

# RELATION OF CORROSION STIMULATORS TRANSPORT AND MODERN CONCRETE PORE MICROSTRUCTURE

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## Abstract

Reinforced concrete service-life depends on a transport rate of corrosion stimulators, especially chlorides, towards the reinforcement through concrete cover layer. Traditional migration tests are able to state the effective diffusion coefficient; however they do not provide the information about the microstructure and its development in time. The electrochemical impedance spectroscopy was applied to study the microstructure of ultra-high performance concrete, ordinary Portland cement concrete and pore concrete. The porosity and electrochemical parameters were related to water and chloride permeability.

Keywords: EIS, UHPC, chloride diffusion, porosity

## 1. INTRODUCTION

The aggressiveness of concrete matrix on carbon steel reinforcement depends on the access of carbon dioxide and chlorides to rebars and, after corrosion activation, also of oxygen from the atmosphere. Diffusion of carbon dioxide is much slower than diffusion of chlorides which is of (mm/a). When chlorides access the concrete matrix and reach the level of reinforcement, steel rebars surface becomes locally active. Critical concentration of chlorides is about 0.2 wt. % per cement and the corrosion rate can increase to values even higher than 10  $\mu$ m/a.

The best way how to slow down chloride diffusion is to make the access and motion of chlorides into concrete bulk more difficult. That is possible by decrease of the volume and size of open pores in its structure. The open pores represent the way for water and diffusing ions to enter the concrete. Closed pores, on the other hand, are fully separated from the surface by concrete matrix and do not participate on diffusion processes [1. 2]. Total porosity influences mechanical, physical and thermal properties of concrete. Open porosity influences, among other, moisture absorption and drying of concrete. Commonly used method for evaluating open porosity is mercury intrusion porosimetry (MIP). Principal of MIP method is in nonwettability of concrete by mercury. The only way how mercury can enter pores is than under applied pressure. The higher pressure is applied, the smaller is diameter of pores that are filled with it and so the distribution of pore size can be determined. Disadvantages of MIP are in simplifications made for data processing. Material is assumed to create pores with non-elastic sides and with regular shape. Also the contact angle and surface tension are independent of pressure. [3, 4]

As an alternative to MIP, electrochemical impedance spectroscopy (EIS) can be used. It allows to determine microstructure of material while measuring at high frequencies (above 1 kHz). To evaluate EIS data, equivalent circuit is necessary to substitute the real material structure. In concrete exist one insulator path (concrete matrix) and two conductive paths: continuous (open-pores structure) and discontinuous (including also cement blockings). Conductive paths can be substituted by resistance; insulators (and discontinuous points) are substituted with capacitance (**Fig. 1**). Theoretical Nyquist spectrum based on equivalent circuit mentioned above shows two capacitive loops (**Fig. 3a**). From those loops, values of resistance and capacitance of circuit



and so those of real concrete can be calculated. Typical for these impedance spectra is: (1)  $R_1$  significantly increases with hydration time and (2) decreases with increasing water/cement ratio (usually corresponds to higher porosity). (3) Values of  $R_0$  and  $R_1$  decrease as thickness of concrete decreases. [5]



Fig. 1 Schematic (a) and simplified (b) representation of concrete structure and (c) equivalent circuit model for concrete. [5]

Nowadays, normalized or standard long-time and accelerated tests are used to characterize diffusion of chlorides in concrete. Using those methods, we obtain only step information about chloride concentration in tested sample. Disadvantage is also that the tests take not less than several weeks or either months. Therefore, ions are very often accelerated by an electrical potential applied to observed system. Accelerated tests deal with the time demands but they introduce problems of material heating and structure changes due to high applied potential [7]. EIS, compared to those, does not influence the structure of material, is non-invasive and can be used for in-situ measurements [2, 6].

### 2. MATERIALS AND EXPERIMENT

For all measurements, samples of pore concrete (PC), ordinary Portland cement concrete (OPC) and ultrahigh performance concrete (UHPC) were used. The pore concrete was of commercial production and the precise preparation procedure is not known. OPC was prepared using commercial concrete mixture Baumit 20 mixed with distilled water (1-1.125 L of water to 10 kg of mixture). The mixture was compacted for 10 minutes at the vibrating table. All types of concrete were cured in humid atmosphere for 28 days.

### 2.1. Mercury intrusion porosimetry

Samples for MIP were cubes with the edge of 5 mm. Those were dried at the temperature of 105 °C until constant weight. For measurements, *AutoPore IV 9500 V1.06* was used. During evacuation of experimental cell, the pressure was 50 µm Hg with 30 min of evacuation time. High pressure measurements were held up to 400 MPa. Three cubes of the same material were placed to measuring cell to keep right conditions for experiment: when less than 20 % of mercury volume is pressed into pores, the measurement has not sufficient accuracy.

### 2.2. Standard diffusion tests

For non-accelerated diffusion test (NaDT), 10 mm thick cylindrical samples of concretes were used. Dry concrete sample was placed between two cells filled with 1.2 % NaOH solution for the first 24 h. Later, one cell was filled with 3 % NaCl solution and this exposition was held for next 13 days.





Fig. 1 Experimental design of accelerated migration tests

Besides the non-accelerated test, accelerated diffusion tests were held according to the standard AASHTO T227 (ASTM C1202): rapid chloride penetration test (RCPM) and accelerated chloride migration test (ACMT). For both, 50 mm thick cylindrical samples were used. The measurement cell (**Fig. 2**) consisted of an anodal space (left) filled with 1.2 % NaOH solution and cathodal space (right) filled with 3 % NaCl solution, between which the sample was placed. Stainless-steel braided electrodes placed inside the cells, close to the concrete surface, were used for applying the potential. During rapid RCPT, potential of 60 V and in case of ACMT, potential of 24 V was applied. During ACMT experiment, samples of anolyte were taken and the amount of chloride ions was determined using ion selective electrode (ISE). From the slope (*K* (*mol·cm<sup>3</sup>·s<sup>-1</sup>*)) of linear regression of concentration – time plot, the diffusion coefficient (*D*) was determined according to equation **(1)** [5].

$$\boldsymbol{D} = \frac{\boldsymbol{V}\boldsymbol{R}\boldsymbol{T}\boldsymbol{L}}{\boldsymbol{S}\boldsymbol{z}\boldsymbol{F}\boldsymbol{c}_{\boldsymbol{k}}\boldsymbol{\Delta}\boldsymbol{E}}\cdot\boldsymbol{K}$$
(1)

Where:  $V(m^3)$  is the volume of the anodal space,  $S(m^2)$  exposed sample area, L(m) thickness of the sample,  $c_k(mo\cdot ll^{-1})$  concentration of Cl<sup>-</sup> in cathodal solution and  $\Delta E(V)$  potential difference.

# 2.3. Electrochemical impedance spectroscopy

Impedance spectra were measured at the samples for diffusion tests using femtostat FAS 1 (Gamry Inst.) and SP-200 (BioLogic Sci. Inst.). At the samples for NaDT, the spectra were measured during the diffusion test, while at the samples for accelerated tests, those were measured before diffusion testing. The frequency range of femtostat FAS 1 was from 10 mHz/10Hz to 100 kHz and for SP-200 from 300 mHz to 3 MHz; both with the amplitude 10 mV. Working electrode was placed at the solution of NaOH and reference and counter electrodes were in the solution of NaCI.



Fig. 3 (a) Theoretical Nyquist spectrum based on equivalent circuit model in Fig. 1c, (b) typical experimental Nyquist spectrum with only low-frequency loop, and (c) simplified equivalent circuit [5]

Due to limited measurement accuracy for high-frequency range, the impedance loop in this range was not recorded. Therefore, the typical Nyquist plot shows just low-frequency loop (**Fig. 3b**) and the equivalent circuit model for the concrete can be simplified (**Fig. 3c**); since the values of  $C_{ICP}$  are much lower than those of  $C_{DCP}$ .



Elements of the equivalent circuit are related to resistance and capacitance of concrete following the equations (2), (3) and (4) [5].

$$R_{CCP} = R_0 + R_1 \approx \frac{\sigma L\xi}{S\varphi\lambda}$$

$$C_{DCP} = C_1 \cdot \left(\frac{R_1}{(R_0 + R_1)}\right)^2 \approx \frac{(1 - \lambda)\varphi S\varepsilon_0 \varepsilon_r}{d}$$
(2)
(3)

$$R_{DCP} = \frac{(R_0 + R_1) \cdot R_0}{R_1} \approx \frac{(L - d)\sigma\xi}{S\varphi(1 - \lambda)}$$
(4)

In the equations,  $\sigma$  ( $\Omega \cdot m$ ) is resistivity of pore solution,  $\varphi$  (%) porosity,  $\xi$  tortuosity of continuous pores,  $\lambda$  the ratio of continuous pores volume and the total volume of pores (including discontinuous pores), d (m) the equivalent thickness of discontinuous points (DPs) at the DCP.

# 3. RESULTS AND DISCUSSION

Impedance spectra were evaluated using EC-Lab program and the results from the samples for accelerated tests are summarised in **Table 1**. Resistance  $R_{CCP}$ , the resistance of continuously connected pores, is inversely proportional to porosity. Values of R<sub>CCP</sub> for UHPC are order (respective three orders) of magnitude higher than those of OPC and PC, which means that UHPC is the less and PC the most porous of the tested concretes, which correlates well with the MIP data.

	PC	OPC	UHPC
R₁ (Ω·m)	1.94	130.50	5353.90
R₀ (Ω·m)	7.53	7.50	3.61·10 <sup>-8</sup>
C <sub>1</sub> (S·s <sup>α</sup> )	6.03·10 <sup>-6</sup>	6.23·10 <sup>-9</sup>	5.24·10 <sup>-10</sup>
R <sub>CCP</sub> (Ω·m)	9.47	138.00	5353.90
$C_{DCP}$ (S·s <sup><math>\alpha</math></sup> )	2.52·10 <sup>-7</sup>	5.57·10 <sup>-9</sup>	5.24·10 <sup>-10</sup>
R <sub>DCP</sub> (Ω·m)	36.8	7.9	1.90·10 <sup>-4</sup>

Table 1 Initial properties of tested concretes determined using EIS.



Fig. 4 Difference of intruded mercury volume - pore size plot from MIP

According to MIP (**Fig. 4**), UHPC contains in its structure mostly pores with size of 0.015  $\mu$ m and 0.12  $\mu$ m, OPC with 0.4  $\mu$ m and 1  $\mu$ m size, and PC with pores between 0.015 and 0.03  $\mu$ m and also macropores with size about 50  $\mu$ m. The total porosity was determined as 7.88±1.13 % for UHPC, 12.69±0.59 % for OPC and 66.26±1.79 % for PC. C<sub>DCP</sub> is, according to equation (**3**), directly proportional to porosity and indirectly to the  $\lambda$  ratio and thickness of DPs. The highest value of C<sub>DCP</sub> was measured for PC, which correlates with its highest



porosity. Low  $C_{DCP}$  of UHPC and significant difference between  $R_{CCP}$  values of UHPC and OPC (which do not correlate with the difference in MIP data) are probably caused by low  $\lambda$  ratio in UHPC, to which is  $R_{CCP}$  also inversely proportional. Therefore, we can say that UHPC structure contains more discontinuous pores and thus higher amount or thicker layer (*d*) of DPs. That is also validated by trend in  $R_{DCP}$  values. Those correspond to the resistance of the continuous part of DCP and according to equation (4), they are inversely proportional to porosity and directly to  $\lambda$  ratio.



Fig. 2 Development of impedance spectra of (a) PC and (b) OPC during NaDT in 1.2 % NaOH solution

Impedance spectra of samples under NaDT conditions (**Fig. 5, Table 2**) show decrease of resistance during its first phase (saturation with NaOH solution) for all tested concretes. During the second phase, when the diffusion of chlorides was determined, the resistance of PC and UHPC develops the same (**Fig. 6**a, **Table 2**) However, after 24 hours of exposition, resistance of OPC shows the opposite trend (**Fig. 3**b). Increase of resistance occurs probably due to hydration processes, during which the concrete ages (cement transforms to CSH gel) and the *continuous pores can be blocked*.



Table 2 Change of resistance of CCP in UHPC during the two phases of NaDT

Fig. 3 Development of impedance spectra of (a) PC and (b) OCP during NaDT with chloride solution.

The difference in permeability of tested concretes can be also expressed by apparent diffusion coefficients (*D*). The values obtained from EIS measurements correlate well with those from the accelerated diffusion tests - ACMT, RCPT (**Table 3**). The difference in values obtained for particular concrete type is caused by measurement errors and different accuracy of methods (various influences according to method).



method		PC	OPC	UHPC
ACMT	K (mol·cm⁻³·s⁻¹)	9.79·10 <sup>-9</sup>	1.19·10 <sup>-10</sup>	1.16·10 <sup>-14</sup>
	DACMT (cm <sup>2</sup> ·s <sup>-1</sup> )	1.50·10 <sup>-6</sup>	2.41·10 <sup>-8</sup>	2.56·10 <sup>-9</sup>
RCPT	R (Ω·m)	51.2	166.5	7480.0
	σ (S·cm⁻¹)	1.95·10 <sup>-4</sup>	6.01·10 <sup>-5</sup>	1.34·10 <sup>-6</sup>
	DRCPT (cm <sup>2</sup> ·s <sup>-1</sup> )	1.64·10 <sup>-7</sup>	5.05·10 <sup>-8</sup>	1.12 <sup>.</sup> 10 <sup>-9</sup>
EIS	R <sub>EIS</sub> (Ω·m)	56.2	159.8	6536.3
	σ <sub>EIS</sub> (S·cm⁻¹)	1.78·10 <sup>-4</sup>	6.26·10 <sup>-5</sup>	1.53·10 <sup>-6</sup>
	D <sub>EIS</sub> (cm <sup>2</sup> ·s <sup>-1</sup> )	1.50·10 <sup>-7</sup>	5.26·10 <sup>-8</sup>	1.29 <sup>.</sup> 10 <sup>-9</sup>

Table 3 Parameters of tested concretes evaluated from accelerated diffusion tests and EIS

### CONCLUSION

We confirmed that EIS can be used for characterization of concrete structure and its permeability. This method shows the same trend in porosity of tested concretes as traditionally used MIP. Advantage of EIS, beside that it can be applied in-situ and is non-destructive, is in obtaining information about pore ordering and their continuity. UHPC, with the highest values of  $R_{CCP}$  and the lowest of  $C_{DCP}$ , was proved to contain less continuously connected pores and so lower permeability for chlorides. Increase of  $R_{CCP}$  values during tests occurs most probably due to pore narrowing by precipitation of complex salts. Another explanation can be in slow aging process of UHPC, during which discontinuous points are created by hydration of cement. In our future work, we will focus on this phenomenon.

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