

Brief note

THE USE OF ELECTRODIFFUSION FOR REMOVING CHLORIDES FROM CONCRETE

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The article presents a description of ion migration in a concrete pore liquid caused by an external electric field. The equation of the flow of aggressive chloride ions is formulated on the basis of partial equations of mass balance. It is assumed that electrochemical potential is in classical form, then an attempt is made to determine the average diffusion coefficient using the inverse diffusion Eq.(3.9).

Key words: chloride, electrodiffusion, concrete, modelling.

1. Introduction

Chlorides present in de-icing substances cause corrosion in the reinforcement of transport structures made of reinforced concrete. Chloride ions diffusing into the concrete cause the depassivation of the steel surface and stimulate electrochemical processes. Over the past few years there have been attempts in foreign countries to remove chloride ions from reinforced concrete structures with an external electric field – cf. [1, 2]. After the concentration of chloride ions in the surroundings of the reinforcement falls below a boundary value, the repassivation of the steel surface begins and corrosion stops. Although methods of removing chloride ions are used commercially, there has been hardly any research so far on the influence of an electric field on the speed of the flow of these ions through concrete pores and the speed of decomposition of bound chlorides. This problem has been researched by cooperating institutes from Austria, Sweden and Denmark [3]. On the basis of that research and the results of measurements of changes in profiles of the concentration of chloride ions in the wall of a road tunnel [4] a mathematical description of the process was proposed in article [5], based on a simple model of Fick's diffusion law. The ion stream was described with the Nernst – Planck equation in which there are components dependent on the diffusion flow, migration caused by an electric field and convection. The diffusion and convection components were disregarded and the stream of chloride ions was researched only in terms of the impact of electric field forces.

2. Technology of removing chlorides from concrete

In order to remove chloride ions from concrete, an electric field is generated with the negative pole of a direct current source connected to the reinforcement and an external electrode connected to the positive pole of that source. A schematic of the process is shown in Fig.1a. Wet cellulose, loam mixtures or porous shotcrete can serve as an electrolyte – cf. [1]. In practice, an electric current of $0.5 - 1.0 A / m^2$ is used. Good results can be achieved after 8 – 10 weeks' exposure to an electric field – cf. [1.4].

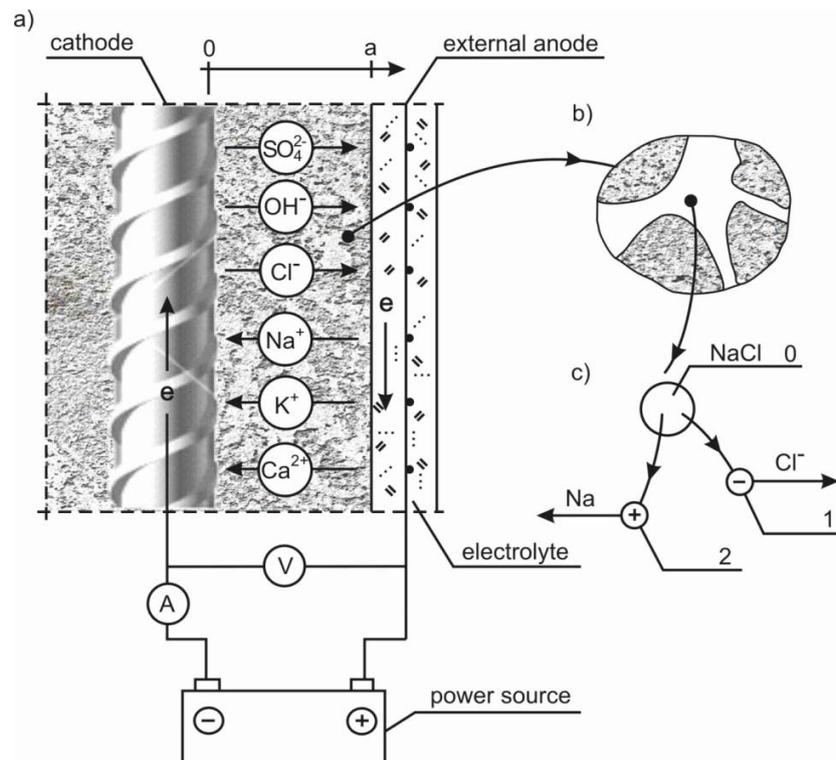


Fig.1. A schematic of the electrochemical extraction of chlorides from concrete.

Article [4] presents a successful attempt to remove chloride ions from the concrete of a 26 m long road tunnel. The thickness of the reinforcement cover was 25–35 mm. The external electrodes and wet cellulose fibre mats were placed with wooden bars. The amperage was 36–40 V, the initial current density was adopted as 0.75 A/m^2 , and then it was decreased to the value of 0.3 A/m^2 . The process lasted for 8 weeks.

3. Electrochemical reactions

After the power source is connected, the reinforcement in the reinforced concrete element becomes the cathode. The reactions of water electrolysis and oxygen reduction occur on the surface of the cathode – cf. [3, 5]



As a result of these reactions additional hydroxide ions appear in the concrete pore liquid.

The electrochemical process mainly occurs in corroded reinforcement located within neutralized concrete whose reaction is slightly acidic. In these conditions corrosion products appear according to reaction [5]



The electric current may cause the reaction of the hydrogen ions produced during reaction (3.3) and the reduction of the secondary ferric oxides produced during the reaction to iron – cf. [5].



Depending on the value of the cathode potential, the reduction of ferric oxides lasts until all ferric oxides are changed into ferrous oxides, or it continues until complete reduction to iron.

On the external anode water electrolysis occurs and chlorine is produced – cf. [3, 5]



If the metal Me of the external electrode is susceptible to corrosion, then the electrode slowly decomposes



The metal ions Me^{n+} transported to the solution may cause a reaction with water molecules [4]



As a result of reactions (3.6) and (3.9), acidity around the anode increases systematically.

The electric field causes the ions present in the concrete pore liquid to move. The negative ions migrate towards the external anode, whereas the positive ions migrate towards the reinforcement (cathode) – cf. Fig.1a. As a result of these migrations, there are changes in the distribution of the concentration of particular ions. In particular, the concentration of chloride ions on the surface of the reinforcement decreases. If the concentration of these ions reaches a smaller value than the critical value, then a passive layer is rebuilt on the steel surface, which protects the reinforcement against further corrosion - cf. [1, 3].

4. Electrodiffusive model

A situation where there is sodium chloride in the concrete cover is considered (Fig.1b). The presence of liquid (moisture) causes the dissociation of chloride into ions – Fig.1c. A simplified model has been adopted, where there are three basic components of the process: sodium chloride – 0, chloride ions – 1, sodium ions – 2, unidirectional flows are described with equations of partial mass balances

$$\rho \frac{\partial C^0}{\partial t} = R^0, \quad \text{component } 0, \quad (4.1)$$

$$\rho \frac{\partial C^1}{\partial t} = R^1 - \text{div } \mathbf{j}^1, \quad \mathbf{j}^1 = \rho^1 \mathbf{u}^1, \quad \text{- component } 1, \quad (4.2)$$

$$\rho \frac{\partial C^2}{\partial t} = R^2 - \text{div } \mathbf{j}^2, \quad \mathbf{j}^2 = \rho^2 \mathbf{u}^2, \quad \text{- component } 2 \quad (4.3)$$

where:

C^α concentration, ρ^α – mass density, R^α – the source of mass components $\alpha=0,1,2$; \mathbf{j}^α – the mass stream, \mathbf{u}^α – the diffusive speed of moving components ($\alpha=1,2$), $\rho = \sum_{\alpha} \rho^\alpha$.

Summing up the sides of Eqs (4.1) - (4.3), and including the principle of mass conservation, we obtain the equation

$$\rho \frac{\partial C}{\partial t} = -\text{div}(\mathbf{j}^1 + \mathbf{j}^2), \quad C = C^0 + C^1 + C^2. \quad (4.4)$$

The stream of chloride ions 1 and the stream of sodium ions 2 are expressed by the dependencies

$$\mathbf{j}^1 = -D^1 \text{grad } M^1, \quad \mathbf{j}^2 = -D^2 \text{grad } M^2 \quad (4.5)$$

where:

D^1, D^2 – the diffusion coefficients, M^1, M^2 – the electrochemical ion potentials.

Including the relation

$$\mathbf{j}^2 = -D^2 \text{grad } M^2 = D^2 \frac{\partial M^2}{\partial M^1} \frac{\partial M^1}{\partial x} = -D^2 k \text{ grad } M^1, \quad (4.6)$$

Eq.(4.4) is transformed to the form

$$\rho \frac{\partial C}{\partial t} = -\text{div}(D \text{ grad } M^1) \quad (4.7)$$

where:

$D = D^1 + kD^2$ is the formulated diffusion coefficient, and k is the numerical coefficient.

The formulated diffusion coefficient D can be found by solving the inverse task. This method was prepared to find the thermal resistance of the wall [6] and to find the diffusion coefficient of water vapour [7]. Equation (4.7) is integrated twice (along the cover thickness and over time) to obtain the expression – cf. [6, 7]

$$D = D^1 + kD^2 = \frac{\bar{J}^1(a) n \Delta t}{\left[\bar{M}^1(a) - \bar{M}^1(0) \right] \Delta t - \int_0^a Q_x [C(x, t + \Delta t) - C(x, t)] dx} \quad (4.9)$$

where:

$\bar{J}^1(a)$ – the average time stream of chloride ions flowing at point $x = a$,

$\bar{M}^1(a), \bar{M}^1(0)$ – the average time values of the electrochemical potentials of chloride ions at points $x=0$ and $x=a$ (Cf. Fig.1a), Q_x – diffusion resistance.

We adopt the dependency used in electrochemistry for describing the electrochemical potential of ions in a solution – cf. [8]

$$M^1 \cong \left(\frac{\partial A_r}{\partial n^1} \right)_{T, V_r, n^{\alpha \neq 1}} = \mu^1 + RT \ln a^1 + z^1 F \varphi \quad (4.9)$$

where:

A_r – the free energy of the solution, n^l – the number of chloride ion moles,

μ^l – the standard potential, a^l – the chloride ion activity, R – the universal gas constant,

T – the absolute temperature, F – the Faraday constant, z^l – the chloride ion value, φ – the electric field potential.

By approximating activity a^l with mole fraction x^l we find the average time difference between the points on the reinforcement surface ($x=0$) and the cover edge ($x=a$)

$$\Delta \bar{M}^l = \bar{M}^l(a) - \bar{M}^l(0) = \frac{I}{M_{cl}} \left[RT \ln \frac{\bar{C}^l(a)}{\bar{C}^l(0)} + z^l F U \right]. \tag{4.10}$$

The above expression denotes the average chloride ion concentration at points $x=a, x=0$, $U = \varphi(a) - \varphi(0)$ is the voltage between the electrodes, and M_{Cl} – is the chloride atomic weight.

5. Attempt to analyse the research results

The numerical values of the formulated diffusion coefficient were estimated on the basis of the research results presented in paper [3]. The research consisted in measuring changes in the concentration of chloride ions in cylindrical samples from cement grout ($w/c = 0.45$) and ones containing an admixture of $NaCl$ with a concentration of 1% in relation to the cement weight. The base of the sample touches two chambers filled with a water solution of $NaOH$ in which the electrodes are dipped. $U = 50V$ and the amperage $I = 40mA$ were used. The content of chloride ions was determined in four layers into which the sample was divided before chemical analysis. Figure 2 shows the results of research [3] which dealt with the chloride ion concentrations C in the concrete pore liquid in relation to the cement weight.

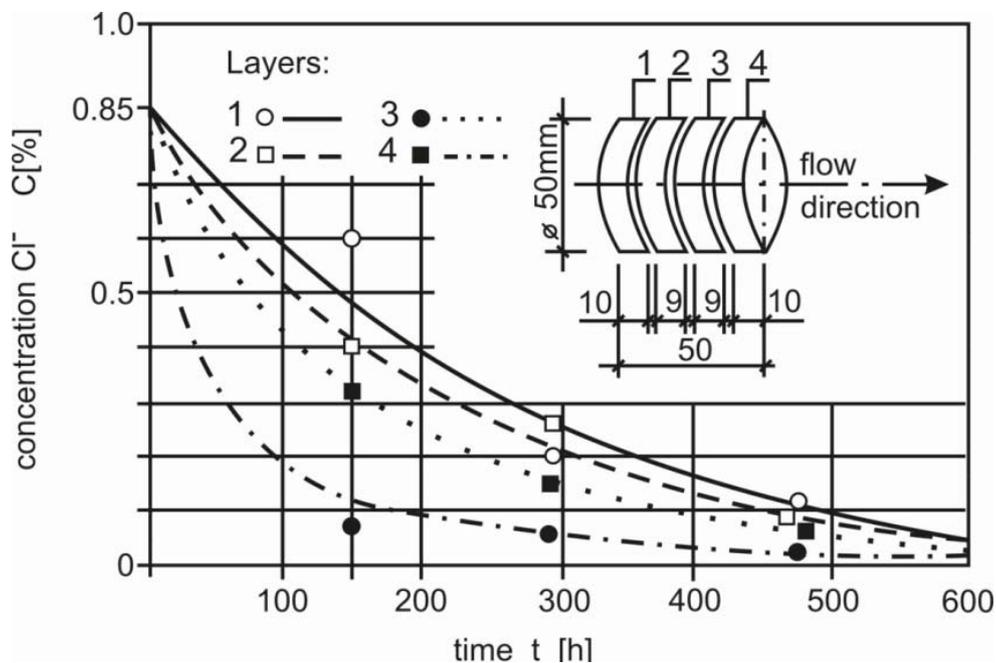


Fig.2. The distribution of chloride concentration in the concrete sample used for numerical analysis.

Taking into account these results, the average value of the chloride ion mass stream at point $x = a$ was determined

$$\bar{J}^l(a) = \frac{\Delta m_{Cl}}{A \cdot \Delta t} = \frac{[C^l(t_i) - C^l(t_{i-1})]g \cdot \rho_c}{t_i - t_{i-1}} \quad (5.1)$$

where:

Δm_{Cl} is the loss of ion mass from layers No.4 over time Δt , A – the flow surface,

$C^l(t_i), C^l(t_{i-1})$ – the concentration of chloride ion concentration in this layer at time t_i

and t_{i-1} , g – the thickness of the layer, ρ_c – the thickness of the cement mass.

It was assumed that at the final stage of the process the flow is stable. Assuming the difference between the concentrations $C(x, t + \Delta t) - C(x, t) \cong 0$, the average values of the formulated diffusion coefficient were calculated from dependency (4.8).

The data used in the calculations and the results obtained are shown in Tab.1.

Table 1. Calculation results.

t_i [hour]	Concentration C [%] in layer		$\bar{J}^l(a) \cdot 10^{12}$ [$\frac{kg}{m^2 \cdot sec.}$]	$\Delta \bar{M}^l \cdot 10^{-8}$ [$\frac{J}{kg}$]	$D \cdot 10^{20}$ [$\frac{kg \cdot sec.}{m^4}$]
	1	4	-	-	-
0	0.846	0.846			
150	0.510	0.110	136.3 ρ_c	1.3620	100.07 ρ_c
290	0.211	0.053	11.31 ρ_c	1.3619	8.30 ρ_c
475	0.114	0.018	5.250 ρ_c	1.3622	3.86 ρ_c
600	0.026	0.009	2.000 ρ_c	1.3617	1.47 ρ_c

6. Conclusions

When the reinforcement of reinforced concrete structures is in danger of chloride corrosion, it is possible to prevent this unfavourable phenomenon by exposing the cover to an electric field. Electric field forces cause a considerable reduction in the concentration of chloride ions in the concrete pore liquid, which leads to rebuilding a passive layer on the surface of the reinforcement and stops corrosion processes.

The process of removing chlorides can be described with multiple diffusion equations, and the main parameter of these equations – the formulated diffusion coefficient can be found by solving the reverse task. The analysis carried out showed that the electrochemical potential of chloride ions largely depended on the amperage, whereas changes in ion concentrations were not very important.

The values of the formulated coefficient calculated with the assumption that the flow was stable decreased over the time of exposure to the electric field. This result is a consequence of major changes in the value of the chloride ion stream flowing into the anode chamber during the initial time of the experiment and a considerable decrease of that stream at the final stage [3]. According to descriptions found in the literature, it has been assumed that the anode appears where the passive layer is damaged and the cathode appears in the surrounding areas. Between these electrochemically active places on the surface of the reinforcement there occurs an exchange of electric charges and the mass of potential-creating components.

The electrochemical process has been described with classic electrochemical dependencies. The balance potential has been determined with the Nernst equation and the voltage with the Tafel equation. The presented model of the corrosion process in the reinforcement has proven that it is possible to lengthen the lifespan of reinforced concrete elements through chloride extraction.

Nomenclature

- A – the flow surface
 A_r – the free energy of the solution
 a^l – the chloride ion activity
 C^α – concentration
 $C^l(t_i), C^l(t_{i-1})$ – the concentration of chloride ion concentration in this layer at time t_i and t_{i-1}
 D^l, D^2 – the diffusion coefficients
 F – the Faraday constant
 g – the thickness of the layer
 \mathbf{j}^α – the mass stream
 M^l, M^2 – the electrochemical ion potentials
 $\bar{M}^l(a), \bar{M}^l(0)$ – the average time values of the electrochemical potentials of chloride ions at points $x=0$ and $x=a$
 n^l – the number of chloride ion moles
 R – the universal gas constant
 R^α – the source of mass components $\alpha = 0, 1, 2$;
 Q_x – diffusion resistance
 T – the absolute temperature
 $U = \varphi(a) - \varphi(0)$ – is the voltage between the electrodes, and MCl – is the chloride atomic weight
 \mathbf{u}^α – the diffusive speed of moving components ($\alpha = 1, 2$), $\rho = \sum_{\alpha} \rho^\alpha$
 z^l – the chloride ion value
 Δm_{Cl} – is the loss of ion mass from layers No. 4 over time Δt
 $\bar{J}^l(a)$ – the average time stream of chloride ions flowing at point $x = a$
 μ^l – the standard potential
 ρ_c – the thickness of the cement mass
 ρ^α – mass density
 φ – the electric field potential

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