made of Portland cement CEM I 42.5N (GOST 30515–2013) of the Topkinsky cement plant and tap
water. The cement paste was prepared in a separate container. After thorough mixing, it was placed in the measuring cell, and the process of measuring its electrophysical characteristics began.

A precision RLC meter Keysight E4980A to measure the spectra of the electrophysical characteristics in the frequency range 20 Hz - 2 MHz at the initial time of the structure formation of the cement paste was used. The measuring cell was a flat capacitor consisting of two rectangular stainless steel plates with a thickness of 1 mm and dimensions 51.0 x 39.5 mm. The distance between the plates was 9.5 mm. The measurement results at intervals of 30 min during the day using a program code written in the LabVIEW environment were recorded.

According to an equivalent circuit consisting of a parallel connected capacitance \( C \) and a resistor \( R \) in this series of experiments the measurement results were recorded. The recalculation of the measured \( R-C \) parameters into the impedance \( Z = Z' + iZ'' \) and admittance \( Y = Y' + iY'' \) components was carried out according to the formulas given in Table 1.

### Table 1. Formulas for converting the measured \( R-C \) parameters of the equivalent circuit into impedance, admittance components and vice versa.

| \( R-C \) parall. | \( Z = Z' + iZ'' \) | \( Y = Y' + iY'' \) |
|-------------------|---------------------|---------------------|
| \( Z' = \frac{R}{1 + (\omega CR)^2} \) | \( Y' = R^{-1} \) | \( Y'' = \omega C \) |
| \( Z'' = -\frac{\omega CR^2}{1 + (\omega CR)^2} \) | \( Y'' = \frac{Z''}{Z'^2 + Z''^2} \) | \( Y'' = -\frac{Z''}{Z'^2 + Z''^2} \) |
| \( R = \frac{Z'^2 + Z''^2}{Z'} \) | \( Y' = \frac{Z'}{Y'^2 + Y''^2} \) | \( Y'' = -\frac{Y''}{Y'^2 + Y''^2} \) |
| \( Y = 1/Y' \) | \( \omega C = Y'' \) | \( R = 1/Y' \) |

### 3. Experimental results

#### 3.1. Parallel \( R-C \) equivalent circuit

Figure 1 shows the frequency dependences of the electrical resistance and capacitance of a measuring cell filled with cement paste, measured at the initial \((t = 0 \text{ min})\), final \((t = 1720 \text{ min})\) moments of time and for the hardening time \(t = 900 \text{ min}\).

![Figure 1. Frequency dependences of resistance (a) and capacitance (b) for three sample holding times.](image-url)
According to Fig. 1a, the resistance values $R$ of the sample rapidly decreases at frequencies up to $\sim 100$ Hz, and then change slightly with increasing frequency. In the frequency range above $100$ Hz, an increase in resistance is observed with increasing holding time. Figure 1b shows that a rapid decrease in capacitance with increasing frequency and increasing exposure time also occurs at low frequencies up to $\sim 1000$ Hz.

In connection with the above, the analysis of the time dependences of the capacitance and resistance values for a measurement frequency of 200 Hz was carried out. The results of measurements are shown in Figure 2.

![Figure 2](image)

**Figure 2.** Dynamics of changes in capacitance (a) and resistance (b) in the "cement-water" system at the initial time of hardening. The measurements were carried out at a frequency of 200 Hz.

According to Fig. 2a, from the moment of mixing the cement with water, the sample capacitance is first to increase up to a time of $\sim 200$ min. After passing the maximum $C \approx 43$ $\mu$F, at first a rapid, and at $t > 900$ min, a slower decrease in the capacitance to the value $C \approx 1$ $\mu$F at $t = 1720$ min occurs. Figure 5b shows that the resistance of the sample changes slightly up to the holding time $t \approx 700$ min. Further, there is a more rapid increase in the $R$ values. Thus, the largest changes in the capacitive component occur at the initial stage of cement paste hardening. Whereas the main changes in the resistive component, occur at the final stage.

The high-frequency section of the $C(f)$ dependence for frequencies $f \geq 100$ kHz is shown in the inset to Figure 1b. The horizontal dashed straight line in the inset corresponds to zero capacitance. It can be seen that at exposure times from 0 to 900 min the capacitive component has a negative sign in the investigated frequency range. This indicates a change in the character of the sample impedance from capacitive to inductive. Thus, the equivalent circuit consisting of a parallel connected resistor and capacitor is not suitable for describing the behavior of the electrophysical characteristics of the "cement-water" system in these frequency-time intervals.

3.2. Analysis of immitance spectra of cement paste

In this section, we will focus on the choice of the parameters of the equivalent circuit that describe the time evolution of the immitance spectra of the cement paste during its hardening. For this, the measured parameters of the equivalent $R-C$ circuit into impedance $Z = Z' + iZ''$ and admittance $Y = Y' + iY''$ components according to the formulas in Table 1 were converted.

The spectra $Z(f)$ and $Y(f)$ obtained at hourly intervals are presented as hodographs of impedance and admittance in Figures 3 and 4, respectively. The points in the figures are experimental data. Lines are calculations for the parameters of the equivalent circuits obtained below. Figure 3a shows the measurement results over the entire range of exposure times from $t = 0$ min to $t = 1720$ min. Figure 3b shows on a larger scale a portion of the spectra up to the exposure time $t = 900$ min, in which a change in the sign of the imaginary part of the impedance at high frequencies is observed.

The low-frequency parts of the hodographs shown in Fig. 3 are typical for non-blocking electrodes with double electric layers and diffusion processes occurring near the interface. Moreover, electric double layers are formed also at the cement - electrolyte phase boundaries. In the initial period of
hardening of the cement paste, the angle of inclination of the low-frequency branches of the hodographs increases with time. Moreover, after a holding time of \( t \approx 300 \) min, the tilt angle practically does not change. A constant phase element (CPE) is well suited for describing such impedance spectra [6 - 8]. This element was proposed first for the analysis of electrochemical processes and dielectric relaxation processes in [9]:

\[
Z_{CPE} = A(i\omega)^S = A\omega^S \left[ \cos(\pi S/2) - i\sin(\pi S/2) \right].
\]

Here \( i = \sqrt{-1} \), \( A \) and \( S \) are phenomenological parameters describing interactions in the near-surface electrode-liquid layer and at boundaries of the phase, as well as interlayer polarization processes. If \( S = 0 \), then \( Z = A = R \), that is, the impedance is resistive. If \( S = 1 \) then \( Z = 1/(i\omega A^{-1}) \), that is, the impedance is capacitive (\( A^{-1} = C \)). At \( S = -1 \), the impedance is inductive \( Z = i\omega A \) (\( A = L \)).

**Figure 3.** Impedance hodographs over the entire range of cement paste holding times (a) and over the time interval of existence of a change in the sign of \( Z'' \) (b). The numbers in Fig. 3b are the measurement times of some spectra from the moment of mixing. Points are experiments, lines are calculations.

The point of intersection of the hodographs with the abscissa at \( Z'' = 0 \) determines the value of the active resistance \( R \), which is the sum of two quantities. One of them characterizes ohmic losses in the interface region of the sample - electrode. The second describes ohmic losses in the sample. Note that at holding times greater than 900 min, the inductive impedance component (\( Z'' \geq 0 \)) disappears and another high-frequency dispersion region appears in the impedance spectra. It is associated with the processes of dielectric polarization in the emerging particles of cement stone.

**Figure 4.** Admittance hodographs. The numbers in the figure are the measurement time of some spectra from the moment of mixing. Points are experiments, lines are calculations.

**Figure 5.** Estimates of the values of inductance (\( L \)) and resistance (\( R \)) depending on the holding time of the cement paste.
In order to characterize in more detail the electrochemical processes occurring at the initial moment of cement paste hardening, we supplemented the analysis of impedance spectra with calculations of admittance spectra. These spectra are shown in Figure 4. It can be seen that they provide more visual information about the immitance spectra at the initial stage of cement paste setting. Whereas the impedance plots in Figure 3a describe the final stage in more detail.

Based on the above considerations, we used two equivalent circuits to describe theoretically the immitance spectra of the cement paste at different holding times. The first circuit contains elements connected in series: inductance $L$, resistor $R$ and constant phase element $Z_{\text{CPE}1}$:

$$Z_1 = R + Z_L + Z_{\text{CPE}1} = R + i\omega L + A_1(i\omega)^{-S_1}. \tag{2}$$

Formula (2) was applied to calculate the impedance spectra up to the exposure time $t = 900$ min.

To describe the impedance spectra at a later setting time of the cement paste, we tested various versions of the equivalent circuits. They were composed of resistors and capacitors connected in series and in parallel. However, the best agreement with experiment was obtained for a circuit in which the elements are connected in parallel: inductance $L$ and constant phase element $Z_{\text{CPE}1}$:

$$Z_2 = (RZ_{\text{CPE}2}) / (R + Z_{\text{CPE}2}) + Z_{\text{CPE}1} = (RA_2(i\omega)^{-S_2}) / (R + A_2(i\omega)^{-S_2}) + A_1(i\omega)^{-S_1}. \tag{3}$$

The parameters included in the equivalent circuits (2) and (3) were estimated using a program written in the VBA programming language in the Excel environment using the Solver add-in. Figure 5 shows the estimated values of inductance ($L$) and direct current resistance ($R$) depending on the setting time of the cement-water mixture. The time dependences of these parameters are similar to the time dependences of capacitance and resistance at a frequency of 200 Hz presented in Figure 2. Only the value of the inductance decreases with time much faster than the capacitance and turns to zero at $t = 900$ min. In addition, the value of the resistance at direct current in the initial hardening period of the cement-water mixture is approximately two times less than at a frequency of 200 Hz.

The estimates of the parameters characterizing the magnitude ($A_1$) and exponent ($S_1$) of the impedances of the constant phase elements $Z_{\text{CPE}1}$ and $Z_{\text{CPE}2}$ are presented in Figures 6 and 7, respectively.

**Figure 6.** Dependences of parameters $A_1, A_2$ of elements with constant phase $Z_{\text{CPE}1}$ and $Z_{\text{CPE}2}$ depending on the holding time of the cement paste.

**Figure 7.** Dependences of parameters $S_1, S_2$ of constant phase elements $Z_{\text{CPE}1}$ and $Z_{\text{CPE}2}$ depending on the holding time.

From Figures 6, 7 it can be seen that the properties of the $Z_{\text{CPE}1}$ element change in the entire range of variation of the holding time not as significantly as the parameters of the $Z_{\text{CPE}2}$ element. Thus, $A_1(t=0)$ is equal to $3100 \ \text{Ohm}(\text{rad}/\text{c})^{S_1}$, and $A_1(t=1720)$ is equal to $5500 \ \text{Ohm}(\text{rad}/\text{c})^{S_1}$. The value of the exponent $S_1$ is close to one. This indicates that the immitance of this CPE is close to the capacitive
imittance. A noticeable break in the dependences \( A_i(t) \) and \( S_i(t) \) is observed in the vicinity of the holding time \( t \approx 300 \text{ min} \), when the quantities \( C(t) \) and \( L(t) \) pass through a maximum.

The parameters of the second CPE, describing the appearance of a new region of dispersion after 900 minutes of holding the cement paste, increase sharply. Then they change more smoothly and their time dependences tend to saturation.

4. Discussion

The processes of dissolution, dispersion, hydration and ion exchange are at the heart of the phenomena that occur after the mixing of cement with water. Later, the processes of adsorption and enlargement of particles supplement them during the crystallization of cement stone. Without dwelling on these processes in detail due to the limited space, we note the following.

After mixing the cement with water, the processes of the initial hardening of the cement paste begin after about 90 minutes of exposure and continue up to about 240 minutes. According to Figures 2a and 5, at this time the values of capacitance \( C(t) \) and inductance \( L(t) \) reach a maximum and then begin to decrease rapidly. The value of \( R(t) \) varies little over this time interval, and kinks are observed in the dependences of the parameters of \( Z_{CPE1} \).

The end-of-setting time for Portland cement is approximately 720 minutes. A sharp transition from the plastic strength of the cement paste to the brittle strength of the hardened cement stone occurs after 720 – 840 minutes of hardening. After 840 – 900 minutes, a period of intense crystallization begins. In this case, gel-like neoplasm’s approach each other and form crystals. Then the crystals grow together and form spatial structures. At this stage of the maturation of the cement paste, the inductive component of the immitance vanishes and a high-frequency dispersion region appears, described by the \( Z_{CPE2} \) element. Obviously, it is associated with polarization processes inside the particles of the formed cement stone.

Equivalent circuit element \( Z_{CPE1} \) describes the low-frequency polarization region. Responsible for this area are the processes of polarization in the near-electrode double electric layer, in the double electric layers at the phase boundaries: "cement grain - electrolyte" and the processes of interlayer polarization at the grain boundaries. During the hardening of the cement paste, the specific contribution from these processes changes, since the amount of free water decreases, and the amount of bound water increases. However, the redistribution of contributions occurs in such a way that the parameters of the resulting process do not change significantly.

5. Conclusion

Thus, the conducted studies of the immitance spectra of the cement paste made it possible to determine the type of equivalent electrical circuits describing the transformation of the spectra at different stages of hardening. The correlation of time dependences of parameters of equivalent circuits with different stages of maturation of cement paste were established.

Acknowledgments

Tomsk State University Competitiveness Improvement Program supported research.

References

[1] Lianzhen X and Xiastes W 2011 Journal of Wuhan University of Technology — Materials Science Edition, 22 983
[2] Heikal M, Helmy I, El-Didamony H and El-Raooof F 2004 Ceramics-Silikaty 48 49
[3] Salem Th M 2002 Cement and Concrete Research 32 1473
[4] Liu K, Cheng X, Li J, Gao X, Cao Y, Guo X, Zhuang J and Zhang C 2019 Composites Part B 177 107435
[5] Yoon S S, Kim H C and Hill R M 1996 Journal of Physics D: Applied Physics 29 869
[6] Macdonald J R 1984 Solid State Ionics 13 147
[7] Barbero U, Becchi M and Freire F C M 2008 J. Appl. Phys. 104 114111
[8] Zhuravlev V A, Suslyaev V I, Zhuravlev A V and Koroven E Yu 2018 Russ. Phys. J. 60 1893
[9] Cole K S and Cole R H 1941 J. Chem. Phys. 9 341