Monitoring of the Penetration of Chloride Ions to the Reinforcement Surface Through a Concrete Coating During Liquid Corrosion

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Abstract. The article is devoted to the study of chloritization of cement concretes during corrosion in liquid aggressive media. With the help of mathematical models, chloride ion concentration profiles are constructed for the thickness of the concrete coating. The possibility of using mathematical models in the description of corrosion of the second type of cement concretes to determine the mass transfer indicators and calculate the corrosion rate of reinforcing steel in concrete is shown. The effect of hydrophobizing additives on the rate of chloride ion transfer through the concrete coating to the reinforcement surface is considered. A study was made of the chlorination of cement concretes taking into account the phenomenon of pore and capillary colmatation. Graphical dependences of the rate of chloride ions transport on the speed and degree of colmatation of pores and capillaries of concretes based on Portland cement during corrosion in liquid aggressive media are presented. Time intervals for the beginning of corrosion of steel reinforcement are established for the corrosion of reinforced concrete in liquid aggressive media containing chloride ions.

1. Introduction

At present, as before, concrete is the main building material.

Reinforcement of concrete structural elements found application in the beginning of the XIX century [1]. Today, reinforced concrete is the most common and important material in the construction industry. It is used for the construction of buildings and various engineering structures such as tunnels, bridges, airports, as well as hydraulic and drainage systems. The efforts of researchers, at present, are focused on expanding the complex of strength and anticorrosive properties of concrete in accordance with the many options for its application.

The main factor causing the destruction of reinforced concrete is the corrosion of steel reinforcement, about 80 % of the damage caused by this phenomenon [2].

In the case of corrosion of reinforced concrete structures, the reinforcement of reinforced concrete is kept for a long time under the protection of a layer of concrete. Over time, particles of aggressive media migrate to the surface of reinforcing bars through the pores of concrete, and due to structural

defects, that are formed when concrete is destroyed during corrosion (Figure 1). Reinforcement corrosion is enhanced by the formation of microcracks in concrete or its partial collapse [3].
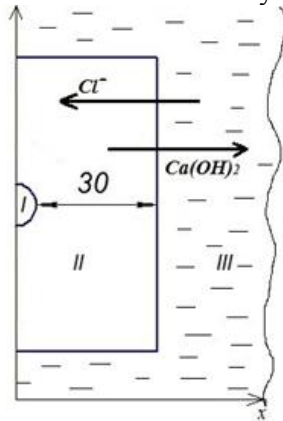
Figure 1. System "steel reinforcement – concrete – aggressive environment": I – steel reinforcement; II – concrete; III – aggressive environment.

Initially, concrete is hydrophilic, like most building materials. The hydrophilicity of concrete is the primary basis of all destructive processes that may occur in it [4]. It`s possible to significantly increase the durability of concrete by reducing the amount of water that can penetrate the concrete [5].

To reduce water absorption resort to the hydrophobization of concrete. Hydrophobic additives impart hydrophobic properties to the walls of pores and capillaries in concrete. The most known chemical additives among water-repellent materials are salts of fatty acids, for example, stearates and oleates of alkali and alkaline earth metals. When using such additives, because of soap reaction with "free calcium hydroxide", an insoluble calcium stearate is formed, which closes the pore surface [6], thus preventing the penetration of liquid into the concrete, and, therefore, the degree of corrosion destruction of the cement stone is reduced.

2. Relevance

Economic losses from corrosion of metals are huge. In the USA, according to the International Association of Engineers NACE, the damage from corrosion and the cost of fighting it are 3.1 % of GDP ($276 billion). In Germany, this damage is 2.8 % of GDP. According to experts from various countries, these losses in industrialized countries are from 2 to 4 % of gross national product [7]. At the same time, metal losses, including the mass of failed metal structures, products, equipment, account for 10 to 20 % of the annual steel production. In our country there is no official statistics that would reflect the economic damage from corrosion, but, according to some estimates [7], it is at least 5 % of GDP. Thus, it is very important to understand the causes of corrosion of building materials, to identify the factors that affect this complex process, to establish and generalize the patterns of mass transfer in concrete and reinforced concrete under the influence of different media.

3. Problem statement

Ensuring the durability of cement concrete has been an important task for scientists and civil engineers for many decades. Many studies are devoted to the fight against corrosion destruction of building materials and to the development of practical recommendations for the protection of reinforced concrete from liquid corrosion. One way to increase the durability of cement concrete is to reduce the water absorption of concrete by hydrophobization. Corrosion resistance of cement stone with hydrophobic additives requires additional research to determine the patterns of mass transfer.

4. Results of experimental studies

4.1 Results of studies of liquid corrosion of hydrophobized concretes

The studies were carried out on tablet samples with a diameter of 50 mm and a thickness of 5 mm (Figure 2) made of Portland cement of the PC 500-D0 brand with a water-cement ratio W/C = 0.3. The cement mark for water resistance W4, W6, W8 was regulated by the hydrophobic additive calcium stearate. It was found [8] that W4 concrete grade corresponds to the concentration of water repellent in the amount of 0.3 % by weight of concrete, W6 concrete grade – 0.5 %, W8 concrete grade – 0.7 %.
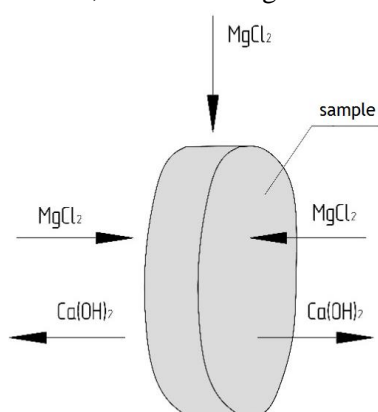
Figure 2. Scheme of the sample for corrosion resistance tests.

Studies of the corrosion resistance of cement stone were carried out [9, 10] on the apparatus for studying mass transfer processes described in the patent of the Russian Federation for useful invention No. 71164. The samples were immersed in aqueous solutions of $MgCl_2$ with a volume of 3000 cm^3 of various concentrations, from which samples for titration with a volume of 10 cm^3 were taken at intervals of 7 days. The concentration of the solution was adjusted in time. At the time of immersion, the age of the samples reached 28 days.

Concentrations of the aggressive environment were adopted in accordance with GOST 27677-88 "Protection against corrosion in construction. Concretes. General requirements for testing", as the concentration allowed for aggressive environment, with different degrees of aggressiveness of the liquid inorganic environment (mildly aggressive, medium aggressive, highly aggressive).

During the experiment it was found that the state close to the equilibrium concentration of calcium cations in the solution is achieved after 14 days of the sample stay in a corrosive environment (Figures 3-5) [8], whereas for samples without hydrophobic additives the equilibrium state occurs after 50 days [9]. After reaching equilibrium in the solution, changes in concentration do not occur due to the difficulty of penetration of the corrosive medium deep into the concrete.

It can be seen from Figure 3 that the kinetic curve of the concentration of calcium cations for samples of the cement brand for waterproof W4 in a solution of $MgCl_2$ with a concentration of 7.5 g/l lies closer to the curve corresponding to a mildly aggressive medium ($C(MgCl_2)$ = 6 g/l) and in a solution of $MgCl_2$ with a concentration of 11.5 g/l lies closer to the curve corresponding to a medium-aggressive medium ($C(MgCl_2)$ = 9 g/l).

It can be seen from Figure 4 that the kinetic curve of the concentration of calcium cations for samples of the cement brand for waterproof W6 in a solution of $MgCl_2$ with a concentration of 11.5 g/l lies closer to the curve corresponding to a mildly aggressive medium ($C(MgCl_2)$ = 9 g/l) and in a solution of $MgCl_2$ with a concentration of 16.5 g/l lies closer to the curve corresponding to a medium-aggressive medium ($C(MgCl_2)$ = 14 g/l).

It can be seen from Figure 5 that the kinetic curve of the concentration of calcium cations for samples of the cement brand for waterproof W8 in a solution of $MgCl_2$ with a concentration of 16.5 g/l lies closer to the curve corresponding to a mildly aggressive medium ($C(MgCl_2) = 14$ g/l) and in a solution of $MgCl_2$ with a concentration of 19.5 g/l lies closer to the curve corresponding to a medium-aggressive medium ($C(MgCl_2) = 18$ g/l).
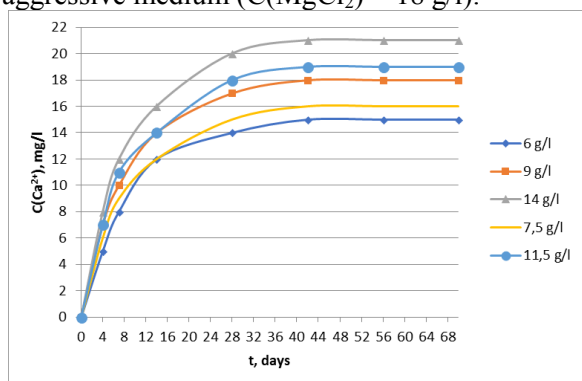
Figure 3. Kinetic curves of the concentration of calcium cations in a solution of $MgCl_2$ of different concentrations for samples from the cement of the brand for water resistance W4.
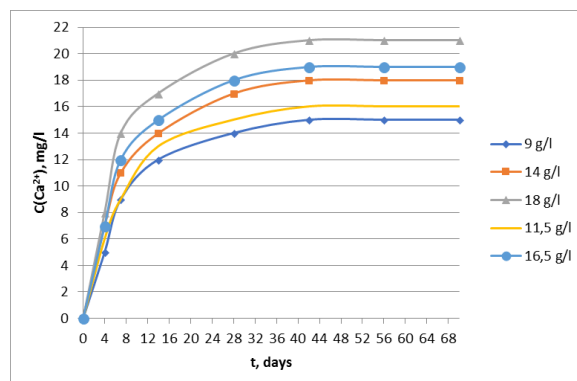
Figure 4. Kinetic curves of the concentration of calcium cations in a solution of $MgCl_2$ of different concentrations for samples from the cement of the brand for water resistance W6.
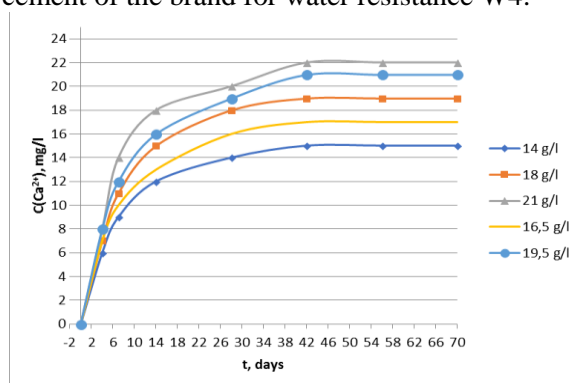
Figure 5. Kinetic curves of the concentration of calcium cations in a solution of $MgCl_2$ of different concentrations for samples from the cement of the brand for water resistance W8.

The results of the research show that the recommendations presented in GOST 27677-88 are conditional. Therefore, for their practical use, it is necessary to carry out preliminary tests for specific concrete grades to determine the range of concentrations depending on the degree of aggressiveness of the medium.

From figures 3-5 it is seen that the equilibrium concentration of calcium cations for concretes of different grades is approximately the same for one type of medium aggressiveness [11]. Thus, knowing the degree of aggressiveness of the medium (the concentration of chloride ions), it is possible to determine the optimal amount of hydrophobic additives sufficient to prevent corrosion damage in concrete.

For $MgCl_2$ concentrations less than 9 g/l, the concentration of the hydrophobic additive of 0.3 % by the concrete weight is sufficient, which corresponds to the W4 water resistance grade. For $MgCl_2$ concentrations of 9-16.5 g/l, the concentration of the hydrophobic additive of 0.5 % by the concrete weight is sufficient, which corresponds to the W6 water resistance grade. For $MgCl_2$ concentrations of 16.5 g/l, the concentration of the hydrophobic additive of 0.7 % by the concrete weight is sufficient, which corresponds to the W8 water resistance grade.

Further studies of the liquid corrosion of cement concretes were carried out in a 2 % solution of $MgCl_2$, which is a highly aggressive medium, so the samples of concrete grades W6 and W8 were tested.

4.2 Results of studies of the rate of chloride ion penetration to the surface of steel reinforcement through concrete coating

To study the processes occurring in liquid corrosion, a research was conducted to determine the degree of leaching of cement stone. Analyzing the profiles of the concentrations of "free calcium hydroxide" over the thickness of the sample in the aqueous salt medium obtained earlier, the concentration of chloride ions entering the concrete cover to the reinforcement bar was calculated (Figure 6) [11].

The obtained concentration profiles allow to predict the time of reaching the chloride-ion concentration necessary for starting the corrosion of reinforcing steel. As a threshold value of the concentration of chloride ions, above which corrosion processes begin to develop on the surface of the reinforcement, 0.4 % by weight of cement is traditionally accepted [3, 12-15]. The threshold value of chloride-ion content for the samples is $2.36 \cdot 10^{-4}$ kg/kg of concrete. To achieve this concentration of chloride ions at the reinforcement surface in concrete at liquid corrosion in a 2 % solution of $MgCl_2$ 174 days are required [12].
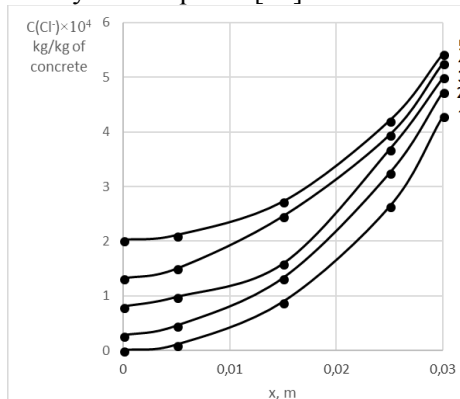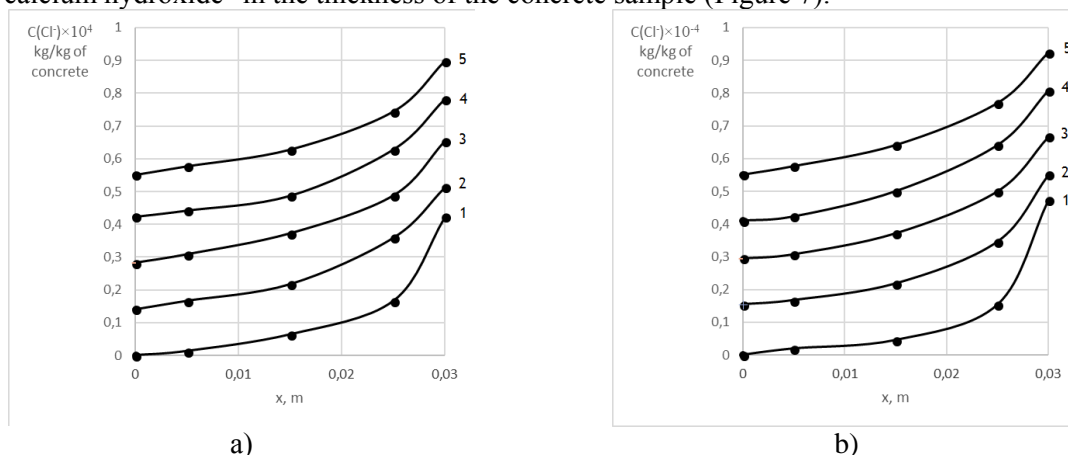

Figure 6. Profiles of chloride ion concentrations in the sample thickness in 2 % solution $MgCl_2$ at τ: $1 - 14$ days; $2 - 28$ days; $3 - 42$ days; $4 - 56$ days; $5 - 70$ days.

Model assumptions about the character of the mass transfer process in the system "solid body – liquid aggressive environment" [16, 17], which were adopted earlier, are confirmed by an analysis of the results of complex physical and chemical studies, that allows to calculate the characteristics of the process of mass transfer of "free calcium hydroxide" in the corrosion of concrete of the second type on the mathematical model developed within the framework of the scientific school of academician S V Fedosov (1) during the corrosion of concrete of the second type, as a result of the action of the selected corrosive medium: 2 % solution of $MgCl_2$ in accordance with known calculation methods [18, 19].

$$\theta\left(\bar{x}, Fo_m\right) = -\frac{Ki_m^*}{6}\left(6Fo_m + 3\bar{x}^2 - 1\right) + \frac{2Ki_m^*}{\pi^2}\sum_{n=1}^{\infty}\frac{(-1)^n}{n^2}\cos(\pi n\bar{x})\cdot\exp\left(-\pi^2 n^2 Fo_m\right) +$$

$$+\int_0^1\theta_0(\xi)\,d\xi + 2\sum_{n=1}^{\infty}\cos(\pi n\bar{x})\int_0^1\theta_0(\xi)\cos(\pi n\xi)\,d\xi\cdot\exp\left(-\pi^2 n^2 Fo_m\right) + \left(Fo_m + \frac{3\bar{x}^2+2}{6}\right)\times$$

$$\times\int_0^1 Po_m^*(\xi)\,d\xi - \int_0^1 Po_m^*(\xi)\cdot\xi\,d\xi + \frac{1}{2}\int_0^1 Po_m^*(\xi)\cdot\xi^2\,d\xi - \frac{2}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}\cdot\cos(\pi n\bar{x})\times$$

$$\times\int_0^1 Po_m^*(\xi)\cos(\pi n\xi)\,d\xi\cdot\exp\left(-\pi^2 n^2 Fo_m\right)$$

(1)

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Here: n – number of terms of the series; ξ – integration coordinate in the range $0 \leq \xi \leq \bar{x}$; Ki_m^* – modified criterion of Kirpichev; Fo_m – Fourier mass transfer criterion; $\bar{x}$ – dimensionless coordinate; $\theta(\bar{x}, Fo_m)$ – dimensionless concentration; $Po_m^*(\xi)$ – modified criterion of Pomerantsev.

According to the expression (1) the profiles of "free calcium hydroxide" concentrations were calculated for the thickness of a cement concrete sample exposed to 2 % solution MgCl$_2$ at different stages of the experiment for concrete grades by water resistance W6 and W8 [8, 18]. Profiles of chloride-ion concentrations were constructed according to the obtained profiles of the concentration of "free calcium hydroxide" in the thickness of the concrete sample (Figure 7).

a)   b)

Figure 7. Profiles of chloride ion concentrations in the thickness of the sample of concrete grades W6 (a) and W8 (b) in 2 % solution MgCl$_2$ at τ: 1 – 14 days; 2 – 28 days; 3 – 42 days; 4 – 56 days; 5 – 70 days.

It has been established that the threshold value of the chloride ion concentration is reached in the concrete of the water resistance brand W6 after 230 days; in the concrete brand for water resistance W8 after 241 days [20].

These calculated data were confirmed by the results of experimental studies of changes in the potential of steel reinforcement in cement samples exposed to aggressive media (Figure 8). During the experiment, it was found that the change in the potential of the reinforcement in a 2 % solution of MgCl$_2$ in a sample without additives begins after 6 months of testing, that is, after about 180 days; in samples with hydrophobic additives - after 8 months, that is, after about 240 days.
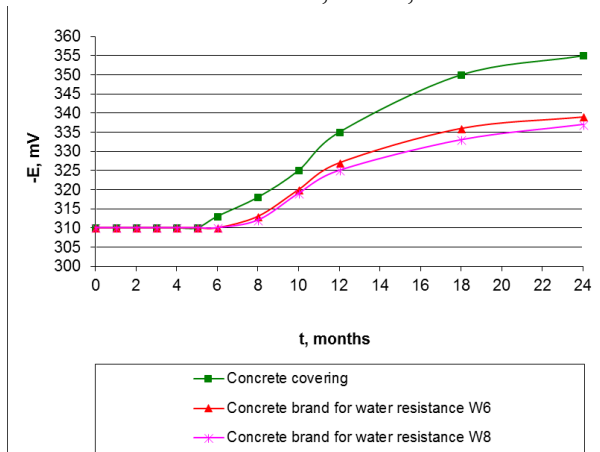
Figure 8. Changing the surface potential of steel reinforcement in cement samples exposed to 2 % MgCl$_2$ solution.

5. Conclusion

Thus, the introduction of hydrophobic additives contributes to the colmatation of pores and capillaries of concrete and allows to inhibit the penetration of aggressive media to the surface of steel reinforcement, as well as to prevent premature corrosion of reinforcement and subsequent destruction of the reinforced concrete products.

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