Brief note

ESSENTIAL FACTORS FOR THE CHANGES IN CONCRETE DURING ELECTROCHEMICAL EXTRACTION

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The objective of the article is to present one of the most significant factors affecting electrochemical removal of chloride ions from concrete. Based on the literature findings, tests were carried out on specimens containing chloride admixtures introduced to the cement grout, on elements subjected to chloride penetration from the solution in laboratory conditions and on fragments of constructions penetrated by chlorides as a result of a long-term exposure to seawater.

Key words: chloride ion penetration, electrochemical extraction, conrete, seawater.

1. Introduction

Corrosion of cast steel in reinforced concrete constructions caused by the activity of chlorides still remains an important problem all over the world. One of the remedies used for repairing constructions affected by this type of aggression is removal of chloride ions from concrete by means of an electro-diffusion technique, commonly called desalination. Desalination requires fixing on the surface of the concrete an anode , which is surrounded by a liquid electrolyte and passing a direct current between the concrete reinforcement, which acts as a cathode and anode. As a result of the voltage applied, chloride ions are attracted towards the anode. Once they reach the surface, they move to the anolite and in consequence they are removed from the concrete [1-14] and [22-23]. Alsabry and Zybura in [20] described ion migration in the concrete pore fluid caused by an external electric field employing the solution to an inverse task of the diffusion equation. Also, in the studies of Alsabry [21] it was attempted to define a model of electrochemical chloride extraction according to the multicomponent medium theory. On the basis of partial equations of mass balance and electric charge, an equation of flow was obtained similar in form to the classic diffusion equation. The equation was used for the formulation of a reverse task, which rendered it possible to determine analytically the coefficient of chloride ion diffusion in the concrete during electrochemical extraction.

2. The effect of the electric current on the extraction intensity

The voltage applied to a system consisting of a reinforcement, concrete, an electrolyte and an external electrode is the fundamental stimulus of the process of electrochemical removal of chlorides. For the assessment of the effect of the voltage applied on the extraction process Arya *et al*. [15] tested cuboid specimens of the size *200x200x120 mm*. Each specimen contained a mild steel bar of the diameter of *10 mm*. The specimens were made of Portland cement, sand and calcareous aggregate. There were two parallel layers in each concrete specimen. The bottom layer did not contain chlorides, whereas chloride of the concentration of *187%* in relation to the cement mass was introduced to the upper layer.

The layer containing the chloride was *75 mm* thick. An N_aOH solution and a titanic mesh (an anode) were placed in a tight fitting plastic frame on the upper surface of the specimen. The scheme of the test is illustrated in Fig.1.
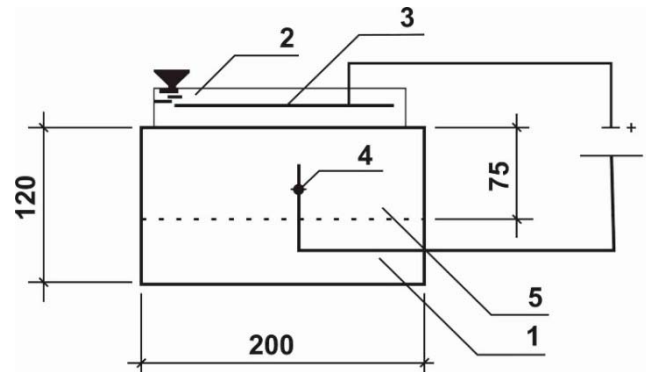
Fig.1. The scheme of tests carried out by Arya et al. [15], Sa'id-Shawqi [16]: 1 – specimen, 2 – electrolyte (0,1 N_aOH solution), 3 – external electrode, 4 – reinforcement bar 5 – upper layer containing Cl^-.

The mass of chloride ions removed was determined on the grounds of an analysis of chloride ion content in the electrolyte. The tests were always made on two identical sets and three values of voltage were applied, namely: *10V*, *20V* and *30V*. A synthesis of the test results is given in Fig.2. It was found that the speed of extraction and the total mass of chlorides removed increased as the value of the voltage applied was increased. An increment in the progress of desalination was caused by a rise in current intensity due to increased voltage.

Figure 3 illustrates the changes in current intensity in time. Each time a new value of voltage was adopted and applied, the current intensity systematically decreased. After 400 hours (about 16 days) the values of current intensity became even and steady.

The decreasing current intensity which was observed is explained by an increase in the electrical resistance of the concrete once the content of chloride ions is reduced. It is also assumed that this phenomenon may be additionally due to the redistribution of $C_a(OH)_2$ from the cement grout as a result of dissolution and reprecipitation [17].

The results of research described in [15] proved a significant rise in the mass of chloride ions removed from the concrete every time the voltage was increased. Ihekwaba and Hope [18] conducted research on the effect of current density on the intensity of chloride extraction. The tests were made on cylindrical specimens *100 mm* in diameter and *200 mm* in height.
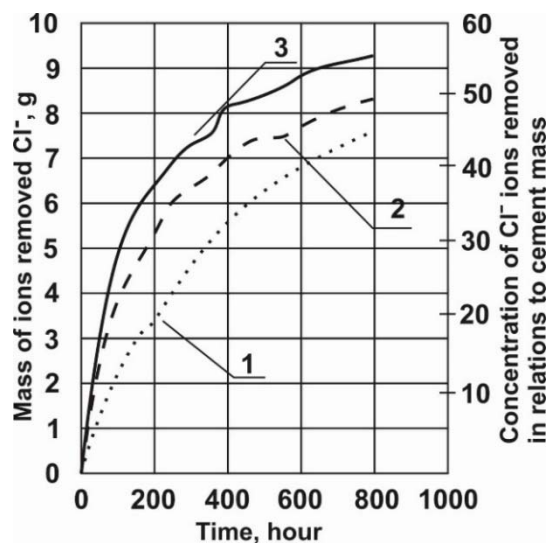

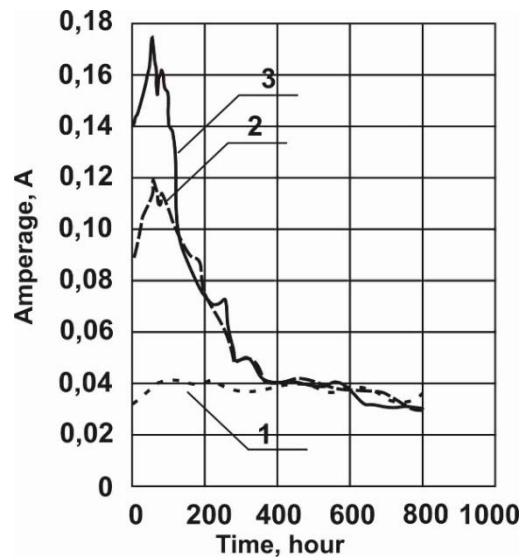Fig.2. The mass of chloride ions removed at different voltage: *10V*, *20V and 30V*, according to [15].

Fig.3. Changes in amperage during the extraction process at different voltage values
$1-10V$, $2-20V$ $3-30V$, according to [15].

Sodium chloride was added to the concrete mix and the initial concentration of chloride ions of *1.7%* and *3.0%* in relation to the cement mass was maintained. The specimens did not contain any reinforcement bars and an electric field was applied with the use of metal <u>electrode wheels</u> placed at the bases. The scheme of the tests is shown in Fig.4. Two current densities were applied: $1A/m^2$ and $3A/m^2$. A saturated water solution of $C_a(OH)_2$ was used as the electrolyte. Each test was repeated on five specimens. Discs *20 mm* in height were cut from each part and the chloride ion content was analyzed Cl^- ion profiles were determined by potentiometric titration with the use of silver nitrate. Free chlorides were removed with hot water, whereas bound chlorides were dissolved in concentrated nitric acid.

Figure 5 shows the results of tests on the chloride ion content in specimens with an admixture of chlorides with the initial concentration of *1.7%* in relation to the cement mass.

The concentration of chloride ions was measured after passing a current of the density of $1A/m^2 i 3A/m^2$ and the content of chloride ions was compared with control specimens isolated from the environment and not subjected to the extraction process.
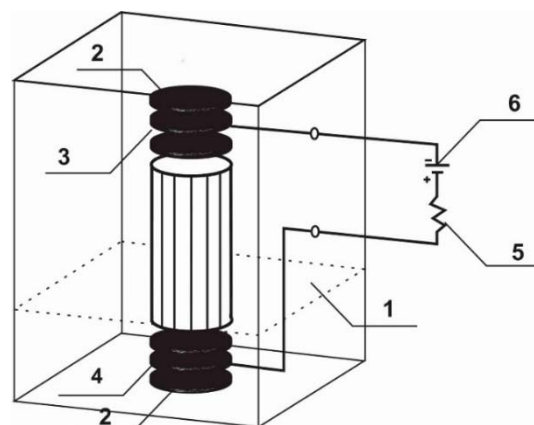

Fig.4. The scheme of chloride extraction tests carried out on cylindrical specimens , according to [18]. 1 – electrolyte $C_a(OH)_2$, 2 – cellulose fiber, 3 – steel cathode, 4 – steel anode, 5 – resistance, 6 – power sources.
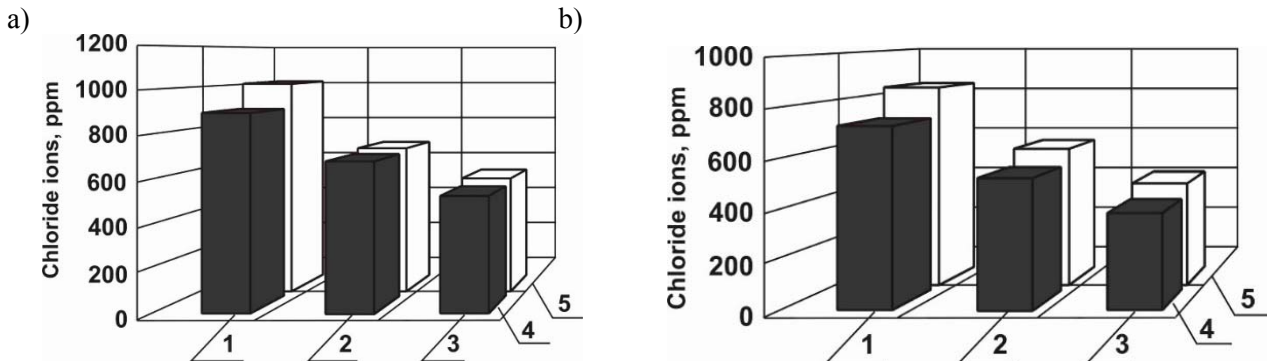
a)   b)

Fig.5. Changes in the chloride ion content after 8 weeks of extraction in specimens with an admixture of chlorides with a concentration of *1.7%* in relation to the cement mass; a) total chloride, b) free chloride; *1 –* control specimen, *2 –* specimen after passing a current of the density of $1A/m^2$, *3 –* specimen after passing a current of the density of $3A/m^2$, *4 –* cathode side, *5 –* anode side, according to [18].

Figure 6 presents similar graphs illustrating changes in the chloride ion content obtained for specimens with an admixture of chlorides with a concentration of *3.0* % in relation to the cement mass. After a comparison of the graphs in Figs 5 and 6 it was observed that the amount of chlorides removed depended on current density. In specimens , in which a current of the density of $3A/m^2$ was passed, the reduction of chlorides was greater than in the case of current density of $1A/m^2$. In specimens with the initial concentration of chlorides of *1.7%* in relation to the cement mass, at the anode part the total chloride was reduced by approximately *26%* at current density of $1A/m^2$, whereas at current density of $3A/m^2$ the amount of chlorides was reduced by about *45%*. Similarly, at the cathode part of these specimens, the total chloride content was reduced by approximately *32%* and *48%* at current densities of $1A/m^2$ and $3A/m^2$, respectively. A less profound effect of current density was observed in specimens with the initial content of chlorides of *3%*. In the anode part, the total chloride ion content decreased by approximately *41%* at current density of $1A/m^2$ and by about *47%* at current density of $3A/m^2$. In the cathode part of the specimens, the concentration of chlorides was similar. A reduction of the total chloride up to *44%* was observed at current density of $1A/m^2$ and up to *46%* at current density of $3A/m^2$. A reduction of the free chloride content was approximately similar to the reduction of the bound chloride content.
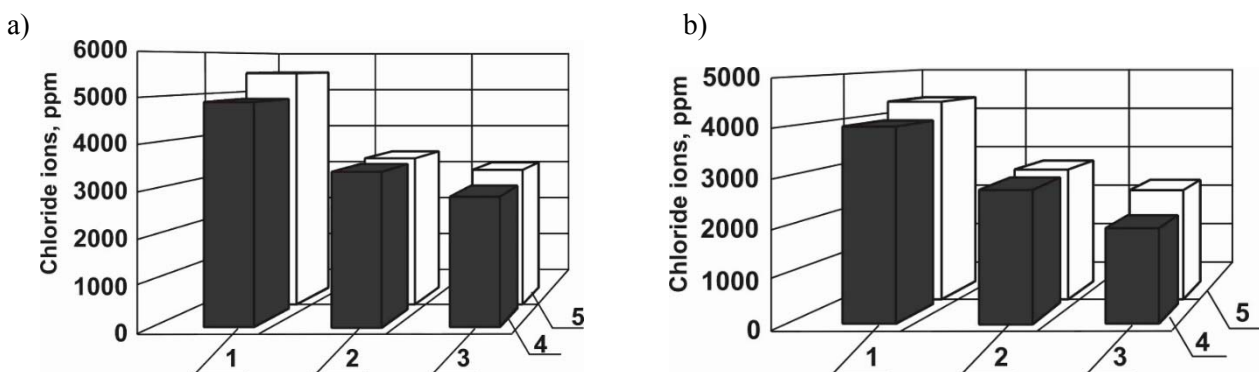
a)   b)

Fig.6. Changes in the chloride ion content after 8 weeks of extraction in specimens with an admixture of chlorides with a concentration of *3%* in relation to the cement mass; a) total chloride, b) free chloride ; *1 –* control specimen, *2 –* specimen after passing a current of the density of $1A/m^2$, *3 –* specimen after passing a current of the density of $3A/m^2$, *4 –* cathode side, *5 –* anode side, according to [18]

Polder [19] investigated the effect of extraction at two different current densities using cuboid elements of the dimensions *500*x*100*x*100 mm*. Each element contained three reinforcement bars *8 mm* in diameter protected by concrete covers of *15, 30, 45 mm* in thickness. Figure 7 illustrates the arrangement of the reinforcement bars and the location of places from which samples to examine the concentration of chlorides were taken.
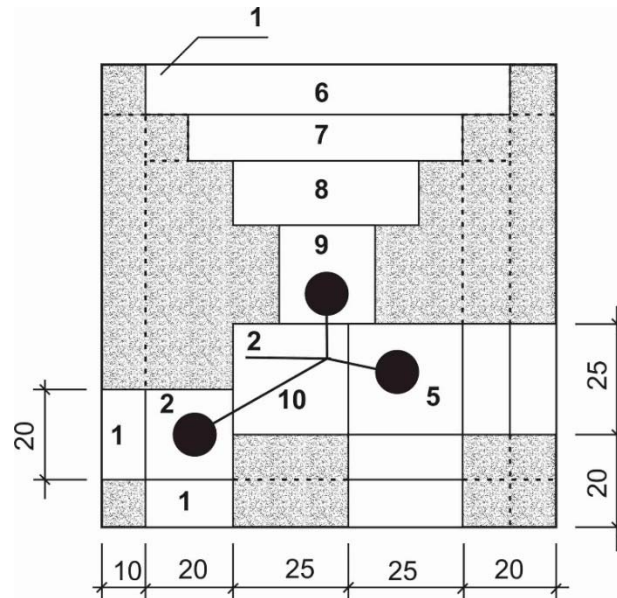

Fig.7.   The scheme of the test element and sampling location for the analysis of chloride concentrations in Polder's research [19]. *1 −* surface covered with an epoxy resin, *2 −* reinforcement bars.

The elements were made of usual Portland cement, silicate aggregate, sand and gravel with the grain size of *32 mm* in diameter. The water-to-cement ratio was *0.4* (*420 kg* of cement per *1 m³* of the mix). The elements were emerged in the North Sea for 16 years, thus absorbing large quantities of chlorides. The process of extraction was carried out for about 6 weeks. The final layer of concrete 10 mm in thickness was cut off and the exposed reinforcement bars were connected to the negative pole of a direct current source. The upper and bottom surfaces were covered with an epoxy resin. The cuboid specimens were placed in PVC cylinders which contained an active anode mesh made of titanium and an electrolyte solution. The scheme of the test is presented in Fig.8. Two types of electrolyte were used: a saturated $C_a(OH)_2$ solution and municipal water. For chloride extraction in the $C_a(OH)_2$ solution, two current densities, i.e., $1A/m^2$ or $4A/m^2$ of steel surface, were used. Extraction in municipal water was carried out by passing a current of $1A/m^2$. The amount of chlorides removed was determined on the basis of analyzing the composition of the electrolyte solution in the cylinder and by examining the samples of ground down concrete taken from various parts of the specimen as shown in Fig.7. The results of analyses of the electrolyte solution are synthesized in Figs 9 and 10, whereas other results are presented in what follows, in the figures illustrating the effect of the initial concentration of chlorides on the progress of desalination. It was found that approximately *40*% of the initial amount of chloride was removed from the concrete applying the current density of $1A/m^2$, while on average *70*% of chloride was removed at current density of $4A/m^2$. Similar results were obtained with the use of municipal water and the saturated $C_a(OH)_2$ solution. After the 8-week treatment, chloride with the concentration of, respectively, *0.3*% to *1*% and *0.3*% in relation to the cement mass, remained around the steel surface after extraction with current density of $1A/m^2$ and $4A/m^2$.
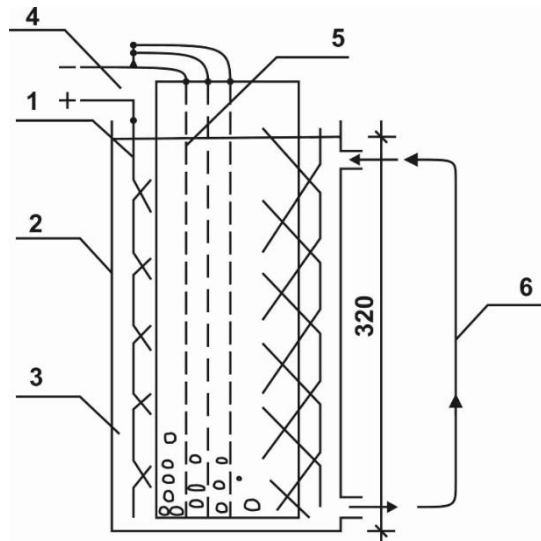
Fig.8.   The scheme of chloride extraction in Polder's investigation [19]. *1* – active titanium, *2* – PVC cylinder, *3* – electrolyte (5,66 l), *4* – power source, *5* – reinforcement bars, *6* – electrolyte flow.
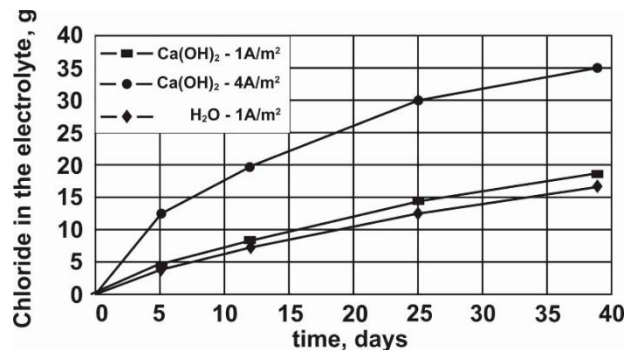

Fig.9.   Changes in the mass of the chloride ions removed, marked in the electrolyte during the examination of samples (1, 4, 7) by Polder [19].
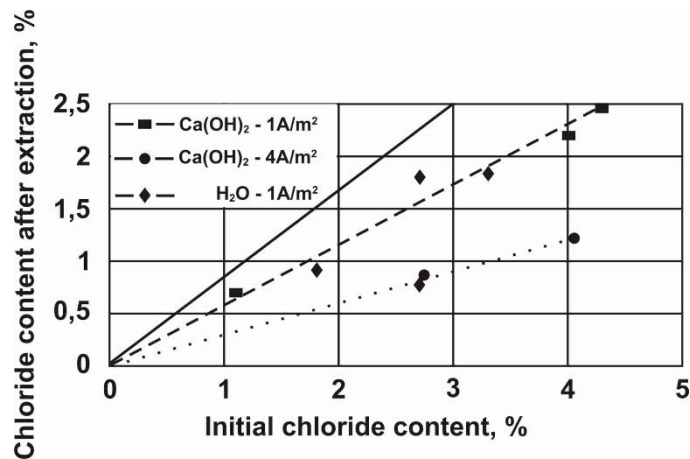

Fig.10.   Chloride concentration after 39 days' removal as a function of the initial chloride content, according to [19].

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Local differences in the effect of chloride ion removal were probably due to the differences in local current density within the concrete and resistances caused by different thicknesses of concrete covers (*15* to *45 mm*) through which the ions migrated.

3. Conclusions

- The mass of chlorides removed increased with a rise in the potential difference applied to the electrodes and the number of reinforcement bars located at identical depth.
- More chlorides were removed from specimens in which the depth of chloride contamination was smaller than the thickness of reinforcement concrete covers.
- When a direct current was passed, not only free chlorides (chloride ions), but also bound chlorides were removed from the concrete.

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