INFLUENCE OF MODERN CONCRETE MICROSTRUCTURE ON THE DIFFUSION OF CORROSION AGENTS

NOVÁKOVÁ Radka[1], KOUŘIL Milan[1], DOBIÁŠ Daniel[2], SEDLÁŘOVÁ Ivona[1], STOULIL Jan[1]

[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

The durability of reinforced concrete structures is limited mainly by the reinforcement material, as which a carbon steel is widely used. Carbon steel corrosion rate increases due to carbonation or contamination with chloride anions. The activation time is strongly influenced by the concrete structure as it influences the diffusion rate of corrosion agents. Therefore, modern ultra-high performance concrete materials are designed to provide less porous structure. Electrochemical impedance spectroscopy (EIS) was used to determine microstructure of different concrete types; ordinary portland cement concrete (OPC), and two ultra-high performance concretes with different water/cement ratio. The microstructure was compared between the different concrete types, and as influenced by the time of curing. Results obtained from EIS correlate well with those of traditionally used mercury intrusion porosimetry.

Keywords: Concrete microstructure, UHPC, OPC, EIS

1. INTRODUCTION

Reinforced concrete structures service life is planned in decades and is achievable under convenient conditions; either outer environment or the combination of construction materials themselves. As the concrete matrix is resistant in common outer environment, problems are mostly with the corrosion of reinforcing material. In hydrated cement, the corrosion rate depends on the moisture level and the accessibility of the reinforcement for aggressive species from outer atmosphere. To prevent their penetration into concrete matrix, materials with low-porous structure are developed. The porosity of cementitious materials mostly depends on the water - cement ratio (w/c ratio). The lower the w/c ratio, the lower is the porosity of the final material. Ultra-high performance concretes (UHPC) have the w/c ratio around 0.2 and show high mechanical characteristics.

In the concrete materials, the mechanical and thermal properties are influenced by its total porosity, while the open porosity influences the moisture absorption to the material and, thus, also the penetration of aggressive agents [1, 2]. Nowadays, the mercury intrusion porosimetry (MIP) is used to determine the open porosity of materials. Its principle is in non-wettability of a concrete material by mercury. Because of that, higher pressure needs to be applied to intrude the mercury into pores. The higher the applied pressure, the smaller pores are filled with it. Therefore, the distribution of the pore size can be determined based on the amount of mercury intruded under certain pressure. Even though MIP gives accurate results, the processing of MIP data brings simplifications; the material is assumed to create regular-shape pores with non-elastic sides, and the contact angle and surface tension are independent on pressure [3, 4].

Electrochemical impedance spectroscopy (EIS) seems to be a good alternative to MIP [5]. When the measurement is held at frequencies above 1 kHz, microstructure of the material can be determined. The equivalent circuit for the evaluation (**Figure 1b**) consists, in the case of concrete material, of three components representing the possible paths through the material (**Figure 1a**). A continuous conductive path (CCP), the open pores, is represented by a resistor. A discontinuous conductive path (DCP), the open pores blocked with thin cement layer (discontinuous point; DP), is represented by a combination of resistor and capacitor. The cementitious matrix is an insulator path (IP) and is represented by a simple capacitor. A theoretical Nyquist spectrum (**Figure 1c**) based on the mentioned equivalent circuit shows two capacitive loops. The resistance and capacitance of the equivalent circuit and consequently the characteristics of the material can be calculated from those. [5]

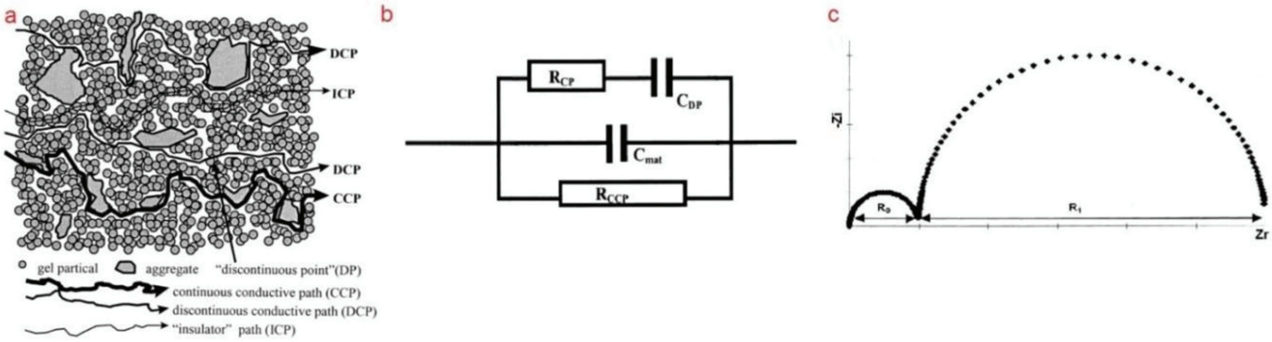

Figure 1 (a) Schematic representation of a concrete structure, (b) an equivalent circuit model for concrete, and (c) a theoretical Nyquist spectrum based on the equivalent circuit model in (b) [5]

2. MATERIALS AND EXPERIMENT

The microstructure of two types of UHPC and an OPC concretes was determined using MIP and EIS methods. The two UHPC types differ in the w/c ratio, which is 0.22 (UHPC1) and 0.26 (UHPC2), respectively. OPC used for microstructure determination was prepared using a commercial concrete mixture Baumit 20 mixed with distilled water (1 - 1.25 L of water per 10 kg of mixture). The mixture was compacted for 10 minutes at a vibrating table. The OPC and UHPC2 types of concrete were cured in humid atmosphere for 28 days. The UHPC1 was tested after the curing time of 28, 60 and 180 days.

For MIP, cube samples with the edge of 5 mm were prepared and dried until the constant weight at the temperature of 105 °C. At the *AutoPore IV 9500 V1.6* device, the evacuation pressure was 50 µm Hg with 30 min of the evacuation time. High pressure measurements were held up to 400 MPa. Due to the experimental setup, three cubes of the same material were used to obtain sufficient accuracy of the results.

For EIS measurements, cylindrical samples (10 cm diameter, 5 cm thickness) were placed between cells filled with solution (**Figure 2**). As electrodes, stainless-steel braided grids were placed inside the cells close to the concrete surface. The measurements were run on the SP-200 (BioLogic Sci. Inst.), the frequency range was between 300 mHz and 3 MHz with the amplitude of 10 mV, and EC-lab software was used for data evaluation.

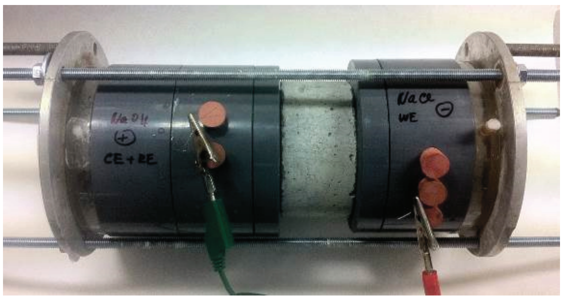

Figure 2 Experimental design of EIS measurement

The high-frequency loop of Nyquist plot (**Figure 3a**) is not recorded due to a limited accuracy of the high-frequency range. Thus, only the low-frequency loop is recorded (**Figure 3b**) and, due to the values of C_{ICP} being much lower than those of C_{DCP}, the equivalent circuit model for the concrete can be simplified (**Figure 3c**). The resistance and capacitance of a concrete are then related to the equivalent circuit according to the equation (1) - (3).

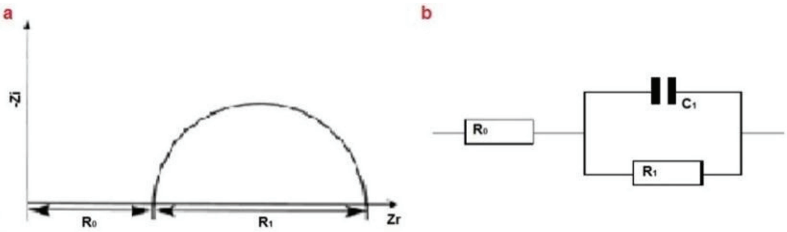

Figure 3 (a) Typical experimental Nyquist spectrum with only low-frequency loop, and (b) the simplified equivalent circuit [5]

$$R_{CCP} = R_0 + R_1 \approx \frac{\sigma L \xi}{S \varphi \lambda} \quad (1)$$

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

$$R_{DCP} = \frac{(R_0+R_1) \cdot R_0}{R_1} \approx \frac{(L-d)\sigma\xi}{S\varphi(1-\lambda)} \quad (3)$$

Where σ *(Ω·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

3.1. Concrete microstructure

The results of the EIS measurements at concretes after 28 day of curing (**Table 1**) show an increase in the R_{CCP} and a decrease in the C_{DCP} values following OPC - UHPC1 - UHPC2 row. Since R_{CCP} is inversely proportional to porosity and λ-ratio; the open-pores fraction of the total porosity (**equation 1**), the UHPCs are less porous (have less and/or smaller pores in their structure) than OPC and within the UHPCs, the one of w/c ratio of 0.26 (UHPC2) shows approx. two times lower porosity than UHPC1 with the w/c ratio of 0.22 after 28 days of curing. This finding may reflect a lack of water in the concrete bulk for completing the hydration process resulting in occurrence of bigger pores in UHPC1 with the lower w/c ratio (**Figure 4**). The C_{DCP} values show the same trend in the total porosity.

Table 1 Initial properties of tested concretes after 28 days of curing determined using EIS

	OPC	UHPC1	UHPC2
R_1 (Ω·m)	130.5	5353. 9	11859.2
R_0 (Ω·m)	7.5	$1.90 \cdot 10^{-4}$	34.6
C_1 ($S \cdot s^{\alpha}$)	$6.23 \cdot 10^{-9}$	$5.24 \cdot 10^{-10}$	$2.34 \cdot 10^{-10}$
R_{CCP} (Ω·m)	138	5353.9	11893.8
C_{DCP} ($S \cdot s^{\alpha}$)	$5.57 \cdot 10^{-9}$	$5.24 \cdot 10^{-10}$	$2.32 \cdot 10^{-10}$
R_{DCP} (Ω·m)	7.9	$1.90 \cdot 10^{-4}$	34.7

According to MIP (**Figure 4**), the total open porosity of OPC was determined as 12.7 %, 7.9 % of UHPC1, and 3.4 % of UHPC2. The most common size of OPC pores was 0.4 and 1 µm, 0.015 and 0.2 µm of UHPC1 and 0.002 - 0.006 µm of UHPC2. That shows the EIS data trend correlates well with MIP results. The EIS-obtained values of R_{DCP} do not correlate precisely with MIP data in the case of UHPC1. More data must be collected to understand the relationship.

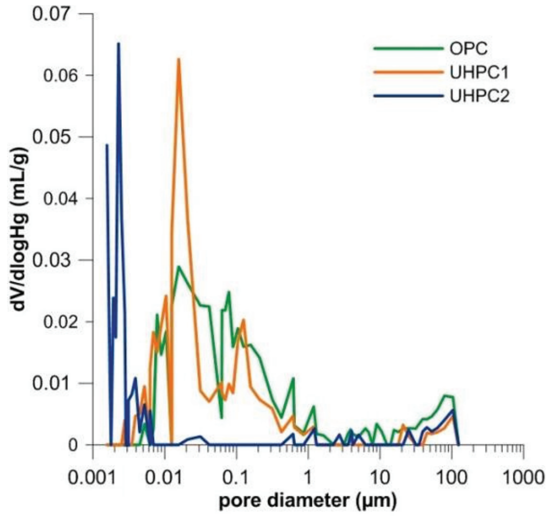

Figure 4 Difference of intruded mercury volume - pore size plot from MIP for concretes after 28 days of curing

According to MIP data measured for UHPC1 after different time of curing (**Figure 5**), the longer the curing takes, the lower pore diameter and total porosity the material shows. Most pores were identified to have 0.015 and 0.12 µm in UHPC1 cured for 28 days. The samples of UHPC1 cured 60 and 180 days have the most pores of a diameter of 0.008, 0.01, and 0.015 µm after 60 days; and between 0.002 and 0.0052 µm after 180 days, respectively. The total open porosity was determined as 7.9, 7.3 and 5 % with increasing time of curing.

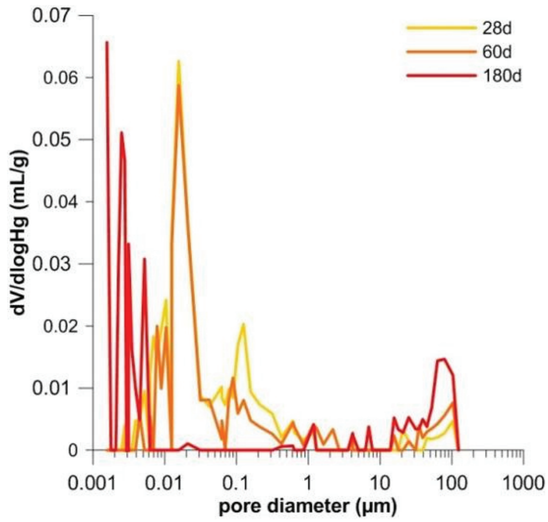

Figure 5 Difference of intruded mercury volume - pore size plot from MIP for UHPC1 after different curing times

The decreasing trend in porosity show also EIS data measured on UHPC1 after different time of curing (**Table 2**). The values of R_{CCP} after 28 and 60 days of curing are of the same order of magnitude, which can be explained while comparing the MIP curves of those materials. High fraction of the pores of both show similar size in a range from 0.008 to approx. 0.13 µm. The significant increase in R_{CCP} of the samples cured for 180 day correlate well with the low open porosity determined by MIP. This trend is also noticeable from the values of C_{DCP} and R_{DCP} that are directly and inversely proportional to porosity.

Table 2 Initial properties of UHPC1 after different curing times determined using EIS

	28 days	60 days	180 days
R_1 (Ω·m)	5353. 9	4524.5	$1.32 \cdot 10^{6}$
R_0 (Ω·m)	$1.90 \cdot 10^{-4}$	35.72	-
C_1 ($S \cdot s^{\alpha}$)	$5.24 \cdot 10^{-10}$	$2.86 \cdot 10^{-10}$	$2.48 \cdot 10^{-11}$
R_{CCP} (Ω·m)	5353.9	4560.2	$1.32 \cdot 10^{6}$
C_{DCP} ($S \cdot s^{\alpha}$)	$5.24 \cdot 10^{-10}$	$2.81 \cdot 10^{-10}$	$2.48 \cdot 10^{-11}$
R_{DCP} (Ω·m)	$1.90 \cdot 10^{-4}$	36.0	-

While related to open porosity, the EIS-obtained characteristics of tester concretes already indicate certain trends (**Figure 6**). As the data of UHPC1 suggest, the resistance of both continuous and discontinuous pores increase with the increasing hydration of cementitious matrix. The trend of the capacitance of discontinuous pores than shows the opposite trend. That is supported by the idea of less porous material, which has less connected pores in its structure (lower λ-ratio). The compactness of the concrete matrix (the type of concrete) would than, in general, shift the curves to either lower, in case of UHPC2, or, respectively, to higher porosity, in case of OPC.

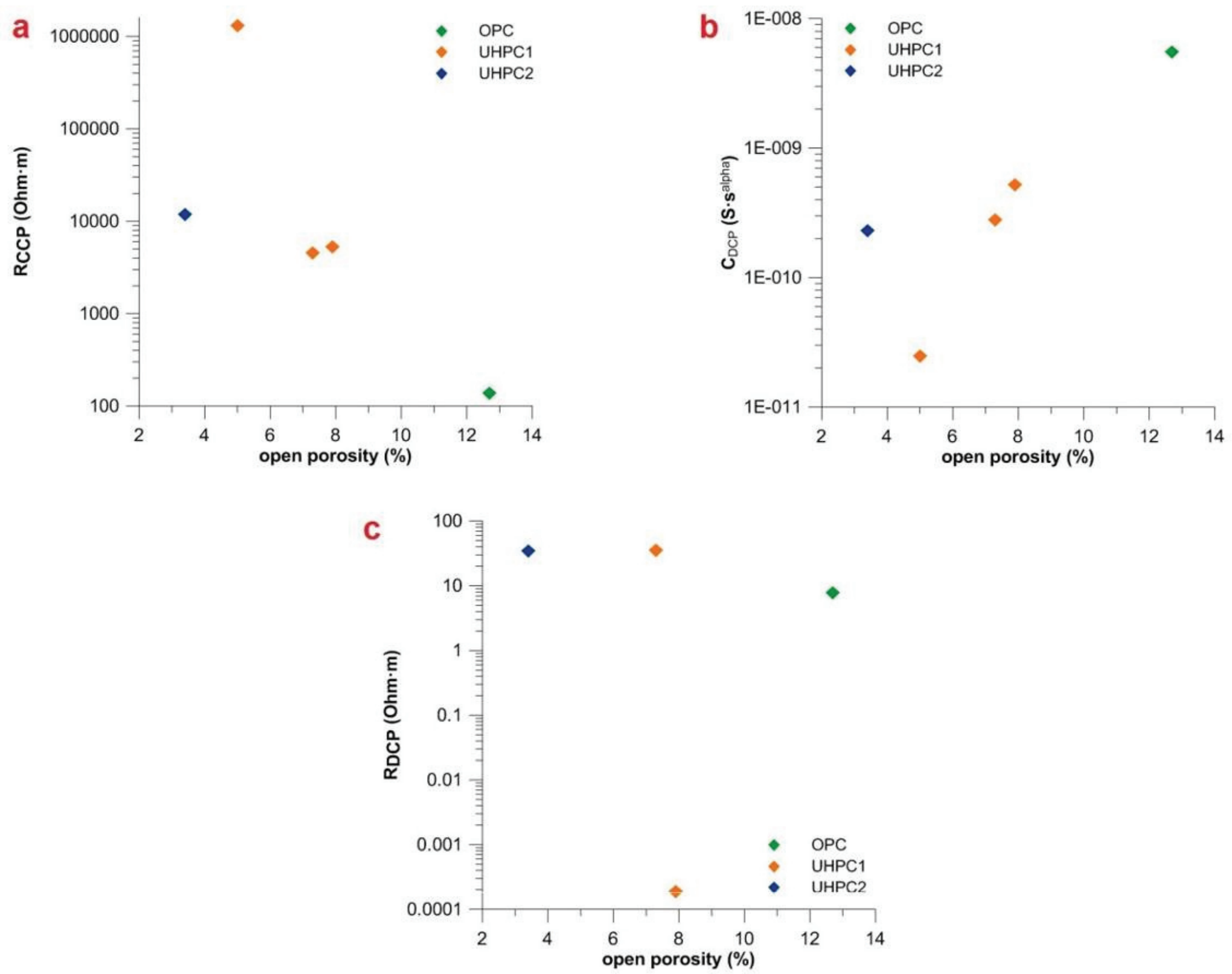

Figure 6 Trend in EIS characteristics of concrete; (a) R_{CCP}, (b) C_{DCP}, and (c) R_{DCP} according to the open porosity

4. CONCLUSION

Using the electrochemical impedance spectroscopy, we have shown that the total porosity of OPC, UHPC1, and UHPC2 decreases as named. This trend corresponds well with the mercury intrusion porosimetry trend of open porosity. The difference in R_{DCP} of UHPC1 (when compared to other concrete types) could be caused by changes in its microstructure over the time as the open-pores fraction is already low and further pore narrowing due to continuous hydration of cement or precipitation of complex salts can occur. The further development of concrete structure over time was also successfully proven using the EIS means to compare the structure of concretes with different curing time. Therefore, our results show that electrochemical impedance spectroscopy might be a useful non-destructive tool for characterizing concrete porosity. However, more laboratory testing and simplification of the technique is certainly required before final applicability in the field.

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