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# ANALYSIS OF CHLORIDE DIFFUSION AND MIGRATION IN CONCRETE PART I – THEORETICAL MODEL

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Abstract
**The first part of 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. In the second part of this paper, theoretical results are referred to our own laboratory studies.**

Streszczenie
**W pierwszej części pracy przedstawiono termodynamiczny model przepływu jonów w cieczy porowej betonu pod wpływem sił pola elektrycznego. Na podstawie bilansu masy w układzie wieloskładnikowym oraz związków fizycznych wyprowadzono równanie migracji jonów. Następnie, ograniczając się do jednego składnika – jonu chlorkowego, sformułowano zadanie odwrotne równania migracji, z którego wyznaczono miarodajny współczynnik dyfuzji. W drugiej części pracy wyniki teoretyczne zostaną nawiązane do własnych badań laboratoryjnych.**

Keywords: **Diffusion of chlorides; Migration of chlorides in the electric field; Flow equation; Converse task; Diffusion coefficient.**

## 1. INTRODUCTION

The chloride-containing environment is conducive to the damage of reinforced concrete structures. That damage is mainly caused by the use of deicing agents and usually occurs in public transport facilities. Because chloride ions belong to the group of the strongest depolarisers, they initiate the corrosion of steel after getting to the rebars. 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. As the corrosion progresses, the increasing volume of reaction products causes cracking and loosening of the concrete cover [1].

The diffusion process under the moisture conditions determines the rate of chloride penetration into the concrete. For this reason, the values of diffusion coefficients are important in evaluating the protective properties of concrete regarding the reinforcement. The diffusion coefficient of chlorides in the water-saturated concrete is usually measured by means of 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 concentration in the 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 the 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 [8] and ASTM C1202-97 [9]. In the standard test, the protective properties of concrete are determined by the total flow of electric charge, whereas none data describing the diffusion are received. The investigation conducted in accordance with the standards [8] and [9] is considered to be the typical one despite the discrepancies in the results from various types of concrete and many critical remarks [11, 12, 14, 15]. So far, the doubts on the extent to which the measurements determine the actual resistance of concrete to chloride ion penetration and to which the conductivity current, have not been resolved. When the potential difference is applied, $OH^-$ ions migrate with $Cl^-$ ions in the same direction but they carry higher charge due to their greater mobility than that of chloride ions [12].

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 [10÷13]. 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 [10, 11], using the results from the migration tests, the apparent diffusion coefficient was calculated from the Nernst-Planck equation which is well-known in the electrochemistry, and then compared with values obtained by analogous techniques that did not involve the electric field. 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 [12, 13].

The effective diffusion coefficient was determined from the tests on chloride penetration into the concrete specimen under the electric field described in the papers [14, 15]. Since the distributions of chloride concentrations in the concrete varied depending on the measurement time, the calculated values of coefficients also significantly differed from each other.

The work [16] proposed that the dependence between migration and diffusion coefficients could be calculated from matching the distribution of concentrations determined in the concrete after completing the tests on migration in the electric field and diffusion in original conditions. 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 two-part paper presents distinct solutions for chloride diffusion and migration. The first part of this paper 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 the concrete.

## 2. EQUATION FOR DIFFUSION PROCESS

Chloride ions migrate inside the 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 the concrete is illustrated in Fig. 1. A free representative volume element X is isolated from the concrete – Fig. 1a. This element contains the concrete skele-ton, 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

$$\frac{\partial \rho^0}{\partial t} = 0, \tag{1}$$

where $\rho^0$ is the mass density of the skeleton with water particles, t is time.

The following anions: $Cl^- - \alpha = 1$, $OH^- - \alpha = 2$ and cations: $Na^+ - \alpha = 3$, $K^+ - \alpha = 4$ and $Ca^{2+} - \alpha = 5$ are the components involved into this process.

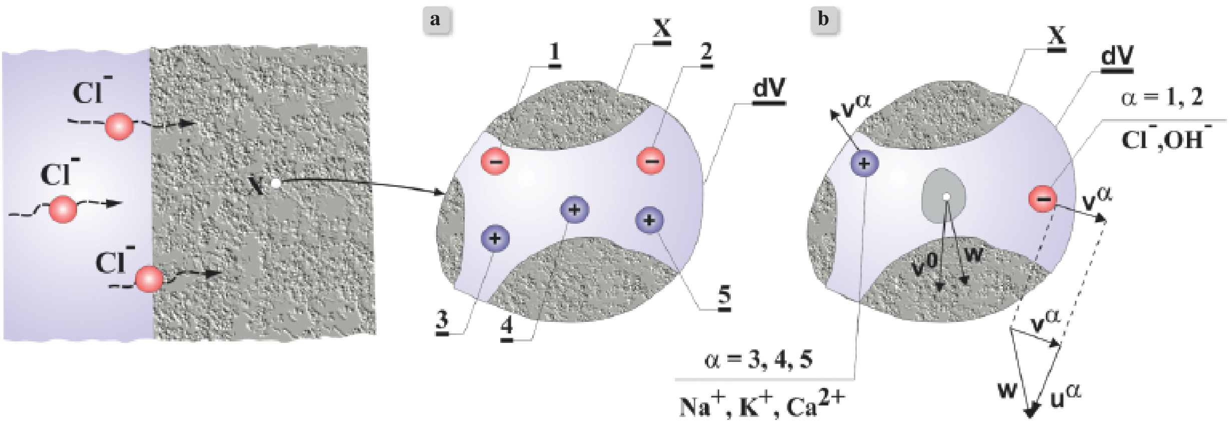

**Figure 1.**
**The model of ion penetration into the concrete: a) a representative volume element isolated from the concrete, b) process components in the representative volume elements and the distribution of component velocities**

The global mass balance of each component α is expressed by the equation [17]

$$\frac{d}{dt}\int_V \rho^\alpha dV = \int_V R^\alpha dV, \qquad \rho^\alpha = \frac{M^\alpha}{N_A} n^\alpha, \qquad (2)$$

where $\rho^\alpha$ is the partial mass density of the component $\alpha$, $M^\alpha$ = const. – its atomic or molecular weight, $n^\alpha$ – number of ions per volume unit, $N_A = 6.02 \cdot 10^{23}$ – Avogadro constant defining the number of ions (or molecules) in one mole of the substance, $R^\alpha$ – mass source of the component corresponding to the gain or loss of mass of the component as the result of chemical reactions, per a unit of volume and time, whereas $\frac{d}{dt}$ is a material time operator. After including the integrated form of the material time operator, the equation (2) is reduced to the following relation

$$\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}\left(\rho^\alpha \mathbf{v}^\alpha\right) = R^\alpha, \qquad (3)$$

where time derivative $\frac{\partial \rho^\alpha}{\partial t}$ denotes the local change in mass density, $\operatorname{div}(\rho^\alpha v^\alpha)$ – the change resulting from the spatial heterogeneity, whereas $v^\alpha$ is the vector of the absolute velocity of the component α.

The following relation occurs in the representative volume element X

$$\rho \mathbf{w} = \rho^0 \mathbf{v}^0 + \rho^1 \mathbf{v}^1 + \ldots + \rho^5 \mathbf{v}^5, \qquad (4)$$

where **w** is the velocity vector of the centre of gravity of the representative volume element, ρ – its mass density.

The velocity vector $\mathbf{v}^\alpha$ of each component breaks down into the velocity vector **w** of the centre of gravity of the representative volume element X and the vector of diffusion velocity $\mathbf{u}^\alpha$ – Fig. 1b

$$\mathbf{v}^\alpha = \mathbf{w} + \mathbf{u}^\alpha. \qquad (5)$$

Substituting the formula (5) into the equation (3) gives the following

$$\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div}\left(\rho^\alpha \mathbf{w}\right) + \operatorname{div}\left(\rho^\alpha \mathbf{u}^\alpha\right) = R^\alpha. \qquad (6)$$

In general theoretical model which was presented in paper [17] following equation of electric charge balance, momentum, energy and entropy inequality were taken into account and then fullfilling residual inequality, the constitutive relations were determined. These relationships were introduced into the equation of the chloride flow, in which was separated part to related chlorides resulting from chemical reactions with other components of the cement binder.

Referring now to presented in the second part of the paper experimental results simplification of the analytical description was introduced. It was assumed that the centre of gravity of the representative volume element X is stationary (**w** = 0) and no chemical reactions take place between the components α. Such an assumption enables to reduce the equation (6) to the following form

$$\frac{\partial \rho^\alpha}{\partial t} + \operatorname{div} \mathbf{j}^\alpha = 0, \qquad (7)$$

where $\mathbf{j}^\alpha$ is the vector of mass flux of the component α

$$\mathbf{j}^{\alpha}=\rho^{\alpha}\mathbf{u}^{\alpha}. \tag{8}$$

For the simplest case, Fick's law can be used to express the mass flux

$$\mathbf{j}^{\alpha}=-D^{\alpha}\operatorname{grad}\rho^{\alpha}, \tag{9}$$

and the common equation of diffusion is obtained

$$\frac{\partial\rho^{\alpha}}{\partial t}+\operatorname{div}\left(D^{\alpha}\operatorname{grad}\rho^{\alpha}\right)=0, \tag{10}$$

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

The derived equations do not include the electric characteristics of ionic components in the pore solution characterised by electrolyte properties. The flow of one mole of ions $\alpha$ is assumed to be driven by the force corresponding to the negative gradient of the chemical potential $\mu^{\alpha}$. One ion $\alpha$ is exposed to the force [18]

$$\mathbf{F}^{\alpha}=-\frac{1}{N_A}\operatorname{grad}\mu^{\alpha}. \tag{11}$$

Electrical charges of all ions $\alpha = 1\div5$ form an electrostatic field with the vector of electric field intensity **E**. Ion $\alpha$ gets the diffusion velocity from that field

$$\mathbf{u}^{\alpha}=u_0^{\alpha}\mathbf{E}=u_0^{\alpha}\frac{\mathbf{F}^{\alpha}}{e^{\alpha}}, \tag{12}$$

where $u_0^{\alpha}$ is the mobility of ion $\alpha$ (velocity of ion $\alpha$ in the electrostatic field with the unit intensity [19]), $e^{\alpha}$– electrical charge of ion $\alpha$.

By substituting the formula (11) into the relation (12), the following is received

$$\mathbf{u}^{\alpha}=-\frac{u_0^{\alpha}}{N_A e^{\alpha}}\operatorname{grad}\mu^{\alpha}. \tag{13}$$

The product $N_A e^{\alpha}$ in the dominator of the above expression (13) is the electric charge of one mole of ions $\alpha$. This charge can be expressed by the Faraday constant F = 96 487 C/mol

$$N_A e^{\alpha}=Fz^{\alpha}, \tag{14}$$

and the dependence (13) can be reduced to this form

$$\mathbf{u}^{\alpha}=-\frac{u_0^{\alpha}}{Fz^{\alpha}}\operatorname{grad}\mu^{\alpha}, \tag{15}$$

where $z^{\alpha}$ is the ion valence.

Chemical potential is expressed by the relation when the activity $a^{\alpha}$ of ion $\alpha$ is approximated by the molar concentration $c^{\alpha}$ ($a^{\alpha}\cong c^{\alpha}$) [19]

$$\mu^{\alpha}=\mu_0^{\alpha}+RT\ln c^{\alpha}, \tag{16}$$

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

After determining the molar concentration with $\rho^{\alpha}$ – the partial mass density of the component

$$c^{\alpha}=\frac{\rho^{\alpha}}{M^{\alpha}}, \tag{17}$$

the gradient of chemical potential takes the following form

$$\operatorname{grad}\mu^{\alpha}=\frac{RT}{\rho^{\alpha}}\operatorname{grad}\rho^{\alpha}. \tag{18}$$

The formula (18) is substituted into the expression (15) and the following relation is obtained

$$\mathbf{u}^{\alpha}=-\frac{u_0^{\alpha}RT}{Fz^{\alpha}\rho^{\alpha}}\operatorname{grad}\rho^{\alpha}, \tag{19}$$

from which, after multiplying both sides by $\rho^{\alpha}$, the following vector of the mass flux of the component $\alpha$ is determined

$$\mathbf{j}^{\alpha}=\rho^{\alpha}\mathbf{u}^{\alpha}=-\frac{u_0^{\alpha}RT}{Fz^{\alpha}}\operatorname{grad}\rho^{\alpha}. \tag{20}$$

By comparing the relations (9) and (20), the diffusion coefficient can be determined from the formula

$$D^{\alpha}=\frac{u_0^{\alpha}RT}{Fz^{\alpha}}, \tag{21}$$

that is well-known in the electrochemistry as the Nernst-Einstein equation.

## 3. EQUATION FOR MIGRATION PROCESS

The concrete specimen exposed to the electric field and chloride ions which migrate in the aque-ous 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 in the pore solution under the voltage U – Fig. 2b. Mass of migrating ions can be determined by modifying Faraday's first law [18]

$$m^{\alpha}=\frac{M^{\alpha}}{Fz^{\alpha}}I^{\alpha}t, \tag{22}$$

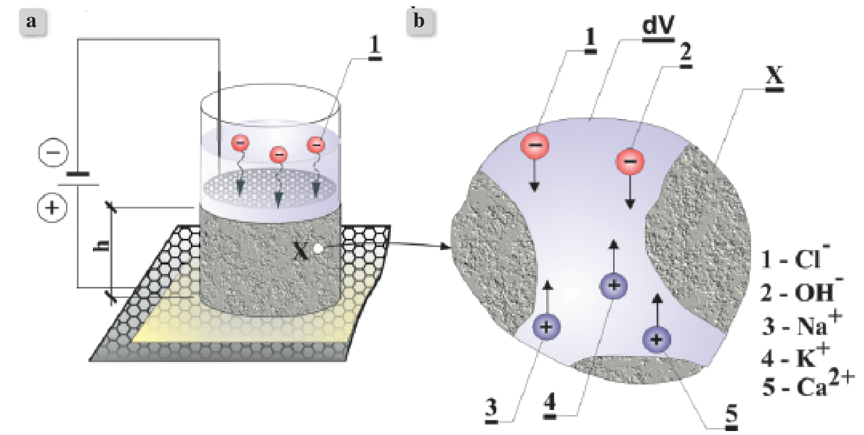

**Figure 2.**
**The model of ion penetration into the concrete during the migration process: a) electric system, b) a representative volume element isolated from the concrete**

where $I^\alpha$ is the intensity of the current flowing along with the component α.

If the mass of component α is related to the flow surface A and time t, the ion mass flux is determined

$$j^\alpha = \frac{M^\alpha}{Fz^\alpha} i^\alpha, \quad i^\alpha = \frac{I^\alpha}{A}, \tag{23}$$

where $i^\alpha$ is the partial current density.

Ohm's first and second laws are taking into account

$$I^\alpha = \frac{U}{R^\alpha}, \quad R^\alpha = \frac{1}{\sigma^\alpha}\frac{h}{A}, \tag{24}$$

as well as the following relation

$$U = Eh, \tag{25}$$

and then, the partial current density is expressed by the following dependence

$$i^\alpha = \sigma^\alpha E, \tag{26}$$

in which electrolytic conductivity per the component α is expressed by the formula [19]

$$\sigma^\alpha = n^\alpha z^\alpha u_0^\alpha e, \quad z^\alpha e = e^\alpha, \tag{27}$$

where e is the elementary charge, whereas $n^\alpha$ is the number of ions α per the volume unit

$$n^\alpha = \frac{\rho^\alpha}{M^\alpha} N_A. \tag{28}$$

Substituting the relation (28) into the formula (27) leads to

$$\sigma^\alpha = \frac{\rho^\alpha}{M^\alpha} z^\alpha F u_0^\alpha, \quad F = N_A e. \tag{29}$$

Then, the formulas (26) and (29) are introduced into the expression (23) and the flux mass of the migrating component is determined by the formula

$$j^\alpha = \rho^\alpha u_0^\alpha E. \tag{30}$$

The mobility of ion α is determined from the Nernst-Einstein equation (21)

$$u_0^\alpha = D^\alpha \frac{z^\alpha F}{RT}, \tag{31}$$

and then, the mass flux is calculated in accordance with the relation (30)

$$j^\alpha = \frac{z^\alpha F}{RT} D^\alpha \rho^\alpha E. \tag{32}$$

The derived relation corresponds to the component expressing the electrostatic interaction in the Nernst-Planck equation which is well-known in the electrochemistry [10, 11].

Taking into account the fact that the migration of ions α occurs in the electric field of intensity E = − grad φ, the following migration equation is obtained in an analogous way to the diffusion process – equations (2)÷(7)

$$\frac{\partial \rho^\alpha}{\partial t} = -\operatorname{div} j^\alpha = \frac{z^\alpha F}{RT}\frac{\partial}{\partial x}\left(D^\alpha \rho^\alpha \frac{\partial \varphi}{\partial x}\right), \tag{33}$$

where φ 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 (33). However, finding numerical values of that coefficient requires the experimental measurement of the concentration distribution of $Cl^-$ 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. Chloride ions exposed to the electric field are squeezed into the concrete structure.

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 $\varphi(0) = U$ at point $x = 0$ and $\varphi(h) = 0$ 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

$$\varphi(x) = U\left(1 - \frac{x}{h}\right), \qquad \frac{\partial\varphi(x)}{\partial x} = -\frac{U}{h}. \tag{34}$$

The diffusion resistance $Q_x$ of the x thick concrete layer and the diffusion resistance Q of the entire a wide area of the tested concrete are taken into account

$$Q_x = \int_0^x \frac{1}{D^1(x')}dx' \rightarrow \quad \frac{dQ_x}{dx'} = \frac{1}{D^1(x')}, \quad Q = \int_0^a \frac{1}{D^1(x')}dx'. \tag{35}$$

Both sides of the migration equation (33) for the component $\alpha = 1$ are multiplied by the quotient $Q_x/Q$ and integrated in the interval (0, a)

$$\int_0^a \frac{Q_x}{Q}\frac{\partial\rho^1}{\partial t}dx = \frac{z^1F}{RT}\int_0^a \frac{Q_x}{Q}\frac{\partial}{\partial x}\left(D^1\rho^1\frac{\partial\varphi}{\partial x}\right)dx. \tag{36}$$

The right-hand side of the equation (36) is integrated by parts, and after substituting the equation (34), the following expression is received

$$\frac{z^1F}{RT}\int_0^a \frac{Q_x}{Q}\frac{\partial}{\partial x}\left(D^1\rho^1\frac{\partial\varphi}{\partial x}\right)dx = \frac{z^1F}{RT}\left|\frac{Q_x}{Q}D^1\rho^1\frac{\partial\varphi}{\partial x}x\right|_0^a -$$

$$-\frac{z^1F}{RT}\int_0^a\left[\frac{\partial}{\partial x}\left(\frac{Q_x}{Q}\right)D^1\rho^1\frac{\partial\varphi}{\partial x}\right]dx =$$

$$= -j^1(a)a + \frac{z^1FU}{RTh}\frac{1}{Q}\int_0^a \rho^1 dx, \tag{37}$$

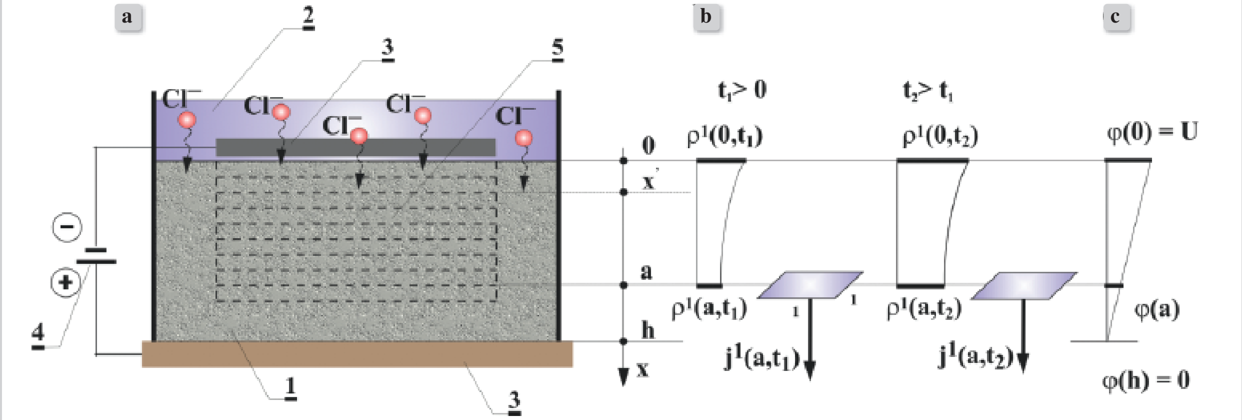

**Figure 3.**
**The principle of conducting laboratory tests with the electric field. Description in the text**

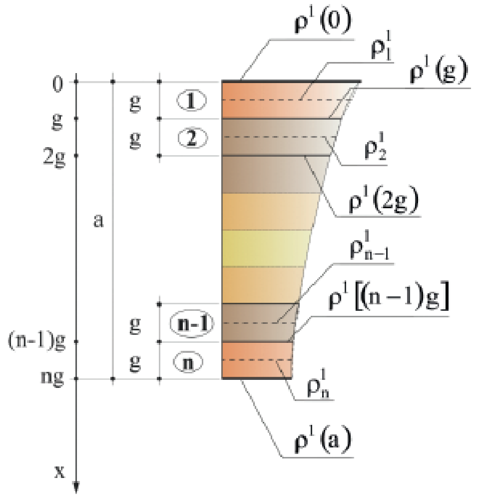

**Figure 4.**
**The polygonal approximation of the distribution curve of the concentration of ions Cl⁻**

in which $j^1(a)$ is the mass flux of $Cl^-$ ions flowing through the plane situated within the distance x = a from the upper edge of the tested element, $\int_0^a \rho^1 dx$ – a definite integral of the function expressing the mass density of ions $Cl^-$.

The following relations are assumed during the transformation of the expression (36)

$$-j^1(a)=\frac{z^1F}{RT}D^1\rho^1(a)\frac{\partial\varphi}{\partial x},\quad \frac{Q_x(a)}{Q}=\frac{Q}{Q}=1,\quad \frac{Q_x(0)}{Q}=\frac{0}{Q}=0. \tag{38}$$

The definite integral $\int_0^a \rho^1 dx$ can be approximated by the trapezoidal rule. The integral is treated as the area of a geometric figure limited by the curve $y = \rho^1(x)$, the interval [0, a] is divided into n equal parts of the length $g=\frac{a}{n}$, and then, the curve of the concentration distribution is replaced by inscribed polygon with vertices in points $A_i$ $(x_i, y_i)$, where $y_i = \rho^1(x_i)$ at $(i = 0, 1, \dots, n-1)$ – Fig. 4. In this way the figure with a curvilinear boundary represents another one consisting of some finite number of trapezia. The area of that simplified figure at sufficiently low **g** is the approximated value of the requested definite integral [20]

$$\int_0^a \rho^1(x)dx \cong g[\frac{\rho^1(0)+\rho^1(g)}{2}+\frac{\rho^1(g)+\rho^1(2g)}{2}+\dots$$
$$\dots+\frac{\rho^1[(n-1)g]+\rho^1(a)}{2}]. \tag{39}$$

The correct result of that simplification is conditioned by technical possibilities for collecting as thin as possible layers g of the grinded concrete required to conduct the chemical analysis.

Regarding practical issues, the areas of trapezia are replaced by the equivalent area of rectangles

$$g[\frac{\rho^1(0)+\rho^1(g)}{2}+\frac{\rho^1(g)+\rho^1(2g)}{2}+\dots+\frac{\rho^1[(n-1)g]+\rho(a)}{2}=$$
$$=g\left[\rho^1_1+\rho^1_2+\dots+\rho^1_n\right], \tag{40}$$

where, in accordance with Fig. 4, $\rho^1_1, \rho^1_2, \dots \rho^1_n$ are the values of the mass density of chlorides inside the length g of individual n parts of the interval [0, a].

Transformations given by the expressions (37), (39) and (40) are substituted into the equation (36), which is then subjected to the time integration scheme in the interval (t, t +Δt)

$$\int_t^{t+\Delta t}\int_0^a \frac{Q_x}{Q}\frac{\partial\rho^1}{\partial t}dxd\tau=-\int_t^{t+\Delta t}\left(j^1(a)a-\frac{z^1FU}{RTh}\frac{1}{Q}g\left[\rho^1_1+\rho^1_2+\dots+\rho^1_n\right]\right)d\tau. \tag{41}$$

Calculating the integral at the left-hand side of the equation (41) leads to

$$\int_t^{t+\Delta t}\int_0^a \frac{Q_x}{Q}\frac{\partial\rho^1}{\partial t}dxd\tau=\frac{1}{Q}\int_0^a Q_x\left[\rho^1(x,t+\Delta t)-\rho^1(x,t)\right]dx. \tag{42}$$

The integral on the right-hand side (41) is replaced by mean values multiplied by time increase Δt

$$-\int_t^{t+\Delta t}\left(j^1(a)a-\frac{z^1FU}{RTh}\frac{1}{Q}g\left[\rho^1_1+\rho^1_2+\dots+\rho^1_n\right]\right)d\tau\cong$$
$$\cong-\bar{j}^1(a)a\Delta t+\frac{z^1FU}{RTh}\frac{1}{Q}g\left[\bar{\rho}^1_1+\bar{\rho}^1_2+\dots+\bar{\rho}^1_n\right]\Delta t. \tag{43}$$

By comparing the relations (42) and (43), the expression determining the coefficient diffusion of chloride ions $D^1=\frac{1}{Q}$ is obtained – it is the converse diffusion resistance for the whole tested zone of the concrete of the range a

$$D^1=\frac{\bar{j}^1(a)a\Delta t}{\frac{z^1FUg}{RTh}\left[\bar{\rho}^1_1+\bar{\rho}^1_2+\dots+\bar{\rho}^1_n\right]\Delta t-\int_0^a Q_x\left[\rho^1(x,t+\Delta t)-\rho^1(x,t)\right]dx}. \tag{44}$$

In this expression, $\bar{j}^1$ (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), $\bar{\rho}_1^1$, $\bar{\rho}_2^1$, and $\bar{\rho}_n^1$ are the averaged in time $\Delta t$ mass densities of ion $Cl^-$ at midpoints of the consecutive intervals [0, g], [g, 2g], …, [(n-1)g, a]. The first term of the dominator determines the stationary part of chloride ion flows, whereas the second one refers to the non-stationary part.

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## REFERENCES

[1] *Ściślewski Z.*; Ochrona konstrukcji żelbetowych (Protection of reinforced concrete structures). Arkady, Warszawa, 1999 (in Polish)

[2] *Castellote M., Andrade C.*; Round-Robin Test on methods for determining chloride transport parameters in concrete. Materials and Structures, Vol.99, 2006; p.955-990

[3] *Castellote M., Andrade C., Alonso C.*; 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, Vol.31, 2001; p.1411-1420

[4] *Della M. Roy, W. Jiang, Silsbee M. R.*; Chloride diffusion in ordinary, blended, and alkali-activated cement pastes and its relation to other properties. Cement and Concrete Research, Vol.30, 2000; p.1879-1884

[5] *Loser R., Lothenbach B., Leemann A., Tuchschmid M.*; Chloride resistance of concrete and its binding capacity – comparison between experimental results and thermodynamic modeling. Cement and Concrete Composites, Vol.32, 2010; p.34-42

[6] *Andrade C., Castellote M., Alonso C., Gonzales C.*; Non-steady-state chloride diffusion coefficients obtained from migration and natural diffusion tests. Part 1: Comparison between several methods of calculation. Materials and Structures, Vol.33, 2000; p.21-28

[7] *Whiting D.*; Rapid determination of the Chloride Permeability of Concrete. Report No. Fhwa/RD-81/119, Portland Cement Association, NTS B No. 82140724, Aug. 1981

[8] Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete. AASHTO T 277-83, American Association of State Higway and Transportation Officials. Washington D.C. 1983

[9] 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

[10] *Andrade C.*; Calculation of Chloride Diffusion Coefficients in Concrete Form Ionic Migration Measurements. Cement and Concrete Research; Vol.23, No.3, 1993; p.724-743

[11] *Andrade C.; Sanjuán M. A., Recuero A., Río O.*; Calculation of chloride diffusivity in concrete from migration experiments, in non steady-state conditions. Cement and Concrete Research, Vol.24, No.7, 1994; p.1214-1228

[12] *Zhang T., Gjørv O. E.*; An electrochemical method for accelerated testing of chloride diffusivity in concrete. Cement Concrete Research, Vol.24, 1994; p.1534-1548

[13] *Zhang T., Gjørv O.E.*; Effect of ionic interaction in migration testing of chloride diffusivity in concrete. Cement and Concrete Research, Vol.25, 1995; p.1535-1542

[14] *Tang L., Nilsson L.O.*; Rapid Determination of the Chloride Diffusivity in Concrete by Applying an Electrical Field. ACI Materials Journal, Title no.89-M6, 1992

[15] *Tang L.*; Electrically accelerated methods for determining chloride diffusivity in concrete-current development. Magazine of Concrete Research, Vol.176, 1996; p.173-179

[16] *Andrade C., Sanjuán M.A.*; Experimental procedure for the calculation of chloride diffusion coefficients in concrete from migration tests. Advances in Cement Research, Vol.23, 1994; p.127-134

[17] *Zybura A.*; Analysis of chloride migration in concrete based on multicomponent medium theory. Archives of Civil Engineering, LIII, No.1, 2007

[18] *Černy R., Rovnaníkowá P.*; Transport processes in concrete. Spon Press; London and New York, 2002

[19] *Kisza A.*; Elektrochemia I – Jonika (Electrochemistry). Wydawnictwa Naukowo-Techniczne, Warszawa 2001 (in Polish)

[20] *Fichtenholz G.M.*; Rachunek różniczkowy i całkowy – II (Differential and integral calculus). Wydawnictwo Naukowe PWN, 2010 (in Polish)