

ACCELERATED CHLORIDE MIGRATION TESTS IN CONCRETE

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Abstract: *Accelerated chloride migration tests are performed on cylindrical samples made of Portland cement concrete. Low voltage electric field is applied as a driving force for both chloride accelerated penetration and extraction. It is verified that the chloride concentration profile measured in samples after 48 hours of electromigration approximately corresponds to the chloride profile after six months of natural diffusion. Potential and effectiveness of the chloride extraction process for the rehabilitation of concrete in terms of lowering the chloride concentration using the DC current is discussed. Experiments show up to 50% decrease in chloride concentration in concrete after 48 hours of extraction driven by electric field with the reverse polarity. Simulation of the process is provided using analytical and numerical solutions of partial differential equations with a simplification in form of the constant diffusion coefficient.*

Keywords: Concrete, Chlorides, Diffusion, Electromigration, Chloride Extraction

1. Introduction

The resistance to penetration of chlorides is one of critical properties of steel-reinforced concrete. The chloride-induced corrosion of steel rebar largely affects the durability of the concrete in saline environments, such as offshore structures, tidal zone structures or in highway engineering (due to the winter deicing maintenance). There are two primary mechanisms by which the ion can migrate inside the pore solution in the concrete. The first one is diffusion where the ions are transported via the concentration gradient; the second one is a convection of ions due to internal (inter-ionic) or externally applied electric potential. As soon as the concentration of chlorides on the rebar surface reaches a critical level, the corrosion of the steel reinforcement starts. The corrosion is accompanied by an expansion of the rust products causing high pressures and, concrete cracking, internal damage and finally spalling of a cover layer. The critical chloride concentration, modeling of the steel corrosion and various concrete impregnation approaches are in researchers' spotlight for more than 30 years (e.g. Blankenhorn, 1978; Tuutti, 1982; Cabrera, 1996; Šmilauer et al., 2013; Němeček & Xi, 2015).

An effectiveness and numerical modeling of chloride extraction from concrete using an external electric field is studied in this paper. Chloride penetration of concrete using both natural diffusion and electromigration and a subsequent chloride extraction in an electromigration chamber is examined.

2. Materials and Methods

2.1 Experimental part

Concrete specimens made of ordinary Portland cement, sand and natural crushed aggregate were used in all experiments used within this study. Table 1 shows its mixture composition. The compressive strength at 28 days was found as 49.7 ± 4.2 MPa and the open (water accessible) porosity $\sim 7\%$.

The concrete was mixed for 2 minutes in a 50l laboratory mixer, subsequently cast into cylindrical and cubic molds and vibrated for approximately 30 seconds. The forms were covered with a foil to prevent water evaporation. The samples were unmolded and submerged into water bath after 48 hours. Cubes

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150x150x150 mm³ were used for compressive strength determination; 50 mm thick slices from cylinders with 100 mm in diameter were used for the chloride migration tests.

Tab. 1: Concrete mixture composition, mass per 1m³.

CEM I-42,5R	Sand 0-4	Aggregates 4-8	Aggregates 8-16	Water	w/c
432 kg	865 kg	288 kg	576 kg	184 kg	0.43

Two kinds of tests on matured samples (at least 28 days old) were performed. First, a natural chloride diffusion test in which the samples were sealed from all sides but the upper surface was submerged in 3% NaCl solution in constant laboratory temperature for 173 days. Second, the accelerated chloride penetration/extraction tests were performed in an electromigration chamber. The chamber consisted of two containers with electrolyte solutions. In case of chloride penetration tests, a 3% NaCl solution was used in the upstream compartment and 0.3 M NaOH solution in the downstream compartment. In case of chloride extraction, both compartments were filled with 0.3 M NaOH and the polarity was switched. A DC power source with a constant electric potential difference 20V was connected to stainless steel mesh electrodes submerged in the electrolytes. The analyzed sample was placed between the two electrodes, and the whole chamber was sealed (Figure 1). The accelerated chloride penetration/extraction run for 48 hours.

After the tests, the total (acid soluble) chloride concentration was analyzed in 5 mm depth-steps. The concrete specimens were drilled in 5 mm steps, the powder collected and mixed with 20% HNO₃. The concentration of chlorides was determined using a chloride ion selective electrode.

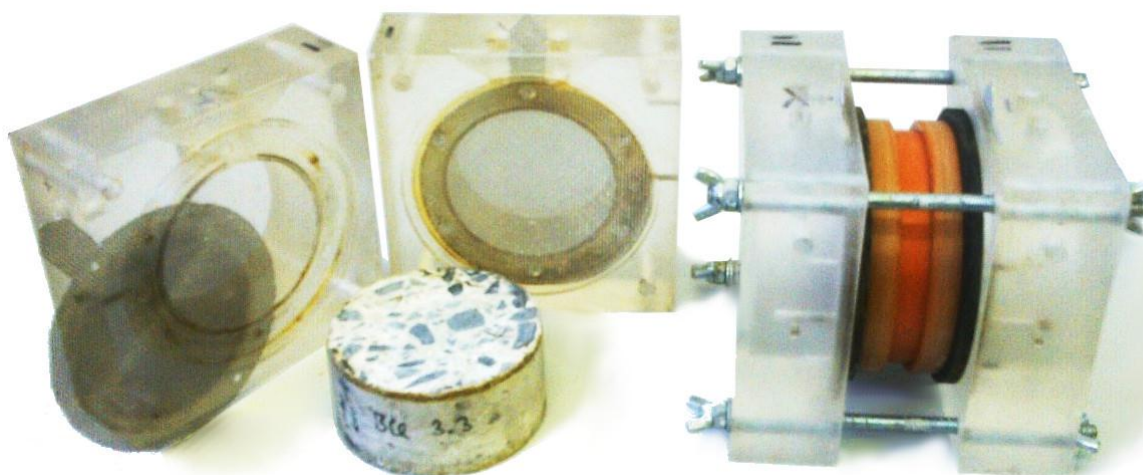


Fig. 1: An electromigration chamber used for accelerated chloride penetration/extraction tests.

2.2. Numerical Part

The concentration profiles were used for the assessment of a diffusion coefficient by employing a non-steady state diffusion equation (the Fick's second law, Eq. 1). The Fick's second law can be used for a pure 1-D diffusion problem in the reference sample and can be written as:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}. \quad (1)$$

For a given boundary conditions of the reference sample, there exists an analytical solution in form of an error function:

$$C(x, t) = C_0 \left(1 - \operatorname{erf} \left(\frac{x}{2\sqrt{Dt}} \right) \right), \quad (2)$$

where x is a distance from the surface exposed to NaCl, t time, $C(x,t)$ is the ion concentration and D is diffusion coefficient.

For modeling of an electromigration experiment, a combination of ion diffusion and ion migration under non-steady state conditions a Nernst-Planck equation can be used (Tang & Nilsson, 1995):

$$\frac{\partial C}{\partial t} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{zF}{RT} \frac{\partial C}{\partial x} \frac{\partial \Phi}{\partial x} \right), \quad (3)$$

where z is the ion valence, R is universal gas constant, F is Faraday's constant and, Φ stands for an electric potential, which is assumed to be constant in time in our case. In this stage of investigation, the diffusion coefficient is, in a simplified way, considered to be constant. The Nernst-Planck equation was solved numerically using the finite difference method (Němeček and Xi, 2015).

3. Results and discussion

The results of natural diffusion test are depicted in Figure 2 which shows a concentration profile of the reference sample after 173 days of a natural diffusion. The chloride diffusion coefficient $D = 4.98 \cdot 10^{-12} \text{ m}^2 \text{ s}^{-1}$ was evaluated from the Eq. 2 as a best fit minimizing the least square error. The red line in Figure 2 exhibits the analytical solution using this diffusion coefficient. The solution agrees well with the experimental results. Chloride concentration profiles of penetrated/extracted samples using the electromigration method are depicted in Figure 3.

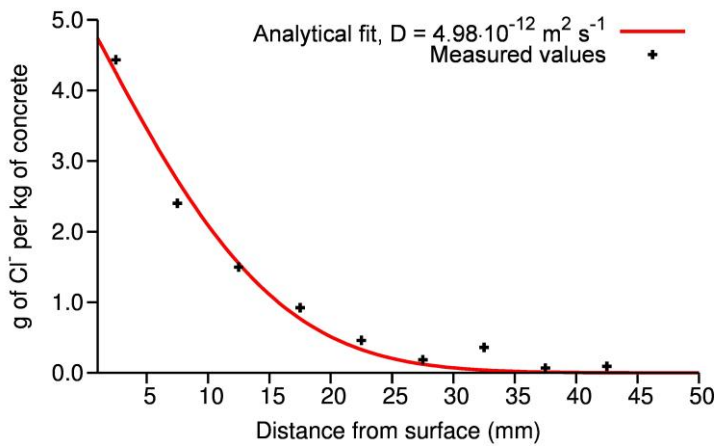


Fig. 2: Chloride concentration profile, natural 1D diffusion of 3% NaCl, 173 days.

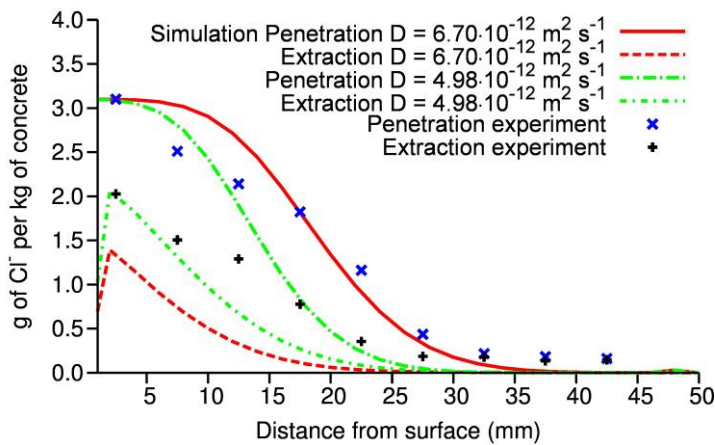


Fig. 3: Chloride concentration profile, chloride penetration/extraction by electromigration at 20 Volts for 48 hours; experiments present an average from three measurements.

The same diffusion coefficient was used for the numerical modeling of the accelerated penetration experiment (Eq. 3). The diffusion coefficient identified from 1-D natural diffusion ($4.98 \cdot 10^{-12} \text{ m}^2\text{s}^{-1}$) seems to be underestimated for the electromigration (the green dash-and-dotted line in Fig. 3). Using the least-square-minimization procedure, the diffusion coefficient for chloride electro-penetration was identified as $6.70 \cdot 10^{-12} \text{ m}^2\text{s}^{-1}$ (the red line in Fig. 3). On the other hand, with this diffusion coefficient the subsequent chloride electro-extraction is significantly overestimated. The difference between the predicted concentrations after extraction (the red dashed line in Fig. 3) and the measured ones can be related to chloride binding in the concrete sample (Yuan et al., 2009; Němeček, 2015). If the original diffusion coefficient ($4.98 \cdot 10^{-12} \text{ m}^2\text{s}^{-1}$) is used for modeling the extraction process, a better agreement to experimental values is found (the green dash-and-dotted line in Fig. 3) also suggesting the reduction in the diffusion coefficient is caused by the binding. Incorporation of the binding phenomena is provided by more sophisticated model (Xi and Bazant, 1999) but is beyond the scope of this paper. Further investigation on the mechanism of chloride extraction and the chloride binding is required.

4. Conclusions

Chloride electromigration experiments showed a speedup in chloride penetration into concrete up to 90 times compared to the natural diffusion test performed at laboratory temperature. Approximately 50% reduction in the chloride concentration was measured after 48 hours of applying a low voltage (20 V) electric field. Therefore, it was found the extraction of chlorides from concrete driven by an electric field is feasible and exhibits a high level of efficiency (i.e. large Cl concentration decrease). The constant diffusion coefficient for the natural diffusion was identified from the experimental data using Fick's second law. The same diffusion coefficient, however, cannot be used in the case of electromigration suggesting different underlying mechanism takes place in the concrete. The diffusion coefficient for chloride penetration in electromigration experiments was identified from experiments numerically using the Nernst-Planck equation solved by finite difference method and it appears to be slightly higher compared to natural diffusion. Also, the numerical predictions of chloride extraction were found to be approximately two times overestimated. It is assumed that the effect of chloride binding (not modeled here) is responsible for such discrepancy.

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