The role of colmatation in liquid corrosion of hydrophobized concrete

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Abstract. To reduce water absorption of cement concretes resort to hydrophobization by introducing special additives in the manufacturing process of the product. In the study of liquid corrosion of hydrophobized cement concretes of the W4, W6 and W8 waterproofness grades in media of various degrees of aggressiveness, the terms for achieving a state close to the equilibrium concentration of calcium cations in the solution were established. Based on the experimental data on the liquid corrosion of cement concretes of various grades in terms of water resistance, the optimum amount of hydrophobizing calcium stearate additive was determined, which is sufficient to prevent corrosion damage in concrete, depending on the degree of aggressiveness of the medium. Tests of strength characteristics of hydrophobized cement concretes of the W4, W6 and W8 waterproof grades were carried out. It is established that when alkali and alkaline-earth stearates are introduced into concrete as hydrophobic additives, its strength is significantly increased compared to non-hydrophobized concrete samples. Some special cases of changes in the mass conductivity coefficient during colmatation of hydrophobized cement concretes of the W4, W6 and W8 waterproof grades are considered and graphically illustrated. Profiles of changes in the rate of colmatation and the thickness of the colmatant layer for cement concretes with and without hydrophobizing additives are presented. The profiles show that over time there is a weakening of the mass flow, which is obviously associated with an increase in the colmatant layer. The rate of colmatation is also reduced due to the fact that the layer of colmatant partially or completely clogged the pores and prevents further penetration of the aggressive medium deep into the concrete.

1. Introduction
Cement concrete always contains interconnected pores of different sizes. Pores can be divided into macropores, capillary pores and gel pores. Gel pore sizes range from a few fractions of nm to several nm. They do not affect the durability of concrete, as they are too small to allow significant transfer of aggressive components. Capillary pores are voids not filled with solid hydration products of hardened cement paste. They have sizes from 10 to 50 nm if the cement paste is well hydrated and made with a low water-cement ratio but can reach up to 3-5 mm if the concrete is made with a high water-cement ratio or poorly moistened. Large pores up to several mm in size are the result of air capture during mixing, which is not removed by compacting the freshly poured concrete. Air bubbles with a diameter...
of about 0.05-0.2 mm can also be introduced into the cement paste intentionally using air-entraping additives in order to ensure resistance to freeze-thaw cycles [1-3].

When determining the resistance to destruction of concrete and its role in the protection of reinforcing steel, it is necessary to take into account not only the total capillary porosity (that is, the percentage occupied by capillaries), but also the size and relationship of capillary pores [4]. Reducing capillary porosity increases the mechanical strength of the cement stone and reduces the permeability of hydrated cement. The decrease in porosity that occurs both in macropores and in micropores plays an important role in increasing the mechanical strength of concretes [5].

The movement of liquids and ions through concrete can occur according to four main mechanisms: capillary suction due to capillary action inside the capillaries of cement stone; permeability due to pressure gradients; diffusion due to concentration gradients and migration due to electric potential gradients [6-8]. The transfer kinetics depends on the mechanism, on the properties of concrete (for example, its porosity and the presence of cracks), on the binding of the transported substances with hydrated cement, as well as on the environmental conditions on the concrete surface (microclimate) and their changes over time [9].

To reduce water absorption resort to hydrophobization of concrete. Hydrophobic additives give the walls of pores and capillaries in concrete hydrophobic properties [10-13]. The most well-known chemical additives among water-repellent materials are salts of fatty acids, such as stearates and oleates of alkaline and alkaline-earth metals. When using such additives, as a result of the reaction of soap with “free calcium hydroxide”, insoluble calcium stearate is formed, which covers the surface of the pores [14].

By reducing water absorption, the amount of aggressive medium entering the concrete is reduced, which means that the degree of corrosive destruction of the cement stone is reduced. Corrosion resistance of cement stone with hydrophobizing additives requires additional research to determine the laws of mass transfer.

2. Methods
Liquid corrosion studies were performed on tablet samples with a diameter of 50 mm and a thickness of 5 mm (Fig. 1), made of Portland cement of the PC 500-D0 brand with a water-cement ratio W/C = 0.3. The brand of cement for water resistance W4, W6, W8 was regulated by a hydrophobizing additive with calcium stearate. It was found that the concrete grade W4 corresponds to the concentration of the additive in the amount of 0.3 % by weight of concrete, the concrete grade W6 – 0.5 %, the concrete grade W8 – 0.7 %.

MgCl2 solution was chosen as the aggressive medium. 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). The concentration of MgCl2 in solutions varied from 6 to 21 g/l.

Studies of the corrosion resistance of cement stone were carried out 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.

3. Results and discussion
In the course of studies on liquid corrosion of hydrophobized concretes in media of various degrees of aggressiveness, it was found that a state close to the equilibrium concentration of calcium cations in solutions is reached after 14 days of the sample's stay in a corrosive environment (Fig. 2-4) [15, 16], whereas for samples without hydrophobizing additives, the equilibrium state occurs after 50 days [15]. After reaching equilibrium in the solution, the concentration does not change due to the difficulty of penetrating the corrosive medium deep into the concrete.
From Fig. 2-4 it is seen that the equilibrium value of the concentration of calcium cations for concretes of various grades is approximately the same for one type of aggressiveness of the medium. Thus, knowing the degree of aggressiveness of the medium (concentration of chloride ions), it is possible to determine the optimal amount of water-repellent additive sufficient to prevent corrosion damage in concrete.

At a MgCl$_2$ concentration of less than 9 g/l, in order to ensure corrosion resistance, the concentration of the hydrophobic additive should be at least 0.3 % by weight of concrete (waterproof grade W4).

At a MgCl$_2$ concentration of 9-16.5 g/l, in order to ensure corrosion resistance, the concentration of the hydrophobic additive should be at least 0.5 % of the mass of concrete (waterproof grade W6).

At a MgCl$_2$ concentration above 16.5 g/l, in order to ensure corrosion resistance, the concentration of the hydrophobic additive should be at least 0.7 % of the mass of concrete (waterproof grade W8).
It is known [17, 18] that when alkaline and alkaline-earth metal stearates are introduced into concrete for hydrophobization in the initial terms, the axial compression strength decreases (in 2-5 times) compared to non-hydrophobized concrete samples. Subsequently, upon hardening, the compressive strength of concrete increases significantly (in 20-40 times), however, no justification has yet been found for such an effect of hydrophobizing additives.

After weathering in aggressive environments, the cement samples were tested for strength. The test results are shown in table 1.

**Table 1.** Changes in the strength of samples under the influence of an aggressive environment

| Concentration of the hydrophobic additive, % | Concentration of MgCl$_2$ in solution, g/l | Estimated fracture stress, MPa |
|---------------------------------------------|------------------------------------------|--------------------------------|
| -                                           | 6                                        | 63.39                          |
| 6                                           | 58.18                                    |
| 7.5                                         | 49.23                                    |
| 9                                           | 38.56                                    |
| 11.5                                        | 34.27                                    |
| 14                                          | 33.84                                    |
| -                                           | 50.48                                    |
| 9                                           | 34.61                                    |
| 11.5                                        | 30.65                                    |
| 14                                          | 29.19                                    |
| 16.5                                        | 27.89                                    |
| 18                                          | 25.63                                    |
| -                                           | 49.2                                     |
| 14                                          | 45.85                                    |
| 16.5                                        | 38.28                                    |
| 18                                          | 34.61                                    |
| 19.5                                        | 28.13                                    |
| 21                                          | 23.47                                    |

An increase in the calculated fracture stress can be associated with structural-phase transformations occurring in a cement stone when exposed to an aggressive environment. A decrease in the calculated fracture stress of samples not exposed to an aggressive environment with an increase in the concentration of water-repellent additive can be due to the fact that the additive is introduced into the structure of the cement stone, causing structural-phase changes.

Model ideas about the nature of the mass transfer process in the studied system “solid – liquid aggressive medium”, which were adopted earlier [15, 19, 20], are confirmed by the analysis of the results of complex physical and chemical studies, which allows us to calculate the characteristics of the mass transfer process of “free calcium hydroxide” at the corrosion of concrete of the second type as a result of exposure to the selected aggressive medium: 2 % MgCl$_2$ solution in accordance with known calculation methods [21].
\[ \theta(\bar{x}, F_{om}) = -\frac{K_i^*}{6}(6F_{om} + 3\bar{x}^2 - 1) + \]
\[ + \frac{2K_i^*}{\pi^2} \sum_{n=1}^{\infty} \frac{(-1)^n}{n^2} \cos(\pi n \bar{x}) \cdot \exp(-\pi^2 n^2 F_{om}) + \int_0^1 \theta_0(\xi) d\xi \]
\[ + 2 \sum_{n=1}^{\infty} \cos(\pi n \bar{x}) \int_0^1 \theta_0(\xi) \cos(\pi n \xi) d\xi \cdot \exp(-\pi^2 n^2 F_{om}) + \]
\[ + \left( F_{om} + \frac{3\bar{x}^2 + 2}{6} \right) \int_0^1 P_{om}^*(\xi) d\xi - \int_0^1 P_{om}^*(\xi) \cdot \xi \cdot d\xi + \frac{1}{2} \int_0^1 P_{om}^*(\xi) \cdot \xi^2 \cdot d\xi - \]
\[ - \frac{2}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \cos(\pi n \bar{x}) \int_0^1 P_{om}^*(\xi) \cos(\pi n \xi) d\xi \cdot \exp(-\pi^2 n^2 F_{om}), \] (1)

Here: \( n \) is number of members; \( \xi \) is integration coordinate in the range \( 0 \leq \xi \leq \bar{x} \); \( K_i^* = \frac{q_c \delta}{k c_0 \rho c} \) is modified Kirpichev criterion; \( F_{om} = \frac{kt}{\delta^2} \) is Fourier mass transfer criterion; \( \bar{x} = \frac{x}{\delta} \) is dimensionless coordinate; \( \theta(\bar{x}, F_{om}) = \frac{c(x,t) - c_o}{c_o} \) is dimensionless concentration; \( P_{om}^*(\bar{x}) = \frac{q_w(x) \delta^2}{k c_0 \rho c} \) is modified Pomerantsev criterion.

It was experimentally established that the coefficient of mass conductivity of the material in the solid phase sharply decreases with time [19]. These data can be approximated by various dependencies [20]. For Fig. 5 special cases of changes in the mass conductivity coefficient \( k \) in the process of colmatation of hydrophobized cement concretes are presented. The mass conductivity coefficient was correlated by an exponential function of the form [21]:
\[ k_b(\tau) = k_{b0} A_1 \tau^B \text{exp}(-B_1 \tau). \] (2)

Here: \( k_{b0} \) is mass conductivity coefficient at the initial time, \( m^2/s \); \( A_1, B_1 \) are analytically selected exponent coefficients.

The physical-mechanical and mass-conducting characteristics of the material remain unchanged during the process: the main such characteristics in this case are the porosity and density coefficients of the concrete and sediment materials.

**Figure 5.** Particular cases of changes in the coefficient of mass conductivity \( k_b \) in the process of colmatation of cement concretes: 1 – without additives; 2 – waterproof grade W4; 3 – waterproof grade W6; 4 – waterproof grade W8
For the exponential dependence of the mass conductivity coefficient, the expressions for determining the colmatation rate, \( \frac{dL(F_{om})}{dF_{om}} \), and the thickness of the colmatant layer, \( L(F_{om}) \), have the form [21]:

\[
\frac{dL(F_{om})}{dF_{om}} = A_1 \cdot \exp(-\hat{B}_1 F_{om}) \cdot \frac{\partial \theta_B(\tilde{R}_k, F_{om})}{\partial \tilde{x}} \cdot \frac{v_{AD} \cdot K_{pc}}{(1 - \varepsilon_{sed})} \cdot \frac{1}{\hat{B}_1 \cdot (1 - \varepsilon_{sed})} \cdot \frac{1 - \exp(-\hat{B}_1 F_{om})}{1 - \exp(-\hat{B}_1 F_{om})}.
\]

Here: \( \hat{B}_1 = \frac{B_1 \delta_{con}}{k_{bo}} \).

To demonstrate the effect of the mass conductivity coefficient, we present the profiles of the colmatation rate, \( \frac{dL(F_{om})}{dF_{om}} \), and the thickness of the colmatant layer, \( L(F_{om}) \), from the Fourier mass transfer criterion, \( F_{om} \), with the same value of the porosity of the sediment layer, \( \varepsilon_{sed} = 0.5 \), for each particular case (Fig. 6).

**Figure 6.** Dependence of the colmatation rate (a), \( \frac{dL(F_{om})}{dF_{om}} \), and the thickness of the colmatant layer, \( L(F_{om}) \), (b) on the Fourier mass transfer criterion, \( F_{om} \), for porosity of the sediment layer, \( \varepsilon_{sed} = 0.5 \): 1 – for concrete without additives; 2 – for concrete of the W4 waterproof grade; 3 – for concrete of the W6 waterproof grade; 4 – for concrete of the W8 waterproof grade.
The profiles show that over time there is a weakening of the mass flow, which is obviously associated with an increase in the colmatant layer. The rate of colmatation is also reduced due to the fact that the layer of colmatant partially or completely clogged the pores and prevents further penetration of the aggressive medium deep into the concrete.

These data correlate with the results of liquid corrosion tests of hydrophobized cement concretes. Water-repellent additives contribute to clogging of pores and preventing the penetration of aggressive media into concrete.

4. Conclusions
It is obvious that the introduction of hydrophobizers and providing colmatation of concrete pores can increase its corrosion resistance and provide the necessary durability of concrete products and structures depending on the aggressiveness of the environment.

Thus, it is possible to predict the rate of corrosion of cement concretes taking into account the movement of the colmatation front, the thickness of the colmatant layer, and to use the phenomenon of colmatation of concrete pores to prevent the development of corrosion processes in further experimental studies.

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