

RELATION OF CORROSION STIMULATORS TRANSPORT AND MODERN CONCRETE PORE MICROSTRUCTURE

NOVÁKOVÁ Radka¹, KOUŘIL Milan¹, STOULIL Jan¹, SPLÍTEK Karel¹, ŠPINAR Vojtěch¹,
DOBIÁŠ Daniel², POKORNÝ Petr²

¹ *University of Chemistry and Technology Prague - Department of Metals and Corrosion Engineering, Prague, Czech Republic, EU*

² *Czech Technical University in Prague - Klokner Institute, Prague, Czech Republic, EU*

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, the 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 $\mu\text{m/a}$.

The best way how to slow down the chloride diffusion is to make the access and motion of chlorides into the 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. The 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. The open porosity influences, among other, the moisture absorption and drying of concrete. Commonly used method for evaluating the open porosity is the mercury intrusion porosimetry (MIP). Principal of MIP method is in the nonwettability of concrete by mercury. The only way how the mercury can enter pores is than under an 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 a regular shape. Also, the contact angle and surface tension are independent of pressure. [3, 4]

As an alternative to MIP, the electrochemical impedance spectroscopy (EIS) can be used. It allows to determine the microstructure of material while measuring at high frequencies (above 1 kHz). To evaluate EIS data, an 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 a resistance; insulators (and discontinuous points) are substituted with a capacitance (**Fig. 1**). A theoretical Nyquist spectrum based on the equivalent circuit mentioned above shows two capacitive loops (**Fig. 3a**). From those loops, values of the resistance and capacitance of circuit and so those of the real concrete can be calculated. Typical for these

impedance spectra is: (1) R_1 significantly increases with the 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 the thickness of a concrete decreases. [5]

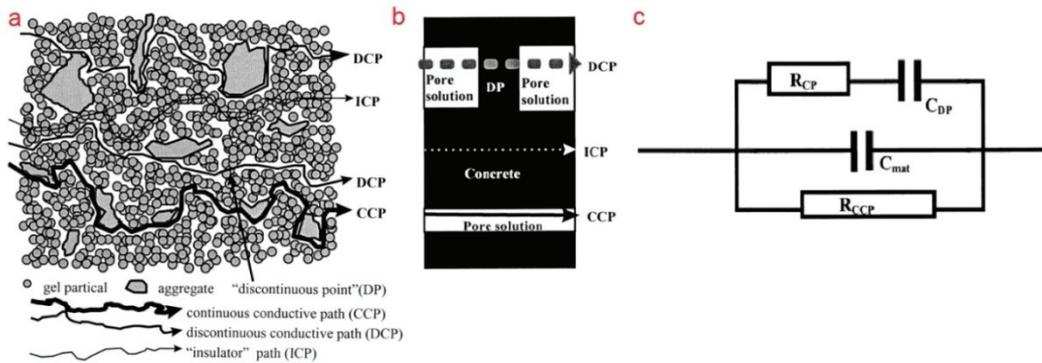


Fig. 1 Schematic (a) and simplified (b) representation of a concrete structure and (c) an equivalent circuit model for concrete [5]

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 the chloride concentration in the tested sample. A 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 the 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 the pore concrete (PC), ordinary portland cement concrete (OPC) and ultra-high performance concrete (UHPC) were used. The pore concrete was of commercial production and the precise preparation procedure is not known. The OPC was prepared using a 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 a 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 μ m Hg with 30 min of the evacuation time. High pressure measurements were held up to 400 MPa. Three cubes of the same material were placed to measuring cell to keep the right conditions for experiment: when less than 20 % of the mercury volume is pressed into pores, the measurement has not sufficient accuracy.

2.2. Standard diffusion tests

For a non-accelerated diffusion test (NaDT), 10 mm thick cylindrical samples of concretes were used. The 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. 2 Experimental design of accelerated migration tests

Besides the non-accelerated test, accelerated diffusion tests were held according to the standard AASHTO T227 (ASTM C1202): a rapid chloride penetration test (RCPT) and an 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 a 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 the ion selective electrode (ISE). From the slope (K ($\text{mol}\cdot\text{cm}^3\cdot\text{s}^{-1}$)) of linear regression of the concentration - time plot, the diffusion coefficient (D) was determined according to equation (1) [5].

$$D = \frac{VRTL}{SzFc_k\Delta E} \cdot K \quad (1)$$

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 ($\text{mol}\cdot\text{l}^{-1}$) concentration of Cl^- in cathodal solution, and ΔE (V) potential difference.

2.3. Electrochemical impedance spectroscopy

Impedance spectra were measured at the samples for the 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. The working electrode was placed at the solution of NaOH and reference and counter electrodes were in the solution of NaCl.

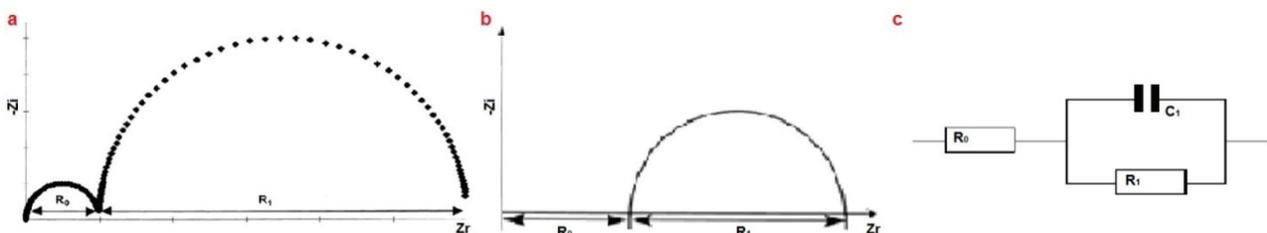


Fig. 3 (a) Theoretical Nyquist spectrum based on the equivalent circuit model in **Fig. 1c**, (b) typical experimental Nyquist spectrum with only low-frequency loop, and (c) the simplified equivalent circuit [5]

Due to a 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} .

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

$$R_{CCP} = R_0 + R_1 \approx \frac{\sigma L \xi}{S \varphi \lambda} \quad (2)$$

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

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

In the equations, σ ($\Omega \cdot m$) is the resistivity of pore solution, φ (%) porosity, ξ tortuosity of continuous pores, λ 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

The impedance spectra were evaluated using EC-Lab program and the results from the samples for the accelerated tests are summarised in **Table 1**. Resistance R_{CCP} , the resistance of continuously connected pores, is inversely proportional to the porosity. Values of R_{CCP} 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.

Table 1 Initial properties of tested concretes determined using EIS

	PC	OPC	UHPC
R_1 ($\Omega \cdot m$)	1.94	130.50	5353.90
R_0 ($\Omega \cdot m$)	7.53	7.50	$3.61 \cdot 10^{-8}$
C_1 ($S \cdot s^\alpha$)	$6.03 \cdot 10^{-6}$	$6.23 \cdot 10^{-9}$	$5.24 \cdot 10^{-10}$
R_{CCP} ($\Omega \cdot m$)	9.47	138.00	5353.90
C_{DCP} ($S \cdot s^\alpha$)	$2.52 \cdot 10^{-7}$	$5.57 \cdot 10^{-9}$	$5.24 \cdot 10^{-10}$
R_{DCP} ($\Omega \cdot m$)	36.8	7.9	$1.90 \cdot 10^{-4}$

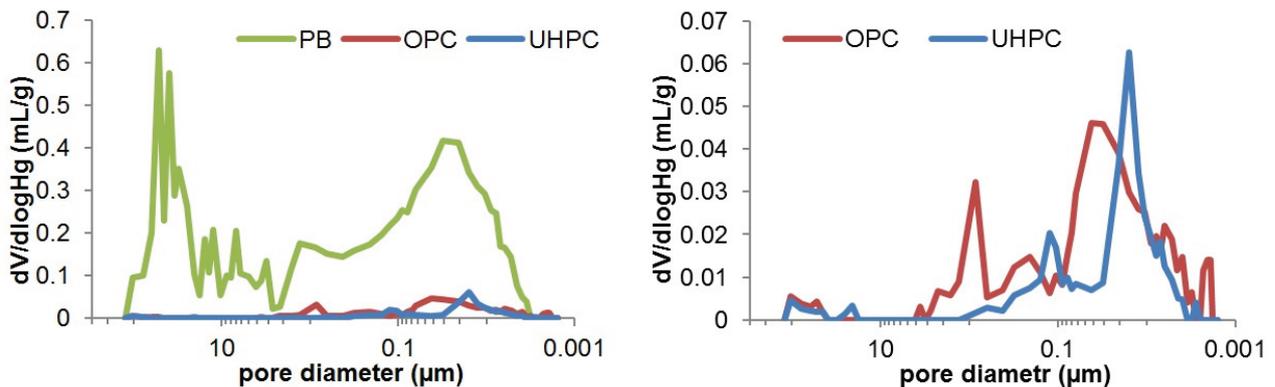


Fig. 4 Difference of intruded mercury volume - pore size plot from MIP

According to MIP (**Fig. 4**), UHPC contains in its structure mostly pores with size of 0.015 μm and 0.12 μm , OPC with 0.4 μm and 1 μm size, and PC with pores between 0.015 and 0.03 μm and also macropores with size about 50 μm . 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_{DCP} is, according to the equation (3), directly proportional to the porosity and indirectly

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

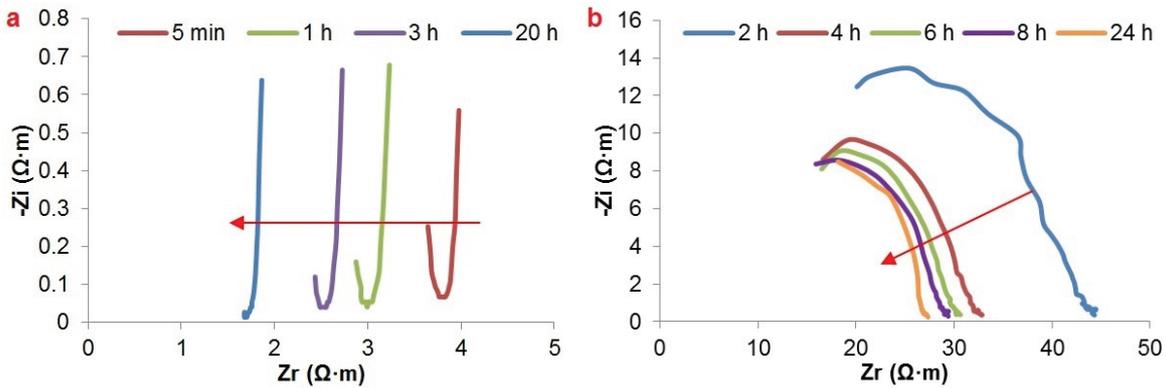


Fig. 5 Development of the impedance spectra of (a) PC and (b) OPC during NaDT in 1.2 % NaOH solution.

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

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

solution	1.2 % NaOH			3 % NaCl				
	80 min	6.5 h	24 h	5 min	20 h	68 h	164 h	312 h
R_{CCP} (Ω·m)	13281	7762	6040	6018	5738	4925	4245	4100

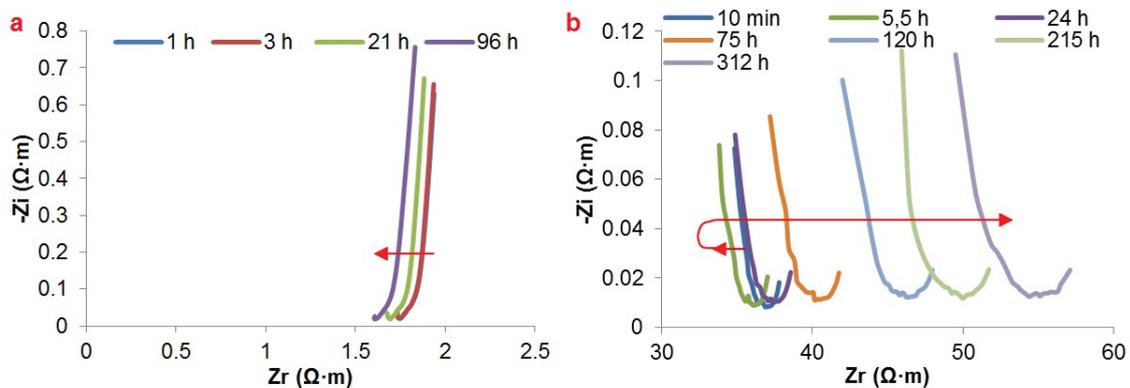


Fig. 6 Development of the impedance spectra of (a) PC and (b) OCP during NaDT with chloride solution.

The difference in permeability of tested concretes can be also expressed by an apparent diffusion coefficient (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 the particular concrete type is caused by measurement errors and different accuracy of methods (various influences according to the method).

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

method		PC	OPC	UHPC
ACMT	K ($\text{mol}\cdot\text{cm}^{-3}\cdot\text{s}^{-1}$)	$9.79\cdot 10^{-9}$	$1.19\cdot 10^{-10}$	$1.16\cdot 10^{-14}$
	D _{ACMT} ($\text{cm}^2\cdot\text{s}^{-1}$)	$1.50\cdot 10^{-6}$	$2.41\cdot 10^{-8}$	$2.56\cdot 10^{-9}$
RCPT	R ($\Omega\cdot\text{m}$)	51.2	166.5	7480.0
	σ ($\text{S}\cdot\text{cm}^{-1}$)	$1.95\cdot 10^{-4}$	$6.01\cdot 10^{-5}$	$1.34\cdot 10^{-6}$
	D _{RCPT} ($\text{cm}^2\cdot\text{s}^{-1}$)	$1.64\cdot 10^{-7}$	$5.05\cdot 10^{-8}$	$1.12\cdot 10^{-9}$
EIS	R _{EIS} ($\Omega\cdot\text{m}$)	56.2	159.8	6536.3
	σ_{EIS} ($\text{S}\cdot\text{cm}^{-1}$)	$1.78\cdot 10^{-4}$	$6.26\cdot 10^{-5}$	$1.53\cdot 10^{-6}$
	D _{EIS} ($\text{cm}^2\cdot\text{s}^{-1}$)	$1.50\cdot 10^{-7}$	$5.26\cdot 10^{-8}$	$1.29\cdot 10^{-9}$

CONCLUSION

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

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