CHARACTERIZATION OF CHLORIDE DIFFUSION INTO REINFORCED CONCRETE

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Abstract

This poster focuses on the characterization of chloride migration from the environment into different types of concrete. Chloride diffusion into reinforced concrete plays an important role in the degradation of reinforced concrete structures. Three types of concrete were tested: conventional concrete, conventional concrete with Portland cement and concrete with the addition of silica fume. These additions led to a reduction in the rate of chloride diffusion. The diffusion rate was determined by means of an immersion test in a solution containing 3% chloride ions. Electrochemical impedance spectroscopy (EIS) was used to further describe the microstructure of the concrete. Open porosity was quantified based on the analysis of the data obtained and these results were correlated with the rate of chloride diffusion. The positive effect of the additives, consisting of limiting chloride migration, was confirmed by the reduction of pore permeability as seen in the EIS data.

Keywords: Chlorides diffusion, steel reinforcement corrosion, concrete additives, silica fume, fly ash

1. INTRODUCTION

Reinforced concrete is a composite material made of a concrete matrix and steel reinforcement to improve mechanical properties. Carbon steel is mostly used as reinforcement. The stability of carbon steel in concrete is important for the durability of the material. Steel reinforcement is naturally protected by formation of stable and protective oxide passive layer once the steel come into contact with an alkaline environment such as a concrete pore solution. Passive layer may be impaired by presence of chlorides that come into concrete from de-icing salts or sea water. Loss of alkalinity by means of carbonation is another but minor cause of corrosion activation of steel reinforcement. Chlorides anions permeability is a key factor for corrosion resistance. The chlorides permeability is influenced by porosity which may result from low compaction of concrete and too high water-to-cement ratio. Another factor that may affect concrete porosity is an electrical current flowing through ion-conductive environment of concrete pores system and hydrated cement binder [1-3].

To create a less porous concrete, additives such as silica fume or fly ash can be used. Silica fume is an amorphous SiO_2 powder with small grain size (diameter below 1 μm). An advantage of using silica fume is that it can fill micropores and make diffusion more difficult. Silica fume is usually used up to 10 % as a replacement for Portland cement. Fly ash is a well-known environmental pollutant and therefore its use in civil engineering seems to be effective. Fly ash particles are spherical, and their effect is to increase the workability of concrete and to reduce the amount of water needed in the concrete mix. Their addition also reduces permeability in the same way as silica fume. On the other hand, high additions of fly ash have a negative effect on the mechanical properties. A fly ash content of 20 % in concrete meets the environmental and economic advantages [4-6]. To describe the influence of the additives on porosity and the diffusion behaviour of chlorides anions is the aim of this paper.

Electrochemical protective techniques are applicable for preventing the corrosion activation (preventive cathodic protection) or for rehabilitation of passivity (electrochemical chloride extraction, realkalization, cathodic protection). All the techniques are based on cathodic polarization of the reinforcement by direct electrical current. Similar approach may be used for electrochemical injection of charged nanoparticles and cationic corrosion inhibitors. On the other hand, all the direct current techniques may influence microstructural properties of cement binder in concrete, which may lead to enhanced permeability of chlorides through concrete [7,8].

2. EXPERIMENTAL PART

2.1. Studied materials

Three types of concrete were studied. The concrete types were different in a binding system. In the case of "**cA**" concrete, the Portland cement binding system was used (CEM I 42.5R), Portland composite-cement (CEM II 42.5R) based on fly ash was used for making the "**cB**" samples and the Portland cement with silica fume was for making the "**cC**" samples. The composition of the samples is shown in the **Table 1**. The water-to-cement ratio is 0.803 for the prepared specimens, this value was chosen to easier observation of transport processes thanks to the higher porosity.

Table 1 Concrete specimens composition in kilograms per cubic meter

Component	**cA**	**cB**	**cC**
CEM I 42.5R	230.5	-	207.4
CEM II 42.5R	-	230.5	-
silica fume	-	-	23.0
water	185.0	185.0	185.0
sand 0-4 mm	1012.3	1012.3	1012.3
aggregate 4-8 mm	256.1	256.1	256.1
aggregate 8-16 mm	512.1	512.1	512.1

Samples were cylindrical with 100 mm in the diameter and 50 mm or 60 mm high (50 mm – samples for electrochemical measurements and 60 mm for diffusion tests). Samples were stored in saturated solution of $Ca(OH)_2$ to eliminate the carbonation on air.

2.2. Diffusion tests

The diffusion tests have been conducted to investigate the process of contamination of concrete by chlorides anions. Concrete samples were coated with Izoban paint (Detecha) except one side that served as an entrance for chlorides from a 3 wt.% NaCl solution (**Figure 1**). The exposition last for 30 and 60 days.

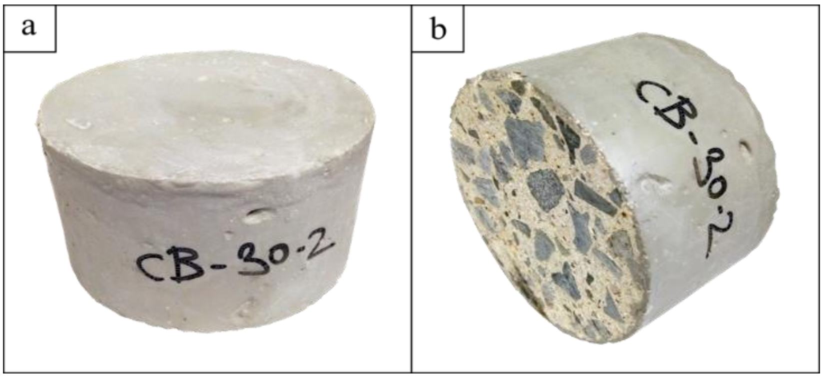

Figure 1 Samples for diffusion tests

Samples after exposition were dried to constant weight at 50 °C. The dried samples were drilled to obtain concrete powder for chloride concentration profile among the sample depth. 2,5 g of drilled powder of a constant weight was put into 250 ml beaker, 50 ml of demineralized water and 10 ml of HNO_3 (concentration 5 mol/l) was added afrewards. An addition of 50 ml of boiling demineralized wated followed and the whole suspension was covered and boiled for 3 minutes on the heater. After that, the suspension was cooled down at ambient temperature. Then the suspension was filtrated on filter paper (Filtrak 389) into small PET medicine bottle.

Analysis of the chloride content in the prepared solution were conducted by potentiometric titration (EasyPlus Titrator APO 15, Mettler Toledo). $AgNO_3$ solution of concentration 0.1 mol/l was used for the titration. The chloride concentrations in solution were converted to wt. % for the initial dry weight of the powder.

2.3. Electrochemical impedance spectroscopy

The electrochemical impedance spectroscopy (EIS) has been chosen to get the information about the sample's microstructure. EIS enables to measure impedance as a function of current frequency. The obtained data are not enough to get information about microstructure, to get them it is necessary to compare the data with model system containing microstructures elements. The impedance spectres were measured on Zahner Zennium X on the software ThalesXT USB (v. 5.3.1). The frequency interval was set from 1 Hz to 12 MHz, the signal amplitude was 20 mV. A measurement cell was made of PMMA (polymethylmethacrylate), the electrodes were made of stainless steel nets with the net size 1mm. The sample was put in this cell with electrolyte (saturated $Ca(OH)_2$), the cell is shown on the (**Figure 2**).

The concrete specimens consist of aggregate and the cementitious binder, between which there is a pore space containing the pore solution. Thus, there are 3 paths for the passing of electric current in the sample. These paths for electrical current are shown on the (**Figure 3**) which represents the structure model. The part of the concrete without pores is a poor conducting path for electric current (CPE1 circuit branch on the **Figure 3**). Isolated pores create a discontinuous path for the electric current (R2 and CPE2 circuit branch on the **Figure 3**). If there are pores and they are connected, there is a good conductivity for electric current (R3 circuit branch on the **Figure 3**). The constant phase element on the (**Figure 3**) represents diversity from ideal condenser. From these constant phase elements is possible to create the structure model. Obtained data have been analysed using Gamry Echem Analyst software (version 6.33). And the system model was fitted on the obtained spectrum.

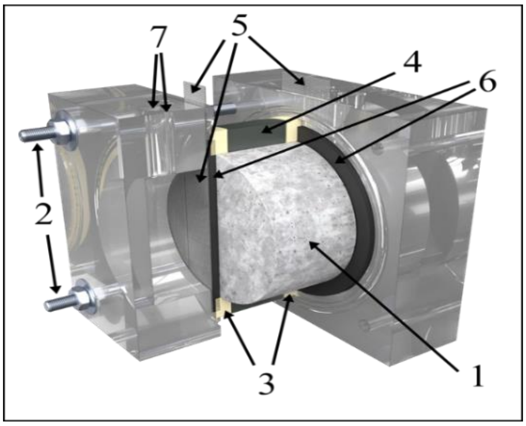

Figure 2 Cell configuration for EIS: (1) sample, (2) tightening system, (3) insulator, (4) central ring, (5) steel electrodes, (6) graphite tissue, (7) pouring and degassing hole

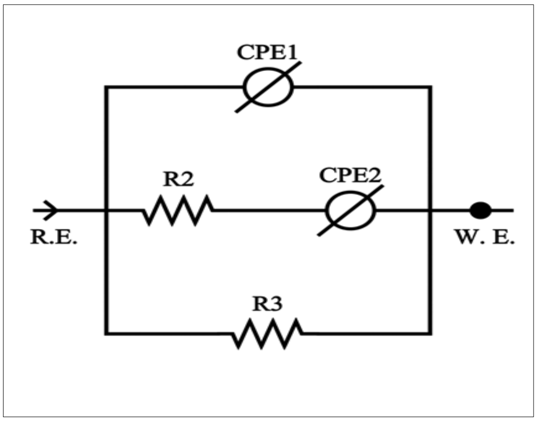

Figure 3 Circuit model used for EIS: CPE - constant phase elements, R - resistors, R.E. - reference electrode, W.E. - working electrode

3. RESULTS

3.1. Diffusion test

The concentration profiles were obtained from the 30- and 60-days diffusion tests. Chloride concentration descended with depth. The concentrations profiles are on the (**Figure 4** and **Figure 5**). The concentration is expressed as a mass of chlorides in the sample powder. The chlorides concentration from higher depths were below the detection limit. The concentration profiles from a 60-day exposure of cB and cC concrete are very similar; protection against chloride diffusion by fly ash does not appear to be very effective in the long term.

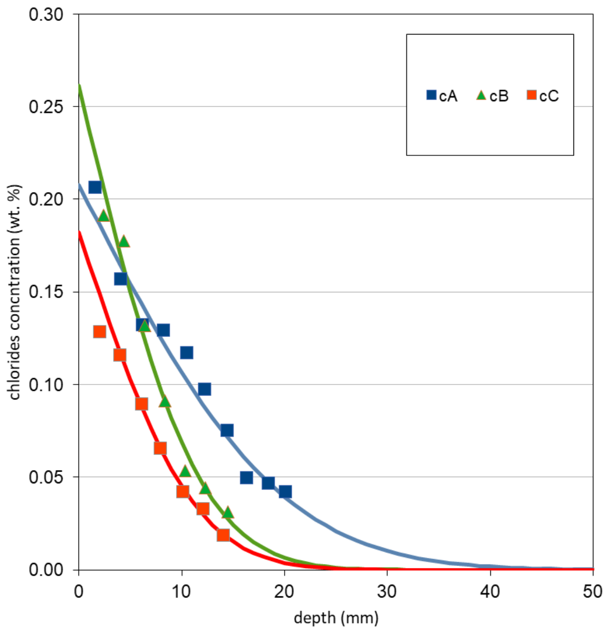

Figure 2 Chloride concentration profile after 30 days of exposition

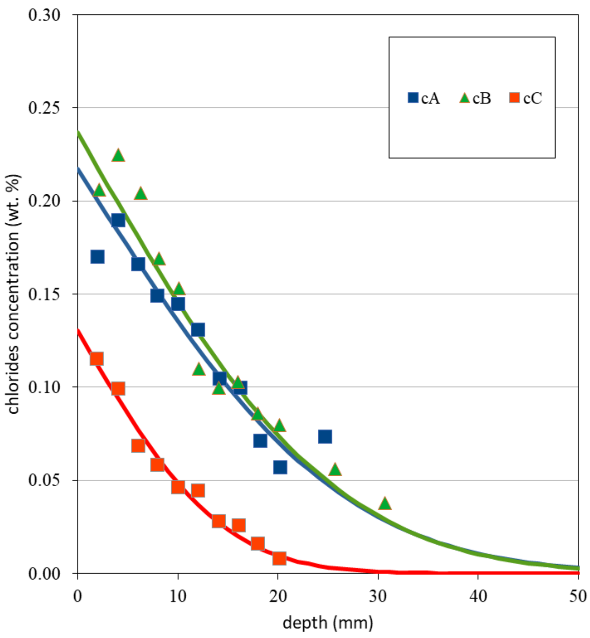

Figure 3 Chloride concentration profile after 60 days of exposition

3.2. Electrochemical impedance spectroscopy

The analysed data showed the difference between the resistances of the material and the resistance of the isolated pores. The highest resistance was shown by the material A (ordinary Portland cement). The comparison of resistance among the sample types shows that the additives have positive effect on reducing the porosity.

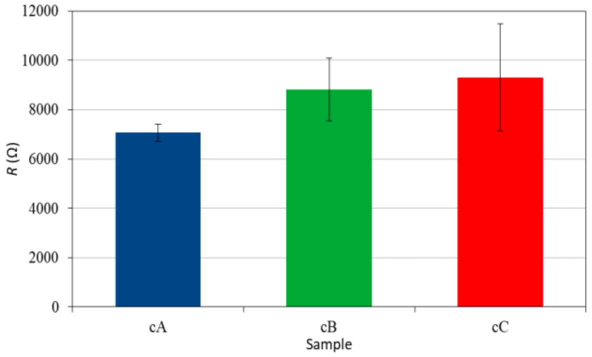

Figure 6 Resistance of discontinuos pores

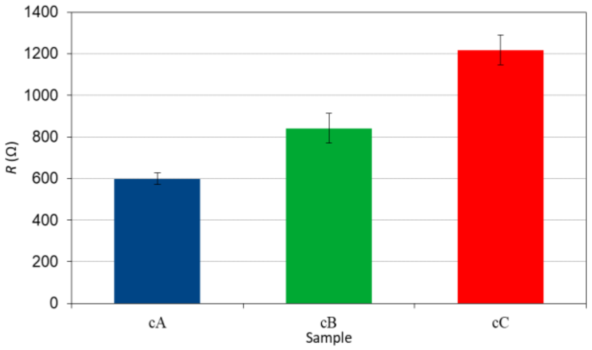

Figure 7 Resistance of continuos pores

The results of resistances obtained from EIS measurement are in the (**Figure 6** and **Figure 7**). The resistance of the interrupted pores (circuit branch 2 on the **Figure 3**) doesn´t show representative data according to the harder spectre fitting (example of spectre on **Figure 8**) and higher divergence. The resistances of the discontinuos pores are shown on the (**Figure 6**).

The resistance of open porosity (circuit branch 3 on the **Figure 3**) is the highest for concrete with silica fume and the lowest for the concrete with basic Portland cement. These values confirm the theory of positive influence of additives on reducing the porosity. The resistances of the continuous pores are shown on the (**Figure 7**).

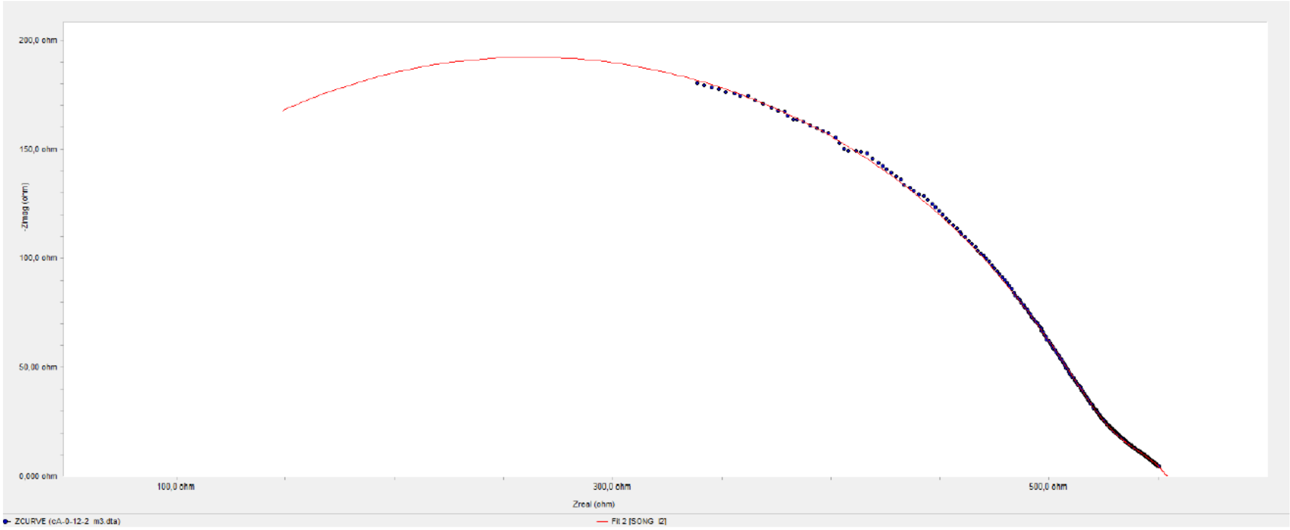

Figure 4 Example of EIS spectrum of specimen type cA

Figure 9 shows an EIS spectrum, which is well fitted with the structure model shown in the (**Figure 3**). This part of the spectrum informs about electrical resistance of the phase elements – resistivity of the material, resistivity of interrupted pores and resistivity of connected pores.

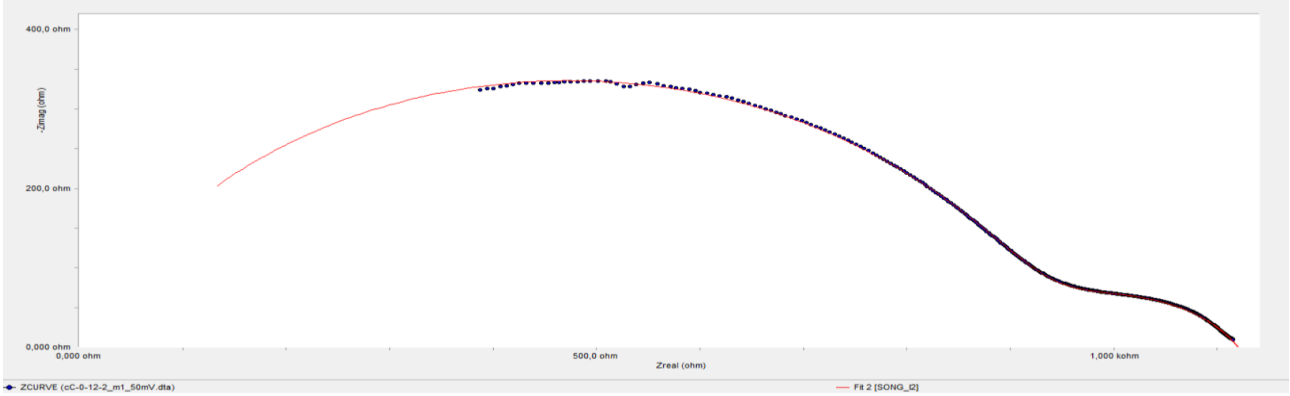

Figure 5 EIS spectrum of specimen type cC

4. CONCLUSION

To conclude, the results from diffusion tests and electrochemical impedance spectroscopy show, that the addition of silica fume has the biggest influence on reducing the open porosity and thus reducing the diffusion of chlorides into concrete. The addition of the fly ash has its benefits too, but according to measured impedance spectres, the porosity seems to be very similar to the concrete based on ordinary Portland cement. According to the diffusion tests the protective behaviour of fly ash isn’t stable in time, because after longer diffusion experiment the difference between the ordinary cement and the cement with fly ash isn’t markable.

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