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MEASUREMENT AND EVALUATION OF CEMENT PASTE POROSITY BY ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

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Abstract. Porosity is an important part of cement paste microstructure, which significantly influences the mechanical properties (especially durability and strength) of cement-based materials. Electrochemical impedance spectroscopy (EIS) is a non-destructive method used to measure the pore system utilizing a range of frequencies of electric current, which is fed to the cement paste by stainless steel electrodes. The pore volume is obtained from the pore resistance and the matrix capacitance measured by EIS. This paper deals with the evaluation of porosity based on resistance values from EIS on a sample of pure CEM I 42.5R Portland cement paste at 3 different hydration times (age 7, 14, 28 days).

Keywords: Electrochemical impedance spectroscopy, cement paste, porosity.

1. Introduction

Cement is one of the most consumed materials in the world. Therefore, many scientists are working on researching, developing, and improving cement-based materials. Porosity is one of the observed properties at the micro-scale that influences strength and durability [1].

Generally, three types of pores can be found in hydrated cement paste – capillary pores, gel pores, and interlayer space. The pore characteristics differ in size, shape, and distribution in the solid matrix. Porosity measurement depends on all these characteristics [2].

The porosity of cement-based material can be accessed either by direct or indirect methods. Direct methods are able to measure the pore sizes from the largest pores in the order of a few millimeters to hundreds or tens of nanometers. Direct methods analyze pore structure from 2D or 3D images of the sample. Therefore, these methods depend on the resolution of an image (pixel size). These methods include 2D images of scanning electron microscopy (SEM), 3D images of X-ray microtomography or X-ray nanotomography, and laser scanning confocal microscopy (LSCM) [3].

Indirect methods use liquid (such as water, gas, mercury, helium, etc.) inside cement paste as a probe. The size of the measurable pores is limited by the lower (tens of nanometers) and upper boundary (hundred of micrometers). Indirect methods of measuring open porosity include mercury intrusion porosimetry (MIP), water saturation, and pycnometry [3–5].

Electrochemical impedance spectroscopy (EIS) can be ranked as the indirect method because a liquid conduct an electric current and thus is involved in the measurement. Using EIS not only detects the porosity and microstructure of concrete [6–9], but also the hydration and shrinkage process [10], corrosion process of reinforced concrete [11, 12], the diffusion of chloride in concrete [13, 14] and the influence of mineral admixtures on cement-based material [15].

Despite some efforts of porosity characterization by EIS [6–9] the methodology is still limited by many uncertainties. Thus, this paper deals with the EIS measurement on pure cement paste samples, evaluation of porosity, and comparison with porosity determined by helium pycnometry.

2. Electrochemical impedance spectroscopy

2.1. Equivalent circuit models for concrete

Electrochemical impedance spectroscopy (EIS) or otherwise known as alternating current impedance spectroscopy (ACIS), is a non-destructive method used to measure the resistance of materials, including cement

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paste and concrete. Electric current (usually alternating current AC) is applied to the samples by a pair of electrodes embedded in the material or attached to their opposite surfaces. The transmitted current with the periodic alternating signal can be decomposed into a series of harmonic signals of sinusoidal shape with different frequencies due to fast Fourier transform [16, 17]. The measurement is taken from the highest frequencies to the lowest, and the impedance is recorded [6, 12].

Cement paste cannot be considered as a single electrical resistor in EIS measurements because the material consists of a bulk matrix and pores. Pores have different shapes, sizes, and distributions in the cement paste structure. For example, capillary pores are connected and with an oblong shape in contrast to a spherical enclosed pores [2]. Electrochemical impedance spectroscopy allows measuring only the capillary pores, and three conductive paths are distinguished as shown in the Figure 1 [6]:

- Continuous conductive path (CCP) – A series of capillary pores connected by pore necks form CCP. The impedance of this path Z_{CCP} equals the resistance of interconnected capillary pores R_{CCP}:

$$Z_{\mathrm{CCP}} = R_{\mathrm{CCP}}. \tag{1}$$

- Discontinuous conductive path (DCP) – The continuity of a capillary path is disturbed by a discontinuous point (DP) formed by a thin layer of cement paste. DP is considered to be a double parallel capacitor with electric capacitance C_{DP}. The resistance of the capillary path is labeled as R_{CP}. The impedance of the path Z_{DCP} is composed of C_{DP} and R_{CP} connected in series as shown the following equation:

$$Z_{\mathrm{DCP}} = R_{\mathrm{CP}} + C_{\mathrm{DP}}. \tag{2}$$

- Insulator conductive path (ICP) – The pores and voids do not form the largest part of cement paste. It is made up of a bulk matrix that acts as an electric insulator. The matrix becomes charged as a result of the current passing through the sample. Therefore it is considered a double parallel capacitor with capacitance C_{mat}. Although cement paste is not a perfect insulator, its resistance R_{mat} can be neglected if the sample is not frozen or dried. Thus, the impedance of this path Z_{ICP} is just equal to the C_{mat}:

$$Z_{\mathrm{ICP}} = C_{\mathrm{mat}}. \tag{3}$$

According to the typical Nyquist diagram (plot of real versus imaginary part of impedance), capacitive loops occur in cement-based materials as shown in Figure 2b. These loops can be replaced by a parallel series of resistors (R) and capacitors (C). An equivalent electric circle containing R and C is necessary to use in order to evaluate the results of EIS measurement [18, 19]. Many equivalent circuits have been published and are summarized in [19].

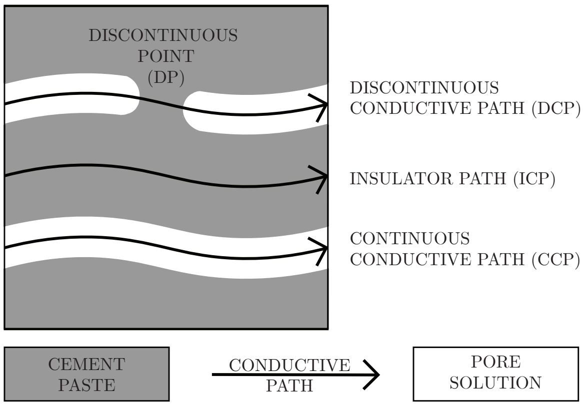

Figure 1. Simplified microstructure of cement paste with illustrated conductive paths.

In this paper, two different models of equivalent electric circuits published by Guangling Song in [6] were used. The first option is the equivalent circuit model (EC), which is composed of all above mentioned paths, as shown in Figure 2a. The capacitance of the solid matrix of the cement paste is relatively low. Therefore the second option assumes the simplification that C_{mat} does not have to be considered in the second equivalent model, as shown in Figure 3.

Furthermore, the electric circuit can be simplified into the simplified equivalent circuit model (SEC) as shown in Figure 2c. Comparing the equivalent models in Figures 2c and 3, the following relations can be deduced [6]:

$$R_0 = R_{\mathrm{CP}} \cdot R_{\mathrm{CCP}}/(R_{\mathrm{CP}} + R_{\mathrm{CCP}}), \tag{4}$$

$$R_1 = {R_{\mathrm{CCP}}}^2/(R_{\mathrm{CP}} + R_{\mathrm{CCP}}), \tag{5}$$

$$C_1 = (1 + R_{\mathrm{CP}}/R_{\mathrm{CCP}})^2 \cdot C_{\mathrm{DP}}, \tag{6}$$

where

R_1 is resistance of (continuous and discontinuous) pores,

C_1 is a capacitance of bulk cement (including C_{DP}),

R_0 is an offset resistance from the origin on real axis of Nyquist diagram.

The theoretical Nyquist spectrum of the EIS consists of arcs. The most important arc of the SEC model is the arc of diameter R_1, see Figure 2d. The position of the center of the arc on the real axis Z is ensured by rotation by the depression angle (α) [20], which is related to the pore size distribution and the others imperfection of the sample [12]. R_0 can be neglected because of high-frequency measurement (nearly to the origin on the real axis of the Nyquist plot) is negatively influenced by surrounding phenomena and the accuracy limitation of most electrochemical equipment [6, 20, 21].

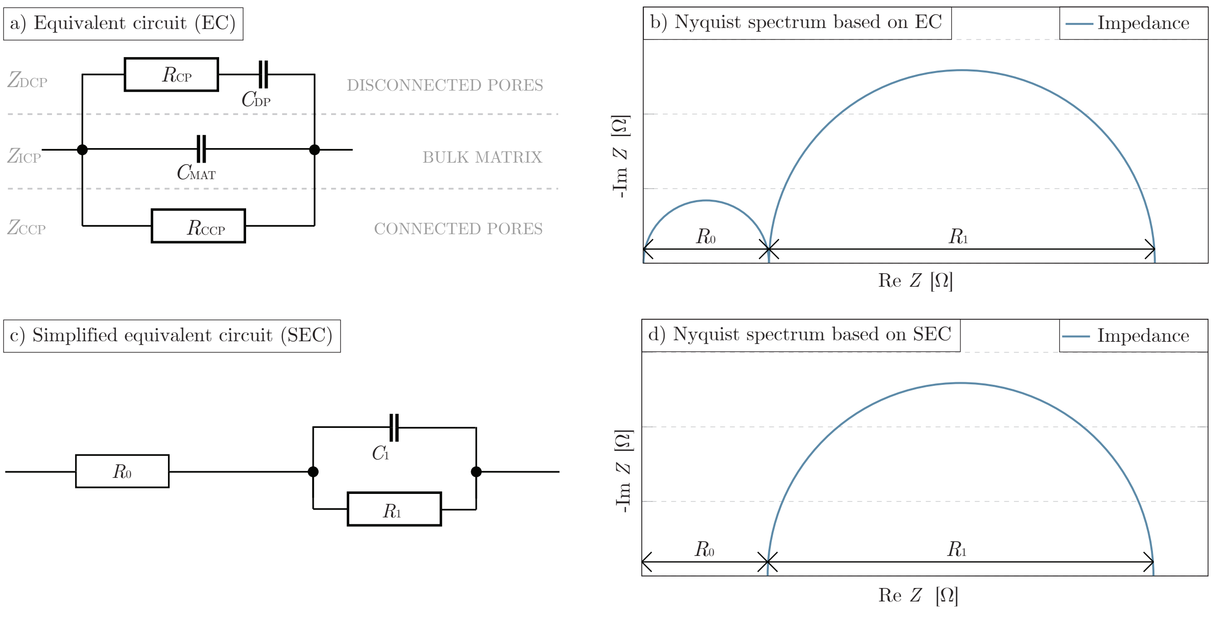

FIGURE 2. Equivalent circuit model (EC), theoretical Nyquist EIS spectrum based on a equivalent model EC, simplified equivalent circuit model (SEC) and theoretical Nyquist EIS spectrum based on a equivalent model SEC [6].

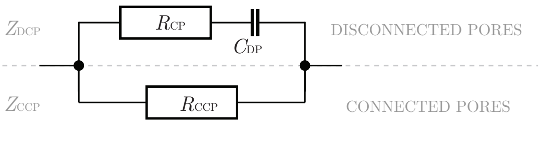

FIGURE 3. Simplified equivalent circuit model for cement paste used to measure of EIS [6].

2.2. Porosity calculation from EIS measurements

Archie's law is the most widely used relationship between the resistivity and porosity of porous material. The relationship was originally derived on the sandstone filled with brine [22] and is defined by the equation:

$$F = A \cdot \phi_0^{-m}, \tag{7}$$

where

F is formation factor,

A is a coefficient,

ϕ_0 is the capillary porosity,

m is Archie's index.

In cement-based materials, the resistivity is dependent on sample dimensions and electrode positions. Thus, it is more convenient to convert the resistance to effective electrical conductivity σ_{eff} as a function of electrode size and position:

$$\sigma_{\text{eff}} = l/(R \cdot S), \tag{8}$$

where

l is the distance between the electrodes in the direction of current,

S is the cross-sectional area of the electrode embedded in the cement paste.

$$\sigma_{\text{eff}} = C \cdot \sigma_0 \cdot {\phi_0}^m, \tag{9}$$

where

σ_0 is the conductivity of conducting medium,

C is a constant depending on the saturation of the sample (assumed to be 1.0 for fully saturated samples),

ϕ_0 is the pore volume fraction,

m is Archie's index.

The exponent m reflects pore complexity and tortuosity and has been found in the range 1.5–4.0 [13, 18].

3. Materials and Methods

3.1. Sample preparation

Cement paste samples were made from CEM I 42.5R with a water to cement ratio of 0.4. A fresh mixture was poured into a silicone-lubricated formwork with dimensions of 54×30×11.7 mm (length, width, height). Additionally, a pair of electrodes from a stainless steel plate was put longitudinally into the formwork. Electrodes were inserted 3 mm above the formwork bottom and 1 mm from formwork edges. The distance between electrodes was set to 10 mm. The scheme of sample setup for EIS measurement is shown in Figure 4. Moreover, the same samples without electrodes were prepared for porosity measurement. The samples were demoulded after 24 hours and placed in 0.5 % limewater solution where retained until the measurement.

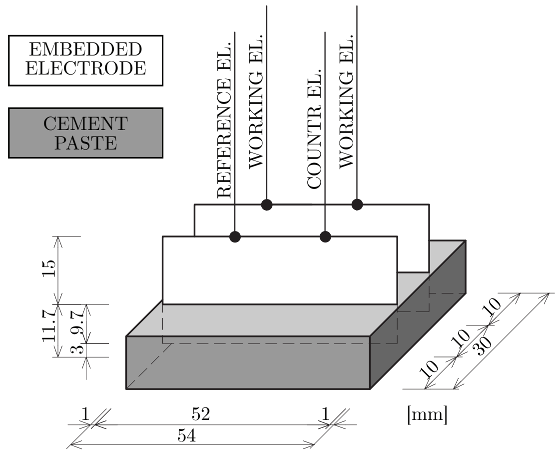

FIGURE 4. An illustration of the sample with embedded and connected electrodes.

3.2. EIS MEASUREMENT

EIS measurement was performed using Zahner Zennium X device and ThalesXT USB software with a frequency range of 12 MHz–100 Hz and 10 steps per decade. The amplitude of sinusoidal voltage was set to 10 mV. The use of a larger potential amplitude is not recommended due to possible changes in the surfaces of the samples [17]. The cables connected two working electrodes to one of the embedded electrodes. The reference electrode and the counter electrode were connected to the other of the embedded electrode [23]. Short coaxial cables were used to reduce the influence of surrounding phenomena and the measurement noise [17]. To ensure consistent measurement results, it was necessary to prevent the drying of the saturated samples. Thus, samples were partly submerged in the water while simultaneously avoiding contact between electrodes and water. Otherwise, the electric current entering the samples would pass through the water, and the results would not correspond to the cement paste. The samples were measured at 3 different ages of hydration – 7, 14, and 28 days. The EIS measurement was taken at five-minute intervals until the values stabilized.

3.3. POROSITY MEASUREMENT

The porosity of the cement paste was determined by helium pycnometry and mercury intrusion porosimetry. After a saturation period of 7, 14, and 28 days, the samples were cut into 2 mm thick slices and dried at 50 °C. Subsequently, sample density, ρ was measured by helium pycnometer Thermo Scientific ATC EVO. The bulk density, ρ_{bulk} of the samples was determined by the gravimetric method. Further, the porosity of the sample was calculated from the equation:

$$\phi_{0,\mathrm{P}} = (1 - (\rho_{\mathrm{bulk}}/\rho)) \cdot 100. \tag{10}$$

4. RESULTS AND DISCUSSION

The example of the EIS results for the C-14d and C-28d samples is shown in Figure 5 as the Nyquist

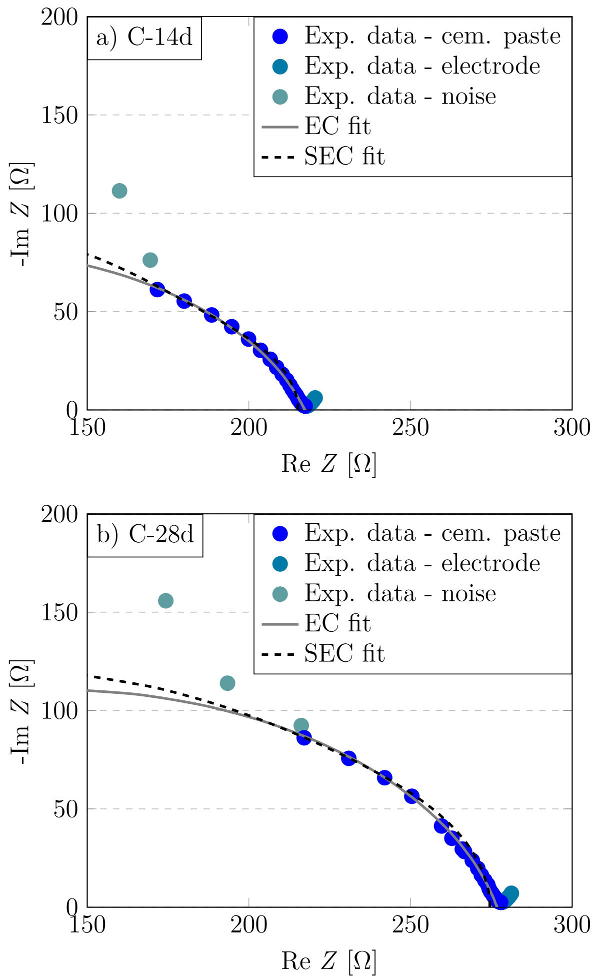

FIGURE 5. Experimental Nyquist EIS spectrum with calculated EC and SEC model fits for samples C-14d and C-28d. Note that only data corresponding to cement paste (blue marks) were used for fitting.

spectrum. Before the resistance and capacitance evaluation, experimental data were corrected and cut off at both ends. That is because the values at low frequencies correspond to the electrodes' resistance and their contact with the material, and values at high frequencies are inaccurate due to the limitations of the measuring device. Further, the data were fitted by the Simplex algorithm with the application of EC and SEC models [6]. The samples were remeasured over time until the resistance values were stabilized. The stabilization period took between the 15–30 minutes, as illustrated in Figure 6.

Table 1 summarizes the resistances and capacities corresponding to the fits based on the EC and SEC models, as well as degree rotation α. The results clearly show almost no differences between resistances R_{CCP} (EC) and R_1 (SEC). Therefore, both values correspond to the continuously connected pores, indicating that C_{mat} for the pure cement paste 7–28 days old can be neglected as considered by the simplified equivalent model. Also, both R_{CCP} and R_1 are increasing with samples age. Such a behavior corresponds

Sample	Equivalent circuit – EC				Simplified equivalent circuit – SEC			
	R_{CCP} [Ω]	R_{DCP} [Ω]	R_{DP} [pF]	C_{mat} [pF]	R_0 [Ω]	R_1 [Ω]	C_1 [pF]	α [rad]
C-7d	201.3	1290	29.1	38.7	0	204.1	41.9	0.81
C-14d	215.2	1577	29.2	40.7	0	217.3	42.0	0.82
C-28d	274.5	1875	21.7	41.6	0	276.8	45.5	0.86

Table 1. Resistance and capacitance of cement paste samples evaluated with different equivalent circuit models: EC, SEC.

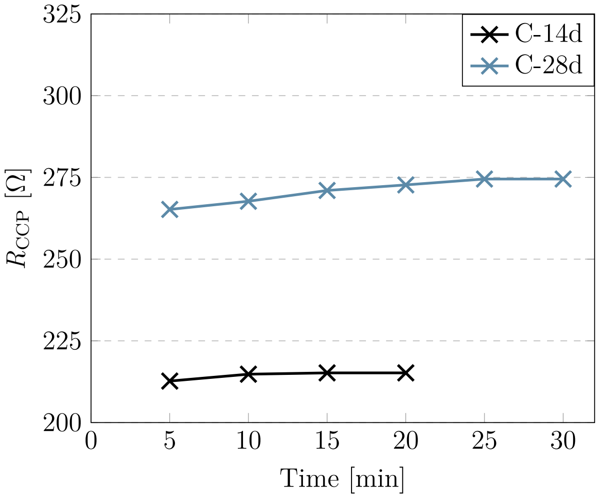

Figure 6. A stabilization period of cement paste resistance at different hydration times. The EC model evaluated R_{CCP}.

Sample	ρ [kg/m^3]	ρ_{bulk} [kg/m^3]	$\phi_{0,\mathrm{P}}$ [%]
C-7d	2320	1687	27.3
C-14d	2287	1687	26.2
C-28d	2234	1685	24.6

Table 2. Porosity evaluated from helium pycnometry.

well to the decreasing porosity due to the ongoing hydration reaction, during which the newly created hydration products occupy space originally formed by capillary pores. Thus, creating more discontinuous paths results in increasing R_{DCP} over time.

The density results measured by helium pycnometry and bulk density are summarized in Table 2 along with the values of calculated porosity (ϕ_0). Again the decrease in porosity corresponds to the hydration process. Initially, the porosity from the EIS measurement could not be directly calculated using Equation (9) and porosity obtained from helium pycnomtery was used for calibration. Another expression, the effective electrical conductivity was easily calculated from resistances R_{CCP} and R_1. The conductivity of the pore solution σ_0 was calculated by the analytical relationship of Snyder [24], which is dependent on the w/c ratio, degree of hydration (DoH), and the amount of Na^+, K^+, OH^- concentration. The DoH was estimated by Cemhyd3d model [25]. Thus, the only unknown term remains Archie's index m. It was found that parameter m is almost identical for both equivalent circuit models EC and SEC and also does not vary with hydration time ranging from 7 to 28 samples age. Therefore, it is possible to calculate the average value of $m = 3.46 \pm 0.02$. Lastly, the porosity ϕ_0 was calculated with the known mean value of paramete m. All the calculated parameters are summarized in Table 3.

5. Conclusions

In this paper, the porosity was measured by electrochemical impedance spectroscopy (EIS) with the aid of helium pycnometry and evaluated using Archie's law. The resistivity of continuous conductive paths was evaluated from the impedance spectrum by the equivalent circuit (EC) and simplified equivalent circuit model (SEC). The minimal differences between resistances R_{CCP} and R_1 were found. Hence, the capacitance of matrix C_{mat} can be neglected in the SEC model. Thus, only the SEC model is sufficient for evaluating the impedance spectra of pure Portland cement paste.

The value of Archie's index m was found to be almost identical between both EC and SEC models and also for 7, 14, and 28 samples age. Thus, the m parameter can be assumed as constant, which would allow porosity from EIS measurement without the aid of another porosity measurement method. Nevertheless, when time changes or supplementary material is added, the porous system also changes. Therefore, further researches on cement-based materials are necessary.

Acknowledgements

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Sample	DoH	σ_0	$\phi_{0,P}$	R_{CCP}	R_1	σ_{eff}		m		ϕ_0
				EC	SEC	EC	SEC	EC	SEC	$m = 3.46$
	[%]	[S/m]	[%]	[Ω]	[Ω]	[S/m]	[S/m]	[-]	[-]	[-]
C-7d	65.5	13.08	27.3	201.3	204.1	0.147	0.145	3.459	3.470	27.3
C-14d	71.7	13.52	26.2	215.2	217.3	0.137	0.136	3.427	3.435	26.5
C-28d	76.8	13.90	24.6	274.5	276.8	0.108	0.107	3.467	3.473	24.5

TABLE 3. The parameters necessary for the porosity calculation by Archie's law.

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