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INFLUENCE OF THE ELECTRICAL FIELD APPLIED IN CHLORIDE MIGRATION TESTS ON THE PROPERTIES OF CONCRETE

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ABSTRACT

Electrically accelerated short-term chloride migration tests have become very popular laboratory techniques, performed in order to obtain quantitative information on the ingress speed of chlorides in concrete. The common model assumption adopted for each chloride migration technique is that the applied electrical field does not alter the concrete, i.e. the permeability of concrete will not change during the test. However, due to the electrical field, not only the chloride ions migrate but also all other ions which are present in the external electrolytes and in the pore solution of concrete. The migration rates of all these ions depend (among other factors) on their mobility, which in the case of chlorides is much lower than for the hydroxyl ions. This can potentially lead to a decrease of the pH of the pore solution and therefore to the dissolution of portlandite or to the reduction of the chloride binding capacity of the cement hydration products.

This study addresses the influence of the electrical field on the properties of concrete. Ageing of the samples by the electrical field was done by performing the migration test with tap water used as the catholyte (instead of the NaCl solution) for 24 hours. Subsequently, the RCM test was performed on pre-aged samples as well as on the reference samples in order to compare their chloride transport properties. The results show that, although the system of concrete/external electrolytes is dynamic (the pH of electrolytes and the current are continuously changing during the test), the investigated chloride transport properties in concrete remain stable.

Key-words: Concrete, chloride, diffusion, migration, permeability

INTRODUCTION

Increasing attention is being paid nowadays to durability and sustainability issues of concrete. In the case of marine structures, the corrosion due to chloride depassivation of the reinforcing steel is the main reason of damage, which entails maintenance work (and costs). Therefore, a proper service life design concrete cover in terms of its quality and thickness vs. the ingress speed of chlorides is of crucial importance. In the case of existing concrete elements/structures exposed to chlorides, the residual service life is estimated based on the information obtained from the element/structure itself – chloride concentration profiles are determined and then the chloride diffusion coefficient is calculated. This information is considered as the most reliable assessment of the condition of concrete as it is measured in real conditions and usually after a long exposure period. However, in the design stage of new concrete elements, only a ’predicted’ or ’expected’ chloride ingress speed is applied. This information is often obtained from electrically accelerated, short term chloride migration tests such as the Rapid Chloride Migration (RCM) test described in NT Build 492 [1] or the Rapid Chloride Permeability (RCP) test given in [2]. The chloride transport properties (the chloride migration coefficient in the case of the RCM test and the total charge passed in the case of RCP test) are obtained for experimental concrete mixtures. The tests are usually performed at the age of 28 days only, often on concrete prepared in laboratory conditions (‘lab-crete’) which additionally may differ significantly from the concrete prepared and cured in industrial scale (‘real-crete’). When having this information, one of the concrete cover design codes is used. In the case of the DuraCrete model [3], the obtained migration coefficient is employed in this model together with empirical factors, which are taking into account e.g. the exposure or curing conditions. Thus, often for the long term service life design of new ‘real-crete’ concrete structures only information collected at early age on ‘lab-crete’ by means of the short term migration test is used. The increasing importance of chloride migration techniques however is not coupled with increased knowledge about these techniques – the tests are very often performed without understanding their background, advantages, shortcomings and limitations, and their output is used as input in the service life design codes. On the other hand, in the recent years there has been a raising discussion about the correctness of the theoretical background of migration techniques. Many issues are addressed, such as multi-species migration, the pH change in concrete and its influence on chloride binding, the non-linear nature of chloride binding [4] or the gradual-shape experimental chloride concentration profile measured after the migration test, which does not match the theoretical, tsunami-shape profiles [4 - 9].

One common assumption for the chloride migration tests is that the applied electrical field (and the resulting current) do not alter the microstructure of concrete, so the chloride transport properties in concrete remain constant during the migration tests. However, during the test not only the chloride ions migrate but also all other ions which are present in the external electrolytes and in the pore solution of concrete. The migration rates of all these ions depend among other factors on their mobility, which in the case of chlorides is much lower than e.g. the mobility of the hydroxyl ions [10]. This can potentially lead to a decrease of the pH of the pore solution and, therefore, to the dissolution of portlandite or to the reduction of the chloride binding capacity of the hardened cement phases. As presented in [11], when the pH in the pore solution of concrete drops from the initial investigated value of 12.5 to 11.5, the binding capacity of the cement hydration products significantly decreases (about 98% of chemically bound chlorides are released back into the pore solution). The reduced binding capacity means that more chlorides are free to penetrate further into concrete, so their transport is facilitated. Additionally, as shown in [12-14], the leaching of calcium and the porosity, which is the most important factor determining the permeability of concrete, are found to increase when the pH level drops, facilitating the ingress of fluids.

This paper presents investigations on the influence of the applied electrical field on the chloride transport properties in concrete. The ageing of concrete by the electrical field was performed on concrete samples without using chloride bearing electrolytes, for 24 hours. Afterwards, the RCM test was performed on the same samples. The current in the circuit, the resistance, the pH and the mass change of the test samples were recorded in both experiments. Subsequently, reference samples were tested for the RCM test only. The chloride transport properties (chloride penetration depths, chloride migration coefficients and total chloride concentration profiles) of both the aged and reference samples were compared. Additionally, the pore size distribution and the pH in the concrete samples were analyzed.

MATERIALS AND METHODS

Materials and concrete mixture proportioning

Conventional concrete consisting of water, Cem I 42.5N, limestone powder, sand 0 - 2 mm, gravel 2 - 8 mm, gravel 2 – 12 mm and polycarboxylate based superplasticizer was mixed, cast in 150 mm cubes and compacted on a vibration table. The mix composition of concrete is shown in Table 1. After 24 hours from casting (during which the molds were covered with plastic foil in order to prevent the evaporation of water) the molds were stripped and the cubes were stored in water until the age of 27 days. Subsequently, cores of 10 cm in diameter were drilled out of the cubes and two discs (5 cm in height and 10 cm in diameter) were extracted from each core (the outermost flat surfaces of the cores were removed) and stored in water until the vacuum saturation was performed prior to the ageing/migration test. A total number of 12 concrete discs were prepared for the tests. Additionally, three 150 mm cubes were tested for compressive strength at the age of 28 days and the average value of 54.5 N/mm^2 was recorded.

Table 1 - Concrete mixture proportions.

Material	Mass [kg/m^3]
Cem I 42.5N	340.0
Limestone powder	40.8
Sand 0 - 2	718.2
Gravel 2-8	659.3
Gravel 2-12	408.5
Water	170.0
Superplasticizer	0.2
Total	2337.1
Air content (estimated)	3%
Workability class	F3

Test methods

Rapid Chloride Migration (RCM) test

The RCM test set-up, which meets the recommendations given in NT Build 492 [1], was used (Fig.1). The vacuum-saturation with limewater (applied pressure of 40 mbar) of three consecutive specimens was performed one day prior to the RCM test. In all performed experiments a voltage of 30 V was applied during 24 hours. Power sources with a constant voltage output (adjustable in the range of 0 – 80 V, accuracy of 0.05 V) were used. The used volume of the catholyte (10% NaCl aq. solution) was approximately 14 litres, while the volume of the anolyte (0.3 M NaOH solution) was about 0.3 litre per one test specimen. After the migration test the samples were split and sprayed with a 0.1 M $AgNO_3$ solution in order to determine the penetration depth of chlorides. Additionally, the total chloride concentration profile was measured on one sample of each test series. The RCM test was performed in total on six reference samples and on six samples previously subjected to ageing by application of the electrical field in absence of any chlorides.

Ageing by the electrical field (modified RCM test)

The ageing of concrete was performed prior to the RCM test, on two series of three samples each. The samples were liquid saturated under vacuum conditions, following the procedure described in [1]. The test set-up and the experimental procedure were the same as used for the RCM test, only the 10% NaCl solution was replaced by tap water and the samples were not split after the test. The external voltage of 30 V was applied for a period of 24 hours. After the ageing, these samples were used for the RCM test.

Resistance and DC current

The resistance was measured by using a commercial LCR meter (accuracy of 2%, frequency of the test AC signal: f = 1 kHz). The 'two electrodes' method [15] was used for measuring the electrical resistance of the samples before/after the vacuum-saturation, after the ageing and after the migration test. Additionally, the resistance of the sample in the test set-up was recorded. This resistance is composed of the resistances of the sample, the anode and the cathode and the electrolytes.

The DC current was measured continuously on one specimen of each experimental series using a digital multimeter (accuracy of 0.01 mA) in a serial connection. The current was logged in a five minutes step during the ageing and the migration experiments.

The pH of the electrolytes and the pore solution of concrete

The pH of the catholyte and anolyte solutions was measured periodically during the ageing of the samples and the RCM test. The pH meter (accuracy of 0.01) was calibrated in the pH range of 4 – 14.

The pH of the pore solution of concrete was measured by means of different colourimetric pH indicators. After the ageing and the RCM test the indicators were sprayed onto the surface of the split concrete samples. The dyed colour of the concrete surface was then observed and compared to the colour of the respective indicator added to different pH reference solutions. The characteristic of the applied colourimetric pH indicators is listed in Table 2.

Table 2 – Characteristic of applied pH colourimetric indicators.

Symbol	Indicator	Chemical name	pH range	Colour in more:	
				acidic solution	alkaline solution
1	Phenolphthalein	Phenolphthalein	8.3 – 10.0	colourless	red – purple
2	Alizarin yellow R	p-Nitrobenzeneazosalicylic acid	10.1 – 12.1	yellow	orange – red
3	Tropaeolin O	p-Sulphobenzenazo-resorcinol	11.1 – 12.7	yellow	orange

Chloride concentration profiles

Immediately after the RCM test was finished, the samples were ground in layers. The surface layer of 0.5 mm was ground at first and then 1 mm layers were ground consecutively until the depth of approximately 35 mm, measured previously on split samples. The grinding process was finished in about 3 hours after finishing the RCM test. About 4 g of concrete powder was collected from the surface layer and about 8 g from all the deeper layers. Afterwards, the powder was sieved on a 0.25 mm sieve and the passing fraction was dried in a ventilated oven at 105°C, until a constant mass was reached. In order to extract the chlorides, 2 g of dried powder from each analyzed layer was poured into a beaker together with 35 ml of distilled water and 2 ml of solution 1 M HNO_3, shook manually for one minute and heated up to reach the boiling point. Next, the solution was cooled down, filtered and its volume was adjusted to 100 ml with distilled water. 10 ml samples were analyzed for the chloride concentration by using an automatic potentiometric titrator and 0.01 M $AgNO_3$ solution as the titrant. The measured concentration was expressed as mass per cent of chlorides in dry concrete.

Pore size distribution

The pore size distribution was measured using the mercury intrusion porosimetry (MIP) technique (Autopore IV, Micromeretics). The maximum applied pressure of mercury amounted to 228 MPa (33.000 PSIA) and the equilibrium time to 20 seconds. The pore size in the range of 900 – 0.005 μm was investigated. Pieces of concrete of approximately 2 grams were tested. The testing included the plain concrete sample, concrete after the ageing and concrete after the RCM test extracted from regions containing penetrated chlorides and free of chlorides.

RESULTS AND DISCUSSION

Resistance, DC current and pH of electrolytes

The measurements of the resistance of concrete samples were performed prior to and after the vacuum saturation, after the electrical field ageing and after the RCM test. Additionally, the resistance was also measured in the test set-up (between the anode and the cathode) prior to and after the ageing as well as prior to and after the RCM test. The registered values of the resistance are presented in Table 3.

Table 3 - Measured values of resistance.

sample no.	1a	2a	3a	4a	5a	6a	1b	2b	3b	4b	5b	6b
treatment	ageing & RCM test						RCM test only					
resistance of sample [Ω]:												
before vacuum saturation	377	385	357	395	383	369	361	371	398	367	364	355
after vacuum saturation	369	376	352	385	378	361	355	364	391	352	356	345
in set-up before ageing	446	456	458	478	466	457	-	-	-	-	-	-
in set-up after ageing	511	532	520	501	502	499	-	-	-	-	-	-
in set-up before RCM	431	422	-	431	455	-	340	357	348	374	355	356
in set-up after RCM	460	439	-	467	484	-	425	454	435	451	431	440
after RCM	449	419	-	438	461	-	417	444	445	433	418	421

As can be seen in Table 3, the resistance of concrete is slightly reduced due to the vacuum saturation, where the air-filled pores are becoming liquid-saturated (therefore also more conductive). The resistance of the sample placed in the test set-up prior to the ageing is increased due to the resistances of the electrodes and the electrolytes (tap water as the catholyte and 0.3 M NaOH solution used as the anolyte), which are additional to the resistance of the test sample. After the ageing the resistance is again increased, which can be attributed to changes in the electrolytes and/or to the increase of the resistance of the sample. A similar trend can be observed comparing the resistance of the test set-up prior to and after the RCM test. Due to the RCM test the resistance of the concrete sample itself is increased by approximately 15 %.

The DC current recorded during the RCM test corresponds well to the measured values of the resistance. As presented in Fig. 1, the current decreases during the ageing and the RCM test – and this can be attributed to the increasing resistance.

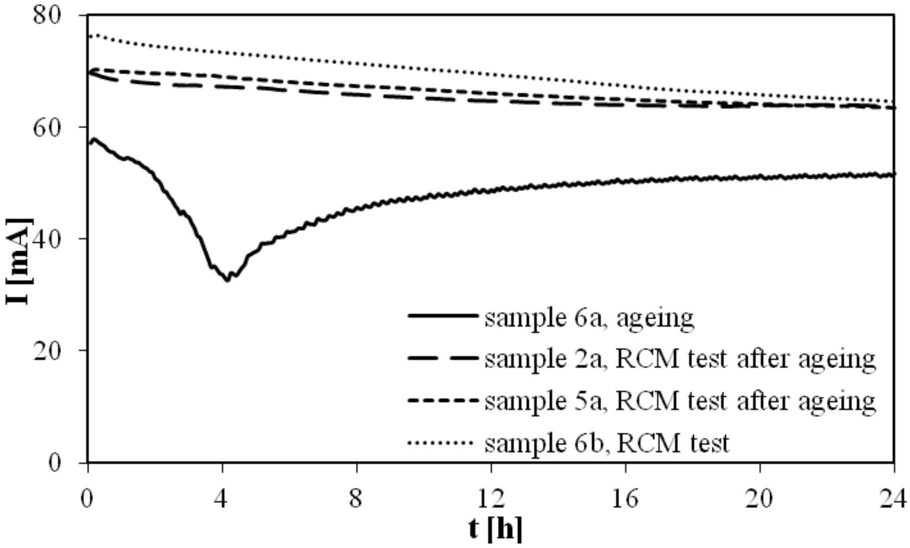

Figure 1 - Development of DC current during the ageing and the RCM tests.

However, the development of the DC current during the ageing is somewhat different than during the RCM test. During the first four hours, the current decreases significantly and then starts to slowly increase until the end of the test. Nevertheless, the final current is still lower than the initial one. The decreasing current during the ageing may be attributed to the increasing resistance of the test sample and to the changes in the conductivity of the electrolytes. During the early stage of the ageing, the amount of ions (the carriers of the current) is low, as tap water is used as the catholyte. The decreasing current in the first hours of the ageing may be attributed to cathodic reactions, as described in [10]. The reduction of oxygen dissolved in water occurs ($O_2 + H_2O \rightarrow 4OH^-$) together with the electrolysis of water ($2H_2O \rightarrow H_2 + 2OH^-$). Because the amount of oxygen decreases the current decreases as well, until the amount of ions generated in the electrode processes increases significantly, so that the conductivity of the solution increases as well. This behaviour does not appear during the RCM test because of the initially highly conductive electrolyte with 10% NaCl. Therefore, during the RCM test the decreasing current may be attributed mainly to the increasing resistance of the test sample.

Fig. 2 a-b shows the pH of the electrolytes measured during the ageing and during the RCM tests. It can be noticed that the pH of the anolyte remains constant, and amounts to approximately 13. On the other hand, the pH of the catholyte increases more significantly during the first hours of the test and then slower. This can be attributed to the generation of hydroxyl ions (OH^-) on the cathode.

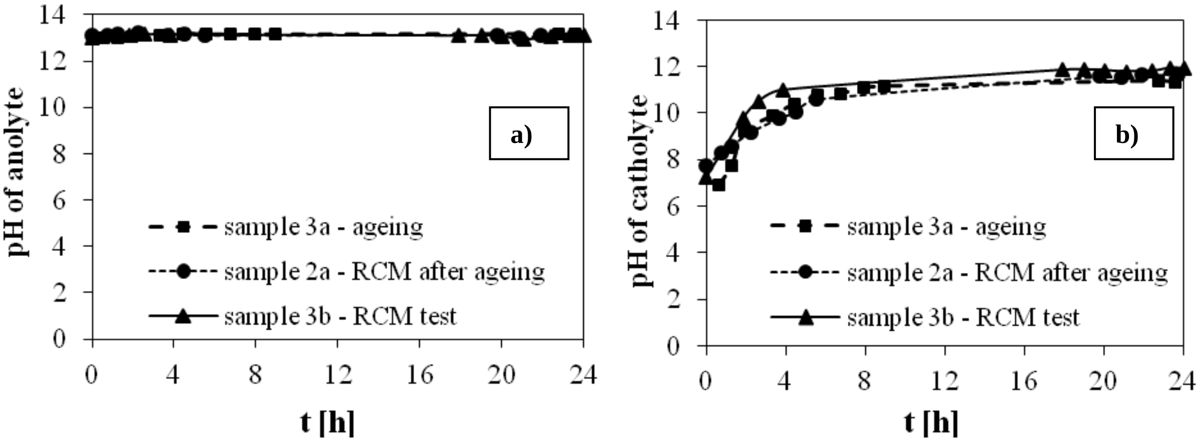

Figure 2 - pH development in the anolyte (a) and catholyte (b) solutions.

pH in concrete

The concrete samples were split after the ageing test and after the RCM test and sprayed with colourimetric pH indicators as described earlier in this paper (see Table 2), in order to observe whether the migration experiment causes a significant pH reduction in the pore solution of concrete. The scheme of colours of the applied indicators at different pH levels is shown in Fig. 3.

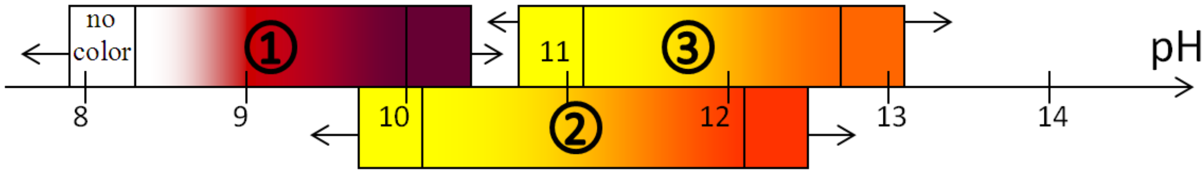

Figure 3 - Scheme of colours of the applied colourimetric indicators at different pH levels (symbols from Table 2)

Figure 4 shows the surface of split samples after spraying with the three indicators.

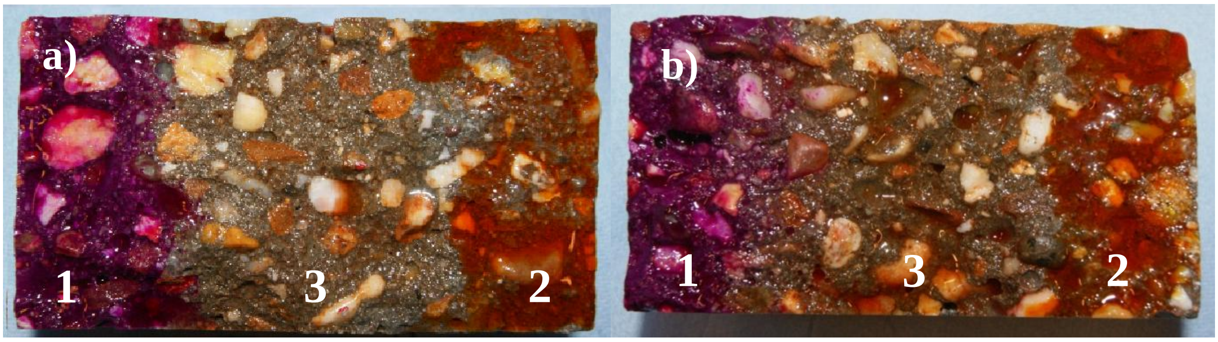

Figure 4 - pH colourimetric indicators sprayed onto the surface of concrete samples after the ageing (a) and the RCM test (b).

The indicator no. 1 was sprayed on the left-hand side of the samples, indicator no. 2 on the right-hand side and indicator no. 3 on the central region of the samples. As can be observed comparing Fig. 3 to Fig. 4, the pH of concrete is greater than 12.7 because indicator no. 3 dyed the surface to orange. The two other indicators confirmed only that the pH is greater than 10 (purple colour of indicator no. 1) and greater than 12.1 (orange-red colour of indicator no. 2). Therefore, it may be concluded that the RCM test does not influence significantly the pH level in the pore solution of concrete, as the reference pH level for OPC concrete containing limestone powder is 13.7 [16].

Pore size distribution

The pore size distribution was analyzed in the plain sample, aged sample and sample after the RCM test, extracted from regions containing penetrated chloride (cathodic side) and regions free of chlorides (anodic side). These results are shown in Fig. 5. It can be noticed that in the plain sample there is a peak at the pore diameter of 5000 nm (50 µm), but this peak is shifted to the finer diameter of about 450 nm (0.45 µm) for aged samples and samples tested for the RCM on the anolyte (chloride free) side. The pore size distribution of the RCM sample containing chlorides has the largest fraction of very fine pores compared to the other samples, with the maximum peak at about 90 nm. The refinement of the pore structure due to the ageing and the RCM test, presented in Fig. 5, is in line with the increasing resistance of the samples.

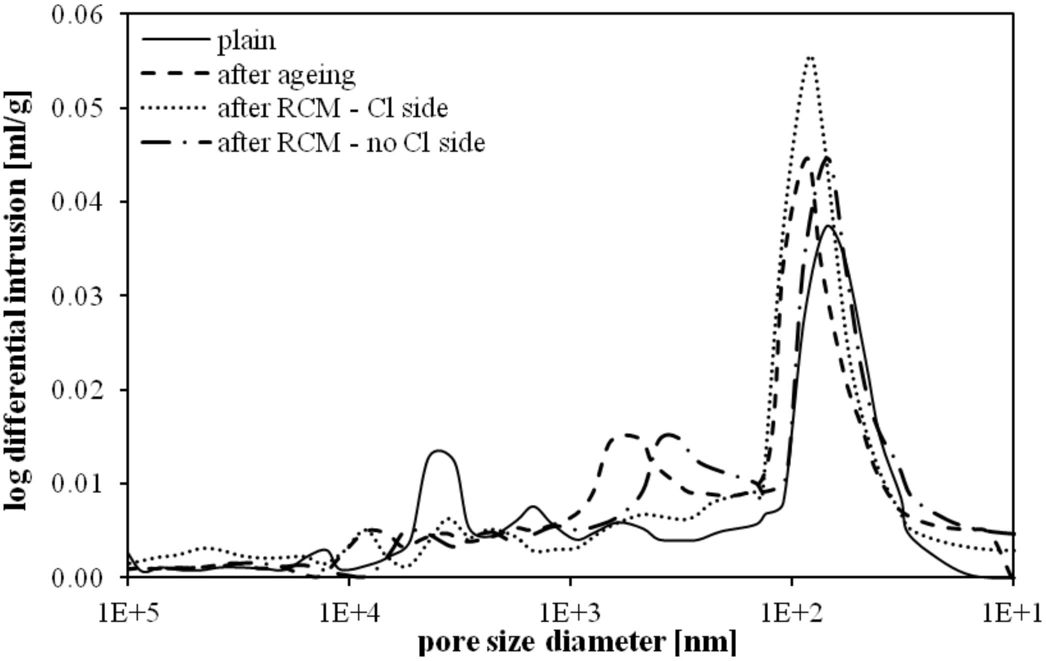

Figure 5 - Pore size distribution measured by the MIP technique

Chloride penetration depth and the D_{RCM} coefficient

The chloride penetration depth (x_d) was measured after the RCM test on the reference samples (tested only for the RCM test) and the aged samples (after ageing and the RCM test). Afterwards, following the equations given in [1], the chloride migration coefficient (D_{RCM}) was calculated. The results are presented in Table 4.

Figure 5 shows the split samples after the ageing and RCM test (a) and the reference sample after the RCM test (b). From Fig. 5 and the data shown in Table 4 it is clear that the ageing by the electrical field did not have any significant influence on the chloride penetration depth or on the migration coefficients, since the obtained values are very similar. The same conclusion can be drawn from the total chloride concentration profiles shown in Fig. 6. The measured profiles are almost identical for the aged sample and for the RCM reference sample.

Table 4 - Measured chloride penetration depths and calculated chloride migration coefficients.

sample no.	1a	2a	4a	6a	1b	2b	4b	5b
treatment	ageing & RCM test				RCM test only			
average x_d [mm]	30.8	31.8	29.7	32.2	32.0	30.5	31.9	32.2
average D_{RCM} [$\times 10^{-12}$ m^2/s]	14.81	15.34	14.11	15.55	15.13	14.38	15.01	15.22

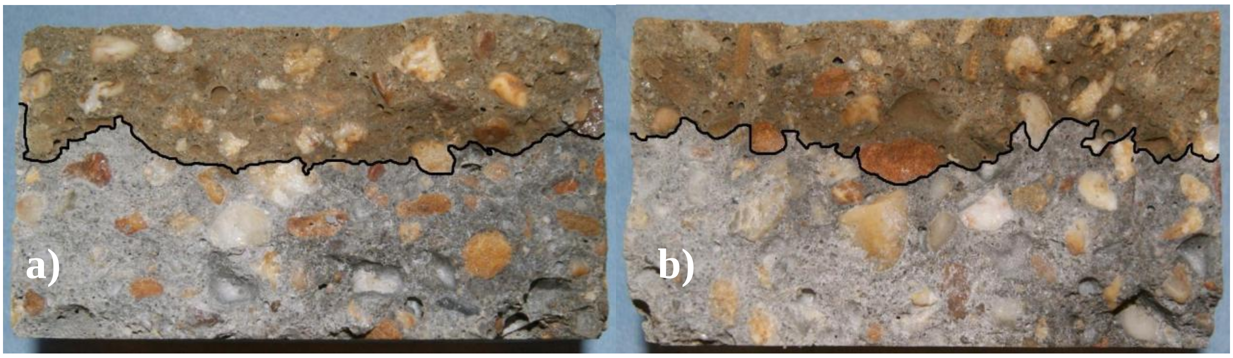

Figure 5 - Chloride penetration depth indicated with $AgNO_3$ solution, measured on (a) sample after ageing and the RCM test and (b) reference sample after the RCM test only

The maximum chloride concentration measured at the surface (Fig. 6) is similar in the two investigated cases, which gives evidence that the binding capacity in both samples is similar as the total chloride concentration measured is composed of the free chloride and the bound chlorides. The gradual shape of the chloride concentration profile is in line with line with experimental data found in literature [5 - 9] and contradicts the theoretical abrupt shape given in [5].

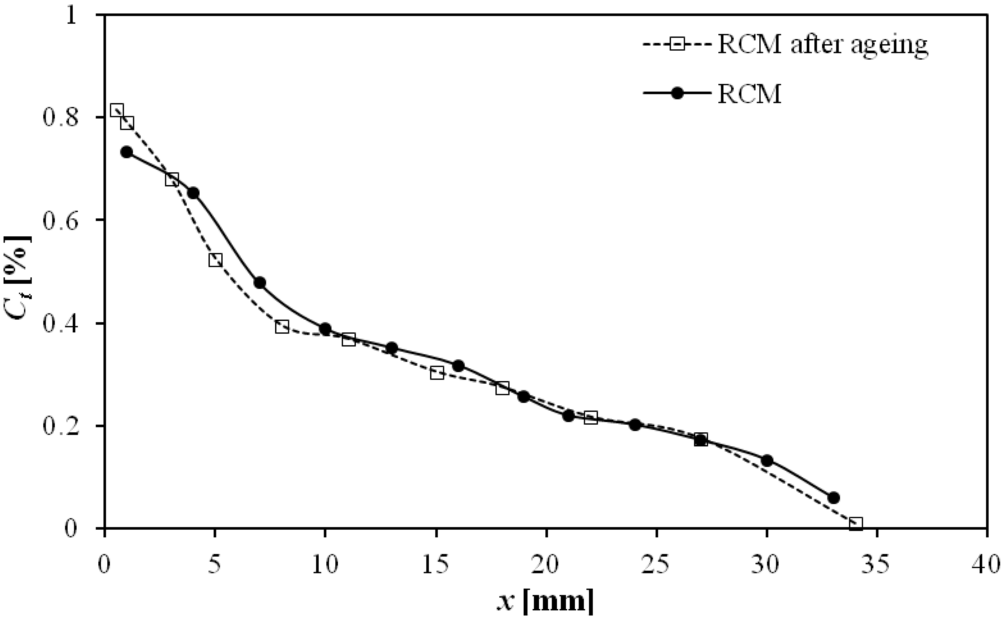

Figure 6 - Measured total chloride (C_t) concentration profiles on the sample 5a (ageing and RCM test) and sample 6b (RCM test only).

CONCLUSIONS

The influence of the electrical field on the properties of concrete was analyzed in this study.
Concrete samples were first aged by the electrical field for 24 hours, by performing the migration test using tap water instead of chloride solution as the catholyte. Subsequently, the same samples were used for the RCM test. The reference samples were tested for the RCM test only. The chloride transport properties in concrete such as the chloride penetration depth, migration coefficients and the total chloride concentration profiles were compared for both experiments, showing very comparable results. Therefore, it is concluded that the electrical ageing of concrete samples did not influence their chloride transport properties.
Additional measurements show that the resistance of the test samples changes during the ageing and migration test – it continuously increases, which also affects the DC current flowing in the circuit. This increase of resistance (decrease of the conductivity) may be caused by refinement of the pore structure which was demonstrated by MIP analyses.
The effect of the electrical field on the pH of concrete was investigated by the application of the colourimetric pH indicators. The results show that there is no significant drop of the pH in the concrete samples during the migration tests.

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