Theoretical Model and Experimental Tests on Chloride Diffusion and Migration Processes in Concrete

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Abstract

This paper focuses on the effect of the electric field on the thermodynamic model of ion flows in the concrete pore solution. The equation for ion migrations was derived from the mass balance in the multi-component system and material constants. Then, using only one component – chloride ion, a reliable diffusion coefficient was determined from the formulated converse task of the migration equation. Taking into account experimentally obtained distribution of chloride concentrations under the electric field, the diffusion coefficient was determined. The distribution of the chloride concentrations was calculated on the basis of that coefficient. And then, it was compared with the measurement results for concentrations of chlorides penetrating into concrete via diffusion. The lowest mean square error between the experimental and calculated distributions of mass densities indicated the reliable value of the chloride diffusion coefficient.

Keywords: diffusion of chlorides, migration of chlorides in the electric field, flow equation, converse task, experimental tests, reliable diffusion coefficient.

1. Introduction

The chloride-containing environment is conducive to the damage of reinforced concrete structures. The corrosion of reinforcement can start when the concentration of Cl\(^-\) ions at the steel surface reaches a critical value of about 0.4% by weight of cement contained in concrete\[1\].

The diffusion coefficient of chlorides in the water-saturated concrete is usually measured by two methods. The first method is based on determining, at the fixed flow, the mass flux of chlorides and calculating the diffusion coefficient according to Fick's first law \[2, 3, 4\]. In the second method, experimentally determined distribution of chloride concentrations in concrete is compared with the result of the diffusion equation solved according to Fick's second law \[5, 6\]. Both methods are long-lasting and provide the results for the ordinary concrete of a rather loose structure. However, conducting the tests on increasingly used high performance concrete in accordance with these rules is difficult because of its considerably higher tightness. That is why accelerated techniques based on forcing the flow of chloride ions through the electric field are undertaken \[1\].

The accelerated methods of chloride permeability in concrete employing the electric field were performed for the first time by Whiting \[7\]. Later, they were adopted as a routine test in standards (AASHTO T277 and ASTM C1202-97). The tests on chloride diffusion coefficient based on their migration in the electric field were usually carried out in two chambers with electrodes. The chambers were separated by a thin specimen of concrete or mortar \[8, 9, 10, 11\]. The steady-state mass flux, and then the value of apparent diffusion coefficient were determined while analysing the concentration changes of chlorides penetrating the cathode chamber through the specimens. In these works \[8, 9\], using the results from the migration tests, the apparent diffusion coefficient was calculated from the Nernst-Planck equation. There was an attempt
to express the differences in the values obtained by migration and diffusion methods by the correction factors adopting the Debye-Hückela model of a central ion surrounded with a cloud of other ions, taking into account the ionic strength according to Lewis and Randall [10, 11].

The effective diffusion coefficient was determined from the tests on chloride penetration into the concrete specimen under the electric field described in the papers [12, 13]. Since the distributions of chloride (concentrations in concrete varied depending on the measurement time), the calculated values of coefficients also significantly differed from each other.

The work [9] proposed that the dependence between migration and diffusion coefficients could be calculated from matching the distribution of concentrations determined in concrete after completing the tests on migration and diffusion. A lower value of the diffusion coefficient obtained from the migration studies was explained by the occurrence of electro-osmosis and the formation of electro-neutral particles of CaCl$_2$.

This paper presents distinct solutions for chloride diffusion and migration and focuses on the effect of the electric field force on the compact, thermodynamic model of ion flows in the concrete pore solution. The derived flow equation was used to formulate the converse task. The second part presents our own laboratory results that, in accordance with the theoretical solution, enable the determination of reliable numerical value of the diffusion coefficient of chlorides in concrete.

2. Equation for diffusion process

Chloride ions migrate inside concrete by means of liquid present in the pores. The pore liquid is a solution containing the dissolved components of hydrated cement. The pore liquid is of electrolyte nature due to the predominating presence of sodium, potassium, calcium, and hydroxide ions. The scheme of chloride penetration into concrete is illustrated in Fig. 1 where a free representative volume element X is isolated from concrete.

![Fig. 1. The model of ion penetration into concrete and the process components in the representative volume element X](image)

This element contains the concrete skeleton, pores and the aqueous solution. In the model, the skeleton and water particles (solvent) are assumed to be the inert component $\alpha = 0$ that is not directly involved in the process. Such an assumption is formally expressed by the relation

$$\frac{\partial \rho^0}{\partial t} = 0,$$

where $\rho^0$ is the mass density of the skeleton with water particles, $t$ is time. The following anions: $\text{Cl}^- - \alpha = 1$, $\text{OH}^- - \alpha = 2$ and cations: $\text{Na}^+ - \alpha = 3$, $\text{K}^+ - \alpha = 4$ and $\text{Ca}^{2+} - \alpha = 5$ are the components involved into this process.

As shown in the article [14] a general theoretical model takes into account the next equation the balance of electric charge, momentum, energy and entropy inequality and then satisfying residual inequality determined constitutive relations. For the simplest case, Fick’s law can be used to express the mass flux

$$j^\alpha = -D^\alpha \text{grad } \rho^\alpha, \quad \frac{\partial \rho^\alpha}{\partial t} + \text{div} \left( D^\alpha \text{grad } \rho^\alpha \right) = 0$$

where $D^\alpha$ is the diffusion coefficient of the component $\alpha$.

The derived equations do not include the electric characteristics of ionic components $\alpha$ in the pore solution characterised by electrolyte properties. The flow of one mole of ions $\alpha$ is assumed to be driven by the force $F^\alpha$ corresponding to the negative gradient of the chemical potential $\mu^\alpha$. One ion $\alpha$ is exposed to the force [15]
where $N_A$ is Avogadro’s number.

The following relation is obtained after transformations and the introduction of the Faraday constant $F = 96487 \text{ C/mol}$:

\[
\mathbf{F}^\alpha = -\frac{1}{N_A} \text{grad} \mu^\alpha, \tag{3}
\]

where $\alpha$ is the ion valence.

Chemical potential is expressed by the relation when the activity $\alpha^\alpha$ of ion $\alpha$ is approximated by the molar concentration $c^\alpha (\alpha^\alpha \cong c^\alpha)$ [16],

\[
\mu^\alpha = \mu_0^\alpha + RT \ln c^\alpha, \tag{5}
\]

where $\mu_0^\alpha$ is the standard chemical potential of ion $\alpha$, $R = 8.317 \text{ J/mol·K}$ – universal gas constant, $T$ – absolute temperature.

After determining the molar concentration with $\rho^\alpha$ – the partial mass density of the component and transformation the following vector of the mass flux of the component $\alpha$ is determined

\[
\mathbf{j}^\alpha = \rho^\alpha \mathbf{u}^\alpha = -\frac{\mu_0^\alpha RT}{Fz^\alpha} \text{grad} \rho^\alpha, \tag{6}
\]

By comparing the relations (2) and (6), the diffusion coefficient can be determined from the formula

\[
D^\alpha = \frac{\mu_0^\alpha RT}{Fz^\alpha}. \tag{7}
\]

3. Equation for migration process

The concrete specimen exposed to the electric field and chloride ions which migrate in the aqueous solution is taken into consideration – Fig. 2a. The electrodes connected to the source of direct current and applied to the specimen of height $h$ cause the one-way migration of ionic components $\alpha$ in the pore solution under the voltage $U$ – Fig. 2b.

![Fig. 2. The model of ion penetration into concrete during the migration test: a) electric system, b) a representative volume element isolated from concrete](image)

Mass of migrating ions $\alpha$ can be determined by modifying Faraday’s first law [15]

\[
m^\alpha = \frac{M^\alpha}{Fz^\alpha} I^\alpha t, \tag{8}
\]

where $I^\alpha$ is the intensity of the current flowing along with the component $\alpha$. 
After Ohm’s first and second laws were taken into account the flux mass of the migrating component is determined by the formula

\[ j^a = \rho^a u_0 E. \]  \hspace{1cm} (9)

Taking into account the fact that the migration of ions \( \alpha \) occurs in the electric field of intensity \( E = - \nabla \phi \), the following migration equation is obtained in an analogous way to the diffusion process \([8, 17]\)

\[ \frac{\partial \rho^\alpha}{\partial t} = - \text{div} j^\alpha = \frac{z^\alpha F}{RT} \frac{\partial}{\partial x} \left( D^\alpha \frac{\partial \phi}{\partial x} \right), \]  \hspace{1cm} (10)

where \( \phi \) is the electric field potential.

4. Determination of the diffusion coefficient on the basis of converse task of the migration equation

Further considerations are limited to one component – chloride ions \( \alpha = 1 \). The diffusion coefficient \( D^1 \) for those ions can be determined by formulating the converse task of the equation (20). However, finding numerical values of that coefficient requires the experimental measurement of the concentration distribution of \( \text{Cl}^- \) ions in the concrete specimens exposed to the electric field. The measurement scheme is illustrated in Fig. 3.

A container with chloride solution 2 is placed in the upper part of the specimen 1 - Fig. 3a. The bottom part of the specimen is placed on the mesh electrode 3. The similar electrode 3 is at the upper surface of the specimen. The electrodes 3 are connected to the source of direct current 4.

![Fig. 3. The principle of conducting laboratory tests with the electric field. Description in the text](image)

The sample is parameterised with the coordinate system, in which the top surface having contact with the chloride solution corresponds to plane \( x = 0 \), whereas the plane \( x = h \) specifies the location of its bottom part. For the purpose of experimental determination of the distribution of chloride ion concentrations \( \rho^1(x) \), the grinded material 5 is collected by layers from the inner part of the specimen. The places, for which the experimental concentrations are determined, are located within the distance \( a \) from the top surface of the specimen. The concentration distributions are determined at time \( t_1 \) and \( t_2 > t_1 \) during the duration of migration – Fig. 3b.

Including the voltage \( U \) between the electrodes, the value of potential \( \phi(0) = U \) at point \( x = 0 \) and \( \phi(h) = 0 \) at the specimen bottom (coordinate \( x = h \)) is assumed, and then the potential distribution along the specimen height is approximated by the linear function – Fig. 3c

\[ \phi(x) = U \left( 1 - \frac{x}{h} \right), \quad \frac{\partial \phi(x)}{\partial x} = -\frac{U}{h}, \]  \hspace{1cm} (11)

After transformations is obtained:

\[ D^1 = \frac{z^1 F U g}{RT h} \frac{\Delta t}{\left[ \rho^1 + \rho^2 + \ldots + \rho^n \right]} - B = \left\{ Q_x \left[ \rho^1(x, t + \Delta t) - \rho^1(x, t) \right] dx \right\}, \]  \hspace{1cm} (12)
In this expression, \( \bar{J}^{\tau}(a) \) is the averaged in time \( \Delta t \) value of the mass flux of chloride ions flowing through the plane situated at a distance \( x = a \) (Fig. 3), \( \bar{\rho}_{1}^{1}, \bar{\rho}_{2}^{1}, \ldots, \bar{\rho}_{n}^{1} \) are the averaged in time \( \Delta t \) mass densities of ion \( \text{Cl}^- \) at midpoints of the consecutive intervals \([0, g], [g, 2g], \ldots, [(n-1)g, a]\). The first term of the denominator determines the stationary part of chloride ion flows, whereas the second term – \( B \) refers to the non-stationary part.

5. Course and results of studies

The experimental studies on the penetration of chloride ions under the electric field and diffusion were planned so as to use the obtained results to calculate the diffusion coefficient on the basis of the theoretical solution and verify the calculated values.

For tests, 18 cylindrical specimens with a diameter of 100 mm and a height of 50 mm were prepared from concrete of class C12/15 with \( w/c = 0.6 \). And the same number of specimens were prepared from concrete of class C90/105 with \( w/c = 0.3 \). The tests started after three months from concreting. Containers with 3% solution of NaCl were tightly attached to the top surface of cylinders. Eighteen specimens were exposed to the electric field inducing the migration of chloride ions, whereas the diffusion of these ions, without the impact of the electric field, was observed in the remaining eighteen ones.

Ions were migrating concurrently in three specimens in parallel in the electric circuit illustrated in Fig. 4.

![Fig. 4. The scheme of equipment unit to conduct tests on ion migration in concrete. Description in the text](image)

The stainless steel cathode 2 with its size adjusted to the cross-section of the tested element was placed in the tank 1. The elements were placed on the wet sponge with platinum plated titanium mesh anode 5 underneath. Before the tests, the specimens were kept in distilled water for 72 hours in order to improve the electrical conductivity of concrete. The soaked specimens were connected to the source of direct current 6 at a voltage \( U = 18 \) V.

The duration of chlorides migration in three first specimens made of concrete of class C12/15 was \( t_1 = 6 \) hours, in the other ones – \( t_2 = 24 \) hours, whereas in the next three specimens – \( t_3 = 48 \) hours. Regarding three specimens made of concrete of class C90/105, the migration of chlorides lasted \( t_1 = 24 \) hours, for the next three specimens – \( t_2 = 48 \) hours, whereas in the other three samples – \( t_3 = 72 \) hours. NaCl solution was replaced every 24 hours. During the whole period of tests, the temperature of solution was constant – about 20 °C.

During the tests on diffusion, three specimens made of concrete class C12/15 were treated with chloride solution for \( t_4 = 90 \) days, the next three specimens for \( t_5 = 180 \) days, and the other three specimens for \( t_6 = 360 \) days. Similarly, three specimens of concrete of class C90/105 were treated with chloride solution for \( t_4 = 90 \) days, the next three specimens for \( t_5 = 180 \) days, and the other three specimens for \( t_6 = 360 \) days.

After completed migration and diffusion, the equipment elements were disassembled, and the specimens were left under ambient conditions for 72 hours. Then, the grinded concrete was collected by layers of thickness \( g = 2 \) mm from consecutive depths of each specimen with “Profile Grinding Kit” of German Instruments AS company. The grinded concrete from corresponding three similar specimens was combined to form the representative material for averaged values.

Distilled water was added to the grinded concrete in a 1:1 weight ratio. The dense solution was stirred every several hours per 24 hours, and then passed through a medium sized filter. The filtration was supported by vacuum from the suction flask connected with the electric pump. Washing out was repeated three times. The experimental solutions were subjected to chemical analysis and the concentration \( c^1 \) [mg/dm^3] of chloride ions in the liquid was determined by argentometric titration according to the Mohr method (PN-ISO 9297) – Tables 1 to 4.

The mass density \( \rho^1 \) of chloride ions was quantified

\[
\rho^1 = \frac{m^1}{V_c} = \frac{3c^1\gamma_c}{\gamma_w}. 
\]

(13)
During the accompanying tests, the volume weight of concrete C12/15 – $\gamma_c = 2460$ kg/m$^3$ and concrete C90/105 – $\gamma_c = 2530$ kg/m$^3$ were quantified. The quantification results for the mass density $\rho^1$ of chloride ions migrating in the concrete specimens exposed to the electric field are presented in Tables 1, whereas the similar results for diffusion of these ions are listed in Tables 2 and 3.

Table 1. Concentration $c^1$ in the experimental solution and mass density $\rho^1$ in concrete of class C12/15 and C90/105 – migration of ions Cl$^-$ under the electric field

| Interval [mm] | Coordinate [mm] | $c^1$ in solution $[\text{mg/dm}^3]$ – C12/15 | Density of mass Cl$^-$ in concrete $\rho^1$ [kg/m$^3$] – C12/15 |
|---------------|-----------------|-------------------------------------------|--------------------------------------------------|
|               | $t_1$ 6 h       | $t_2$ 24 h                                | $t_3$ 48 h                                       |
| 0 ÷ 2         | 1               | 712                                       | 1052                                            | 1172                                            |
| 2 ÷ 4         | 3               | 316                                       | 644                                             | 724                                             |
| 4 ÷ 6         | 5               | 256                                       | 408                                             | 592                                             |
| 6 ÷ 8         | 7               | 76                                        | 218                                             | 420                                             |
| 8 ÷ 10        | 9               | 20                                        | 150                                             | 404                                             |
| 10 ÷ 12       | 11              | 10                                        | 72                                              | 308                                             |
| 12 ÷ 14       | 13              | –                                         | 36                                              | 236                                             |
| 14 ÷ 16       | 15              | –                                         | 27                                              | 188                                             |
| 16 ÷ 18       | 17              | –                                         | 22                                              | 148                                             |
| 18 ÷ 20       | 19              | –                                         | 3                                                | 116                                             |
| 20 ÷ 22       | 21              | –                                         | 0                                               | 36                                              |
| 22 ÷ 24       | 23              | –                                         | –                                               | 12                                              |
| 24 ÷ 26       | 24              | –                                         | –                                               | 6                                               |
| 26 ÷ 28       | 25              | –                                         | –                                               | 4                                               |

| Interval [mm] | Coordinate [mm] | $c^1$ [mg/dm$^3$] – C90/105 | $\rho^1$ [kg/m$^3$] – C90/105 |
|---------------|-----------------|-----------------------------|-------------------------------|
|               | $t_4$ 90 days   | $t_5$ 180 days              | $t_6$ 360 days               |
| 0 ÷ 2         | 1               | 1530                        | 1534                          | 1521                                            |
| 2 ÷ 4         | 3               | 864                         | 897.12                        | 1232                                            |
| 4 ÷ 6         | 5               | 720                         | 753.88                        | 960                                             |
| 6 ÷ 8         | 7               | 446.4                       | 613.8                         | 817                                             |
| 8 ÷ 10        | 9               | 316.8                       | 460.8                         | 640                                             |
| 10 ÷ 12       | 11              | 190.8                       | 309.6                         | 525                                             |
| 12 ÷ 14       | 13              | 104.4                       | 261                            | 430                                             |
| 14 ÷ 16       | 15              | 54                          | 196.2                         | 341                                             |
| 16 ÷ 18       | 17              | 7.2                         | 75.6                           | 264.4                                           |
| 18 ÷ 20       | 19              | –                           | 27                             | 136.2                                           |
| 20 ÷ 22       | 21              | –                           | 16.2                           | 96.8                                            |
| 22 ÷ 24       | 23              | –                           | 6.9                            | 75                                              |
| 24 ÷ 26       | 24              | –                           | –                              | 23.4                                            |
| 26 ÷ 28       | 25              | –                           | –                              | 22.3                                            |
| 28 ÷ 30       | 29              | –                           | –                              | 23.1                                            |
| 30 ÷ 32       | 31              | –                           | –                              | 5.3                                             |

Table 2. Concentration $c^1$ in the experimental solution and mass density $\rho^1$ in concrete of class C12/15 – diffusion of ions Cl$^-$
6. Quantification of the diffusion coefficient of ions $\text{Cl}^-$

On the basis of the distribution measurements of mass density $\rho_1^{\prime}$ of chloride ions migrating in concrete under electric field, the reliable value of the diffusion coefficient was obtained using the relation (25).

First of all, the experimental results of the specimens of C12/15 class were grouped into a computational zone I of $a = 13$ g = 26 mm range, which included thirteen sampling depths of the material – Fig. 5. Fig. 5a illustrates the distribution of the mass density of chlorides in the consecutive sampling depths of the specimen. The results obtained during the migration period $t_1 = 6$ hours are marked with the light colour, the darker colour indicates the results for the migration period $t_2 = 24$ hours, whereas the darkest colour indicates the results for the migration period $t_3 = 48$ hours.

![Fig. 5. Computational scheme – concrete of class C12/15: a) mass density in isolated layers, b) computational zones](image)

Taking into account the averaged mass density of chloride ions in the layers 1, 2, ..., n–1 was determined

\[
\bar{\rho}_1^I(t) = 0.5 \rho_1^I(t), \quad t = t_1, \quad t = t_2, \quad t = t_3,
\]

the averaged value of the mass density in the whole computational zone I was determined.

\[
\bar{\rho}^{\prime}_1(t) = 0.5 [\rho_1^1(t)+\rho_2^1(t)+...+\rho_{n-1}^1(t)].
\]

The averaged mass flux $\bar{j}^I(a)$ of chloride ions flowing out from the boundary area of the computational zone I was determined on the basis of the definition, and the mass density $\rho_n^1$ of chloride ions present in the last layer n, outside the zone I was calculated

\[
\bar{j}^I(a) = \frac{m^1}{At} = \frac{g}{t} \rho_n^1, \quad t = t_1, \quad t = t_2, \quad t = t_3,
\]

where $m^1$ is the mass of chlorides flowing through the section of the area A at time t.

For the denominator of the expression (12), the term describing the non-stationary part of chloride ion flows is assumed to be proportional to the term expressing the stationary course

\[
B \equiv \omega F_{\text{Ug}} \left[ \bar{\rho}^{\prime}_1 + \bar{\rho}^{\prime}_2 + ... + \bar{\rho}^{\prime}_{n-1} \right]/At,
\]

where $\omega$ is the proportionality factor.
The conditions similar to the stationary ones ($\omega = 0$) were assumed and the expression (12) was reduced to

$$D_1 = \frac{\sqrt{\pi} a k}{z' \text{Fug}_g \rho_{j}^{1} \left( t \right)} .$$

(18)

The calculations on the basis of consecutively isolated zones II ÷ XIII were performed analogously. The quantification results are obtained in choices zones I, II, XII and XIII are presented in Table 5. According to the relations (12) and (18), the contribution of the non-stationary influence was estimated proportionally to the component expressing the stationary part. By increasing in sequence the proportionality factor by 0.1 within $\omega = 0.1 \div 0.5$ range, the value of the diffusion coefficient of chloride ions was estimated taking into account the non-stationary course of the migration – Table 4.

| Zone | $t$ [h] | $D_1 \cdot 10^{12}$ [m$^2$/s] | $D_{ns} \cdot 10^{12}$ [m$^2$/s] |
|------|--------|-------------------------------|-------------------------------|
|      |        | Non-stationary influence      | Non-stationary influence      |
|      |        | 10% | 20% | 30% | 40% | 50% | 10% | 20% | 30% | 40% | 50% |
| I    | 6      | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | 24     | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | 48     | 0.02 | 0.02 | 0.03 | 0.03 | 0.03 | 0.04 | 0.03 | 0.03 | 0.04 | 0.04 |
| II   | 6      | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | 24     | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | 48     | 0.04 | 0.05 | 0.06 | 0.06 | 0.08 | 0.09 | 0.08 | 0.09 | 0.09 | 0.09 |
| XII  | 6      | 9.15 | 10.06 | 11.89 | 12.81 | 15.55 | 18.30 | 11.89 | 12.81 | 15.55 | 18.30 |
|      | 24     | 3.58 | 3.94 | 4.66 | 5.02 | 6.09 | 7.17 | 4.66 | 5.02 | 6.09 | 7.17 |
|      | 48     | 4.23 | 4.65 | 5.50 | 5.92 | 7.19 | 8.46 | 5.50 | 5.92 | 7.19 | 8.46 |
| XIII | 6      | 12.37 | 13.61 | 16.08 | 17.32 | 21.03 | 24.74 | 16.08 | 17.32 | 21.03 | 24.74 |
|      | 24     | 4.88 | 5.37 | 6.34 | 6.83 | 8.29 | 9.75 | 6.34 | 6.83 | 8.29 | 9.75 |
|      | 48     | 4.43 | 4.87 | 5.75 | 6.20 | 7.52 | 8.85 | 5.75 | 6.20 | 7.52 | 8.85 |
| $\overline{D}$ | 2.41 | 2.65 | 3.13 | 3.37 | 4.10 | 4.82 | 3.13 | 3.37 | 4.10 | 4.82 |

The reliable value of the diffusion coefficient $D_{ns}$ was determined by comparing the distribution of the mass density of chloride ions calculated according to the well-known solution for the diffusion

$$\rho_{1}^{cal}(x,t) = \rho_{0,cal}^{1} \left( 1 - \text{erf} \frac{x}{2 \sqrt{D_{ns}^{1} t}} \right) ,$$

(19)

with, previously presented in Table 4, mass densities of these ions $\rho^{j}(x,t)$ determined during the diffusion tests at time $t_4 = 90$ days, and $t_5 = 180$ days, and $t_6 = 360$ days. In the dependence (19), $\rho_{0,cal}^{1}$ is the calculated mass density of chlorides at the edge of the element, erf – the Gauss error function, $t$ – time.

To determine the most convergent calculated and experimental results, the mean square error was calculated

$$s = \sqrt{\frac{\sum_{i=1}^{n} \left[ \rho_{1}^{cal}(x,t) - \rho^{1}(x,t) \right]^2}{n - 1}} ,$$

(20)

between the expected values $\rho_{1}^{cal}(x,t)$ and the ones obtained from the diffusion tests $\rho^{1}(x,t)$ at time $t_4 = 90$ days and $t_5 = 180$ days and $t_6 = 360$ days. In the above formula, $n$ means a number of experimental results.
Fig. 6a illustrates the calculated and experimental distributions of the mass density of chloride ions in concrete of class C12/15. A dotted line indicates the results calculated on the assumption that the diffusion coefficient corresponds to the stationary conditions. Whereas the solid lines indicate the results calculated on the assumption that the diffusion coefficient $D_{ns} = 3.37 \times 10^{-12}$ m$^2$/s is reliable at the time $t_4 = 90$ days (line 1) the diffusion coefficient $D_s = 2.41 \times 10^{-12}$ m$^2$/s is reliable at the time $t_5 = 180$ days (line 2) and $t_6 = 360$ days (line 3).

Fig. 6b illustrates the calculated and experimental distributions of the mass density of chloride ions in concrete of class C90/105. Similarly as before, dotted lines indicate the results calculated on the assumption that the diffusion coefficient $D_{ns} = 0.31 \times 10^{-12}$ m$^2$/s corresponds to the stationary conditions, whereas the solid lines indicate the results calculated on the assumption that the diffusion coefficient $D_s = 0.53 \times 10^{-12}$ m$^2$/s is reliable at the time $t_4 = 90$ days (line 1) and the diffusion coefficient $D_s = 0.40 \times 10^{-12}$ is reliable at the time $t_5 = 180$ days (line 2), and $D_s = 0.31 \times 10^{-12}$ is reliable at the time $t_6 = 360$ days (line 3).

The analysis of test results related to the distribution of chloride concentrations in the specimens of concrete C90/105 was conducted in a similar way. Mass densities $\rho$ of chlorides migrating in the electric field listed in Table 2 were used to establish four computational zones I ÷ IV and to determine the values of diffusion coefficients $D_s$ under stationary conditions, considering the non-stationary effects – $D_{ns}$ and their average values – Table 5.

### Table 5. The list of calculated results for the diffusion coefficient of ions Cl$^-$ concrete of class C90/105.

| Zone | $t$ [h] | $D_s \times 10^{-12}$ [m$^2$/s] | $D_{ns} \times 10^{-12}$ [m$^2$/s] |
|------|--------|-------------------------------|-----------------------------------|
|      |        | Non-stationary influence      | 10%  | 20%  | 30%  | 40%  | 50%  |
|      |        |                               | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
| I    | 6      | 0.00                          | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 |
|      | 24     | 0.10                          | 0.11 | 0.13 | 0.14 | 0.17 | 0.20 |
|      | 48     | 0.06                          | 0.06 | 0.07 | 0.08 | 0.09 | 0.11 |
| II   | 6      | 0.08                          | 0.09 | 0.10 | 0.11 | 0.13 | 0.16 |
|      | 24     | 0.22                          | 0.24 | 0.28 | 0.30 | 0.37 | 0.43 |
|      | 48     | 0.15                          | 0.17 | 0.20 | 0.21 | 0.26 | 0.30 |
| III  | 6      | 0.30                          | 0.33 | 0.39 | 0.43 | 0.52 | 0.61 |
|      | 24     | 0.46                          | 0.50 | 0.59 | 0.64 | 0.78 | 0.91 |
|      | 48     | 0.32                          | 0.36 | 0.42 | 0.45 | 0.55 | 0.65 |
| IV   | 6      | 0.69                          | 0.75 | 0.89 | 0.96 | 1.17 | 1.37 |
|      | 24     | 0.63                          | 0.70 | 0.82 | 0.88 | 1.07 | 1.26 |
|      | 48     | 0.41                          | 0.45 | 0.53 | 0.58 | 0.70 | 0.82 |
| $D_s$|        | 0.31                          | 0.34 | 0.40 | 0.43 | 0.53 | 0.62 |
7. Conclusions

This paper presents the theoretical and experimental model of chloride ion migration under the electric field in concrete and the method of determining the reliable value of the diffusion coefficient of these ions. The flow processes were expressed by the global mass balance of all components of the representative volume element isolated from concrete. The diffusion equation was derived on the basis of the simplifying assumptions of the centre of gravity of the representative volume element, the lack of chemical reactions, and according to Fick’s first law, the simplest form of material constants. Electric properties of ionic components of the pore solution were expressed by the electrostatic forces proportional to the intensity of the electric field. After taking into account the relations defined by Faraday’s and Ohm’s laws, the migration equation for all main ions in the solution filling the concrete pores under the applied voltage was derived. The inverse task of the migration equation, limited to only one component, was formulated in order to determine analytically the diffusion coefficient of chloride ions.

The diffusion coefficient, determined on the basis of short time migration tests in the electric field, were allowed the calculation of correct distributions chloride’s concentration:

- in ordinary concrete of class C12/15 at the time \( t = 90 \) days taking into account 30% of the non-stationary influence and at the time \( t = 180 \) days under the steady conditions,
- in high performance concrete of class C90/150 at the time \( t = 90 \) days taking into account 40% of the non-stationary influence and at the time \( t = 180 \) days under the steady conditions.

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References

[1] Ściślewski, Z., 1999. Protection of reinforced concrete structures. [in Polish], Arkady, Warszawa.
[2] Castellote, M., Andrade, C., 2006. Round-Robin Test on methods for determining chloride transport parameters in concrete, Materials and Structures 99, pp. 955-990.
[3] Castellote, M., Andrade, C., Alonso, C., 2001. Measurement of the steady and non-steady-state chloride diffusion coefficients in a migration test by means of monitoring the conductivity in the anolyte chamber. Comparison with natural diffusion tests, Cement and Concrete Research 31, pp. 1411-1420.
[4] Della, M., Roy, W., Jiang, Sielsbee, M. R., 2000. Chloride diffusion in ordinary, blended, and alkali-activated cement pastes and its relation to other properties, Cement and Concrete Research 30, pp. 1879-1884.
[5] Loser, R., Lothenbach, B., Leemann, A., Tuchschmid, M., 2010. Chloride resistance of concrete and its binding capacity – comparison between experimental results and thermodynamic modeling. Cement and Concrete Composites 32, pp. 34-42.
[6] Andrade, C., Castellote, M., Alonso, C., Gonzales, C., 2000. Non-steady-state chloride diffusion coefficients obtained from migration and natural diffusion tests. Part 1: Comparison between several methods of calculation, Materials and Structures 33, pp. 21-28.
[7] Whiting, D., 1981. Rapid determination of the Chloride Permeability of Concrete. Report No. Fhwa/RD-81/119, Portland Cement Association, NTS B No. 82140724, Aug. 1981.
[8] Andrade, C., 1993. Calculation of Chloride Diffusion Coefficients in Concrete Form Ionic Migration Measurements, Cement and Concrete Research 23(3), pp. 724-743.
[9] Andrade, C., Sanjuán, M. A., 1994. Experimental procedure for the calculation of chloride diffusion coefficients in concrete from migration tests, Advances in Cement Research 23 July, pp. 127-134.
[10] Zhang, T., Gjorv, O. E., 1994. An electrochemical method for accelerated testing of chloride diffusivity in concrete, Cement Concrete Research 24, pp. 1534-1548.
[11] Zhang, T., Gjorv, O. E., 1995. Effect of ionic interaction in migration testing of chloride diffusivity in concrete, Cement and Concrete Research 25, pp. 1535-1542, USA.
[12] Tang, L., Nilsson, L.O., 1992. Rapid Determination of the Chloride Diffusivity in Concrete by Applying an Electrical Field, ACI Materials Journal, 89-M6.
[13] Tang, L., 1996. Electrically accelerated methods for determining chloride diffusivity in concrete-current development, Magazine of Concrete Research 176 September, pp. 173-179.
[14] Jaznik M., Zybara, A., 2009. Modelling the Carbonated Concrete Realkalization, Journal of Civil Engineering and Management 15(2), pp. 159-168.
[15] Černý, R., Rovnaníkowá, P., 2002. Transport processes in concrete. Spon Press; London and New York.
[16] Kisza, A.; Electrochemistry I. Wydawnictwa Naukowo-Techniczne, Warszawa 2001 [in Polish].
[17] Andrade, C., Sanjuán, M. A., Recuero, A., Río, O., 1994. Calculation of chloride diffusivity in concrete from migration experiments, in non-steady-state conditions, Cement and Concrete Research 24(7), pp. 1214-1228.
[18] PN-ISO 9297: Determination of chlorides. Titration method with silver nitrate in the presence of chromate as indicator (Mohr Method) [in Polish].
[19] Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete. AASHTO T 277-83, American Association of State Highway and Transportation Officials. Washington D.C. 1983.
[20] Standard Test Method for Electrical Indication of Concrete’s Ability to Resist Chloride Ion Penetration. ASTM C 1202 – 91 American Society for Testing and Material, Philadelphia 1991.
[21] Wieczorek, G., 1993. Effect of chloride corrosion of reinforcing steel in concrete. Research papers ITB. Series: Monographs; Warsaw.