Pore colmatation in case of liquid corrosion of concrete

S V Fedosov¹, V Eu Rumyantseva², V S Konovalova² and A S Evsyakov²

¹Moscow State University of Civil Engineering (National Research University), department of technologies of cohesive materials and concretes, 129337, Yaroslavskoe av., 26, Moscow, Russian Federation
²Ivanovo State Polytechnic University, department of natural sciences and technosphere safety, Sheremetyevsky av., 21, Ivanovo, 153000, Russian Federation

E-mail: fedosov-academic53@mail.ru, varrym@gmail.com, kotprotiv@yandex.ru, smart47@rambler.ru

Abstract. Pore colmatation plays a positive role, since a decrease in the permeability of cement concrete due to the deposition of insoluble corrosion products in the pores leads to a slowdown in corrosion processes. To test a mathematical model of pore colmatation of cement concretes under liquid corrosion, a study of mass transfer processes occurring when samples from Portland cement are exposed to a liquid aggressive medium was conducted. The article presents equations that allow us to determine the rate of pore colmatation and the thickness of the layer of colmatant formed in the pores during liquid corrosion of cement concretes. Based on the results of experimental studies of liquid corrosion of cement stone, the mass transfer parameters were determined in the investigated system «cement concrete – 2 % MgCl₂ solution». Based on the obtained data, the values of the colmatation rate and the thickness of the layer of colmatant of cement concrete were calculated during liquid corrosion in a 2 % MgCl₂ solution. It has been established that over time, the rate of mass transfer processes occurring in concrete decreases due to the difficulty of penetration of aggressive medium deep into concrete due to the deposition of corrosion products in the pores.

1. Introduction
Concrete is a capillary-porous material penetrated by a very fine network of pores and capillaries of various sizes [1]. When concrete is moistened, the smallest pores and capillaries are filled with an aggressive medium that reacts with calcium hydroxide to form insoluble reaction products that seem to clog these capillaries. Colmatation of pores and capillaries occurs, which leads to a decrease in the permeability of concrete [2, 3].

When cement stone is corroded, calcium hydroxide is dissolved in the outer layer of concrete [4, 5]. Calcium hydroxide is washed out of the concrete pores, while almost all the silica gel remains in the product pores, causing their partial clogging (colmatation) [5, 6]. Thus, the corrosion process becomes to some extent self-locking. The more silicic acid gel is formed during corrosion, the denser and less permeable it is for calcium ions, the more the process is inhibited over time [7].
2. Relevance

To assess the depth of corrosion damage, various equations are proposed for predicting the stability of concrete in an aggressive environment [8-12]. These equations take into account the rate of concrete corrosion in the initial period, the rate of heterogeneous reactions and the nature of control (kinetic or diffusion), the kinetics of the internal diffusion process with a constant diffusion coefficient over time, the porosity of the cement stone, the dependence of mass transfer coefficients on the structure and composition of concrete, as well as the composition and concentration of aggressive media, relative humidity (saturation level) and the concentration of calcium ions in the pore solution, the formation of calcite and the dissolution of hydration products, simultaneous impact of the force load and negative impact of aggressive media on concrete and reinforced concrete structures.

Based on the theory of mass transfer processes, equations are proposed for the mathematical description of the kinetic dependences of the corrosion process, which are most often encountered in practice. These equations describe extensive and intensive processes of concrete corrosion inhibition [13-16]. However, the developed models do not fully take into account the process of colmatation of the pores and capillaries of concrete, which remains completely unexplored.

3. Problem statement

Since pore colmatation influences the development of mass transfer processes and the rate of concrete corrosion, it is necessary to conduct research on the factors affecting the rate of colmatant deposition in the pores and the spread of the colmatation front. Establishing the regularities of mass transfer processes in the case of liquid corrosion of concrete, taking into account the pore colmatation, will allow using natural and artificial colmatation to prevent the development of corrosion damage.

4. Results of experimental studies

For the exponential dependence of the change in the mass conductivity coefficient over time, 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 [17]:

\[
\frac{dL(F_{om})}{dF_{om}} = A_1 \cdot \exp(-\bar{B}_1 F_{om}) \cdot \frac{\partial \theta_B(R_s, F_{om})}{\partial \bar{x}} \cdot \frac{v_{AD} \cdot K_{pc}}{(1 - \epsilon_{sed})} \tag{1}
\]

\[
L(F_{om}) = \frac{\partial \theta_B(R_s, F_{om})}{\partial \bar{x}} \cdot A_1 \cdot K_{pc} \cdot v_{AD} \cdot \bar{B}_1 \cdot (1 - \epsilon_{sed}) \cdot [1 - \exp(-\bar{B}_1 F_{om})]. \tag{2}
\]

Здесь: \( \bar{B}_1 = \frac{B_1 \delta_{con}^2}{\rho_{CaO}} \); \( A_1, B_1 \) are experimentally determined exponent coefficients; \( \delta_{con} \) is the thickness of the concrete layer, m; \( k_B \) is coefficient of mass conductivity of the transferred component of calcium hydroxide in concrete, m²/s; \( F_{om} = \frac{k_B \cdot \tau}{\delta_{con}} \) is Fourier mass transfer criterion; \( \theta_B = \frac{C_{B,a} - C_B(x, \tau)}{C_{B,a}} \) is dimensionless concentration; \( C(x, \tau) \) is the concentration of «free Ca(OH)₂» in concrete at the time \( \tau \) at an arbitrary point with the \( x \) coordinate, in terms of CaO (kg CaO/kg of concrete); \( C_B \) is concentration of «free Ca(OH)₂» in concrete at the initial moment of time at an arbitrary point with the \( x \) coordinate, in terms of CaO (kg CaO/kg of concrete); \( \frac{d\theta_B(R_s, F_{om})}{d\bar{x}} \) is mass flow of the transferred component; \( v_{AD} \) is stoichiometric coefficient depending on the reaction; \( \epsilon_{sed} \) is porosity of the sediment layer, which characterizes the volume of voids in the sediment layer; \( K_{pc} = K_p \cdot C_{B,a} \) is density coefficient.

For Figure 1 the profiles of the dependence of the colmatation rate, \( \frac{dL(F_{om})}{dF_{om}} \), and the thickness of the colmatant layer, \( L(F_{om}) \), on the Fourier mass transfer criterion, \( F_{om} \), for the porosity of the sediment layer \( \epsilon_{sed} = 0.5 \), for the changing value of the mass flow, \( \frac{d\theta_B(R_s, F_{om})}{d\bar{x}} \), are presented.
Figure 1. The dependence of the colmatation rate \((b)\), \(\frac{dL(F_{om})}{dF_{om}}\), and the thickness of the colmatant layer \((c)\), \(L(F_{om})\), on the Fourier mass transfer criterion, \(F_{om}\), for the porosity of the sediment layer \(\varepsilon_{sed} = 0.5\), for the value of the mass flow \((a)\), \(\frac{\partial \theta (R_{c}F_{om})}{\partial x}\): 1, 2 – constant; 3 – changing along an inclined linear relationship; 4 – changing exponentially.

The results of the research presented in Figure 2 show that after 70 days of testing, the concentration of \(Ca^{2+}\) cations in the liquid phase reaches constant values, and after 150 days, a state close to equilibrium occurs in the system under study [18, 19]. The values of mass transfer characteristics were calculated using a mathematical model of liquid corrosion of the second type of cement concretes [19, 20].

Figure 3 shows that over time, the coefficient of mass conductivity decreases according to an exponential law, which corresponds to a deceleration of the mass transfer processes occurring in concrete during liquid corrosion due to the formation of corrosion products in the pores.
Figure 2. Kinetic curve of Ca$^{2+}$ cations in a 2 % MgCl$_2$ solution for a cement concrete sample.

Figure 3. Change in the value of the coefficient of mass conductivity in the system «cement concrete – 2 % solution of MgCl$_2$» over time.

Using equations (1) and (2), the calculation of the rate of colmatation of cement concrete without additives and the thickness of the colmatant layer under liquid corrosion in 2 % MgCl$_2$ solution was performed (Figures 4 and 5).
5. Figure 4. Change in time of colmatation rate $\frac{dL(Fo_{m})}{dFo_{m}}$ for liquid corrosion in 2 % MgCl$_2$ cement concrete solution.

5. Figure 5. Change in time of the thickness of the layer of colmatant $L(Fo_{m})$ during liquid corrosion in a 2 % solution of MgCl$_2$ cement concrete.

The form of the obtained curves corresponds to the dependencies calculated using the mathematical model of colmatation, shown in Figure 1 (curve 4). The established values of the rate of colmatation of cement concrete under liquid corrosion in 2 % MgCl$_2$ solution and the thickness of the colmatant layer correspond to the values predicted by mathematical modeling, which allows us to judge the adequacy of the developed model of pore colmatation of cement concretes.

5. Conclusion
Having an understanding of the kinetics of mass transfer processes and the mechanism of natural colmatation during liquid corrosion of cement concretes, it is possible not only to predict the durability of concrete, but also to control the processes of corrosion destruction, affecting the rate of corrosion by artificial colmatation of the pores and capillaries of concrete.

References
[1] Mehta P K and Monteiro P J M 2006 Concrete: Microstructure, Properties, and Materials (New York: McGraw-Hill) p 683
[2] Yanakhmetov M R, Chuykin A E and Massalimov I A 2015 Nanotechnologies in construction: a scientific internet-journal 7 1 pp 63-72
[3] Mukhametshin V V and Kadyrov R R 2017 Nanotechnologies in construction: a scientific internet-journal 9 6 pp 18-36
[4] Stepanova V F, Rozental N K, Chekhniy G V and Baev S M 2018 Construction materials 8 pp 69-73
[5] Nikolopoulos C V 2015 Journal of engineering mathematics 91 1 pp 143-163
[6] Bazhenov Y M, Erofeev V T, Rimshin V I, Markov S V and Kurbatov V I 2016 Engineering Solid Mechanics 4 4 pp 219-225.
[7] Qiao H, Shi Y, Chen D, Cao H and Gao S 2015 Chongqing Daxue Xuebao 38 6 pp 129-137
[8] Levandovskiy A N, Melnikov B E and Shamkin A A 2017 Magazine of Civil Engineering 1 (69) pp 3-22
[9] Sugiyama T, Ritthichaup W and Tsuji Y 2008 Cement and Concrete Research 38 pp 49-67
[10] Ovchinnikov I I, Snezhkina O V and Ovchinnikov I G 2017 *IOP Conference series: Materials and engineering* **262** 012041
[11] Leonovich S N, Shalyi E E and Kim L V 2019 *Science and Technique* **18** 4 pp 284-291
[12] Gusev B V and Fayvusovich A S 2019 *Industrial and civil engineering* 7 pp 58-63
[13] Patel R A, Perko J, Jacques D, Schutter G D, Ye G and van Breugel K 2018 *Construction and Building Materials* **165** pp 833-845
[14] Gilmudtinov T Z, Fedorov P A, Latypov V M, Lutsyk E V and Latypova T V 2017 *Journal of Engineering and Applied Sciences* **12** 15 pp 4406-4413
[15] Hoang N D, Chen C T and Liao K W 2017 *Measurement* **112** pp 141-149
[16] Isgor O B and Weiss W J 2019 *Materials and structures* **52** 3
[17] Fedosov S V, Rumyantseva V E, Krasilnikov I V, Konovalova V S and Evsyakov A S 2018 *Magazine of Civil Engineering* **7** (83) pp 198-207
[18] Fedosov S V, Rumyantseva V E, Krasilnikov I V and Konovalova V S 2018 *IOP Conference Series: Materials Science and Engineering* **456** 012039
[19] Fedosov S V, Rumyantseva V E, Krasilnikov I V, Konovalova V S and Evsyakov A S 2018 *IOP Conference Series: Materials Science and Engineering* **463** 4 042048
[20] Fedosov S V, Rumyantseva V E, Konovalova V S and Loginova S A 2018 *International Journal for Computational Civil and Structural Engineering* **14** 3 pp 161-168