



# CARBONATION OF CONCRETE TAKING INTO ACCOUNT THE CRACKS IN THE PROTECTIVE CONCRETE LAYER

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## ABSTRACT

Nowadays, the application of the reinforced concrete structures for the construction of various national economy facilities all around the world is growing. Although this material appeared more than 150 years ago, from the position of the complex safety and lifetime of any facility of the national economy it is understudied. If a reinforced concrete structure is operated in the normal conditions with time the emergency situation can happen due to the change of the operation conditions. The typical reason of such failure is an impact of the aggressive gas and air environment of the atmosphere. The most wide-distributed aggressive gas regarding to the reinforced concrete structures is carbon dioxide. As a result of the interaction of the aggressive environment and components of the hardened cement paste, the concrete loses its protective properties regarding the reinforcement. The presence of cracks in the protective concrete layer of the reinforced concrete structures also promotes the increase of access of the aggressive environment to the zone of the reinforcement. This article considers the main approaches to the study of the kinetics of concrete neutralization under the impact of carbon dioxide. The results of the accelerated tests of the reinforced concrete samples are specified, in which the cracks of the set crack width are formed at CO<sub>2</sub> concentration 2% and relative humidity 75%. The method of recording of the impact of cracks in the reinforced concrete structures on the rate of the concrete carbonation was offered.

**Keywords:** reinforced concrete, carbon dioxide, carbonation, cracks, carbonation in crack, lifetime, corrosion.

## INTRODUCTION

More than 75% of the building structures of the building and structures are subjected to the aggressive impact of the operation environment. According to the data of the author of this work [1], the costs of the repair and the reinforcement of the structure exceed 5% of the total world gross profit. In Russia, the volume of losses from corrosion is estimated as 330-410 million dollars annually. One of the main reasons of the insignificant lifetime of the reinforced concrete structures is an aggressive impact of the external environment, in particular, the carbon dioxide contained in the environment that facilitates the corrosion of the reinforcement due to the neutralization of the protective concrete layer. The aggression of the atmosphere is constantly growing: according to the latest data, the concentration of the carbon dioxide in the air exceeded the level of 400 ppm [2], which is approximately 30% higher than the values of the last century, on the base of which the normative documents of the anticorrosion protection of concrete and reinforced concrete structures are based. The process of concrete carbonation can be considered as an interaction of two groups - minerals of the hardened cement paste and molecules of carbon dioxide [3-4]. The mathematical model of the physical and chemical interaction of the data of the groups is described by the system of the differential equations of second order in the private derivatives where the diffusion, dissolution and chemical interaction of carbon dioxide (group A) and soluble components of the hardened cement paste (group B) are taken into account simultaneously:

$$\left. \begin{aligned} \frac{\partial C_A}{\partial t} &= D_A^* \frac{\partial^2 C_A}{\partial x^2} + R(C_A) \\ \frac{\partial C_B}{\partial t} &= D_B^* \frac{\partial^2 C_B}{\partial x^2} + \frac{K_B S_B}{P_B} (C_{B\infty} - C_B) + R(C_B) \end{aligned} \right\} (1)$$

where:  $C_{A,B}$  is the concentration of the  $i$ -th substance;  $R_{A,B}$  is a function characterizing the decrease of the component from the unit of volume of the environment as a result of the reaction;  $D_A^*$ ,  $D_B^*$  are the efficient coefficients of diffusion;  $K_B$  is a kinetic coefficient of the dissolution of the solid phase;  $S_B$  is a specific internal surface of the hardened cement paste;  $P_B$  is the concrete porosity.

The analytical solution of the equation systems (1), based upon the simplification of the physical and chemical processes of concrete corrosion, has a view of the general dependency of "square root of time":

$$x = a\sqrt{t} \quad (2)$$

where  $a$  is a complex parameter.

The coefficient  $a$  depends upon many factors. For example, according to the data obtained from the authors [5-7], the concrete carbonation is mainly influenced by the efficient coefficient of the carbon dioxide diffusion in concrete, the reaction capacity of concrete and the carbon dioxide concentration.

Kishitany reveals such factors as a water-cement ratio and the characteristics of the used cement and a filler. Smolczyk *et al.* point the influence of the concrete compression strength [8].



Besides the technological factors and characteristics of the initial materials, the climatic conditions and (or) environment [9] play an important part. If the coefficient  $a$  characterizes the properties of the concrete and the carbon dioxide concentration, for taking into account the impact of the environment in different works it was offered to use the correction factors (coefficient of operation conditions), in particular, in the work [9] the coefficient  $m_i$  ( $m_1 \dots m_4$ ):

$$x = m_i \sqrt{at} \quad (3)$$

The coefficient  $m_i$  in the function (3) takes into account the following conditions:

- $m_1$  is a decrease of the carbonation rate at the humid and wet operation mode;
- $m_2$  is a decrease of the carbonation rate for the structures operated in the open air;
- $m_3$  is a dependence of the carbonation rate from temperature;
- $m_4$  is an increase of the carbonation rate at the increased concentration of the carbon dioxide regarding the normal conditions (300 ppm).

Besides the operation conditions, the availability of cracks can influence the kinetics of the carbonation process. As it is known, the acting Russian design norms allow the existence of the cracks of the particular width of a long-term or a short-term opening in the reinforced concrete structures. In this case, the availability of cracks till now is not taken into account in the method of calculation of the concrete carbonation and equations (2) and (3) can be applied only to those structures that do not have any cracks during the operation. Such structures are very rare. Furthermore, according to the acting norms, for example, GOST 28042-2013 "Reinforced concrete slabs for buildings and structures. Technical conditions" besides the power cracks the shrinkage cracks are allowed up to 0.1 mm crack width.

Now the achievements in the field of binder, chemical additives and technologies of concrete allow to obtain the concrete of the low and extremely low permeability (W8 and higher). In its turn, in the international construction practice, the so-called high quality concrete is more often used, with the durability of 60-150 MPa, water resistance of which can reach W12 and higher. It is evident that the application of such concretes decreases significantly the corrosive resistance of the concrete and reinforced concrete structures in the operated aggressive environments [12].

However, according to the various sources, the availability of cracks in the more durable (solid) concrete is more dangerous than in the non-durable (porous) concrete. It is connected to the fact that at the low concrete permeability the absorbing capacity of the crack walls is decreasing [1] causing the diffusion of the carbon dioxide inside the crack within a short time.

The author of the works [13-14] offers to determine the time of neutralization of the parallel crack walls in the acid gas environments by the following dependence:

$$t = \frac{m_0 x^4 D^* K_s^2}{C_0 a_{cr}^2 D_d^2 K_f^2} \quad (4)$$

where  $t$  is the time of crack opening;  $m_0$  is a reaction capacity of the concrete;  $x$  is a thickness of the protective concrete layer;  $D^*$  is an efficient coefficient of diffusion of the acid gas in concrete;  $C_0$  is a concentration of the acid gas in the air in the relative units;  $D_d$  is a coefficient of diffusion of the acid gases in the air;  $a_{cr}$  is the width of the crack opening;  $K_s$  is a sinuosity coefficient of the crack walls;  $K_f$  is a coefficient of the section form. A similar formula is used in the work [15]:

$$t = \frac{8m_0 x^4 D^*}{a_{cr}^2 D_d^2} \cdot \frac{c_x}{(c_0 - c_x)} \quad (5)$$

where  $t$ ,  $m_0$ ,  $x$ ,  $D^*$ ,  $C_0$ ,  $D_d$ ,  $a_{cr}$ , are the same as in the formula (4),  $c_x$  is the content of carbon dioxide in the cavity of the crack on the border of the carbonation (relative units).

In the foreign works, we can see the calculation of the efficient coefficient of the diffusion of carbon dioxide in the crack [16]:

$$D_{eff} = \frac{A_{ucr} D_{ucr} + A_{cr} D_{cr}}{A_{tot}} \quad (6)$$

where  $D_{eff}$  is an efficient coefficient of the carbon dioxide diffusion,  $A_{tot}$  is the total square of the concrete surface,  $A_{cr}$  is the square of the concrete surface with a crack,  $A_{ucr}$  is the square of the concrete surface without a crack,  $D_{cr}$  is a coefficient of the carbon dioxide diffusion in the crack,  $D_{ucr}$  is a coefficient of the diffusion of the carbon dioxide without a crack.

To take into account the sinuosity, connectivity of the crack walls that decelerate the efficient coefficient of diffusion in the equation (6), an additional coefficient  $\beta$  is used:

$$D_{eff} = \frac{A_{ucr} D_{ucr} + A_{cr} \beta D_0}{A_{tot}} \quad (7)$$

where  $\beta$  is a geometric factor,  $D_0$  is a coefficient of the carbon dioxide diffusion in the air.

The application of the above mentioned functions (4), (5), (7) is difficult for the practical calculations. Also, the formulas (4), (5) are based upon the fact that at the neutralization of the crack walls the absorption of the acid gas stops and that the gas is coming inside the concrete along the crack. In reality, the acid gas is absorbed constantly.

Accordingly, the authors of this work offers to use the approach described in the work [9] where the well-known diffusion function is taken as a base but in addition to the earlier applied correction coefficients ( $m_i$ ) the



impact of the cracks shall be taken into account as the fifth coefficient of the working conditions  $m_5$ :

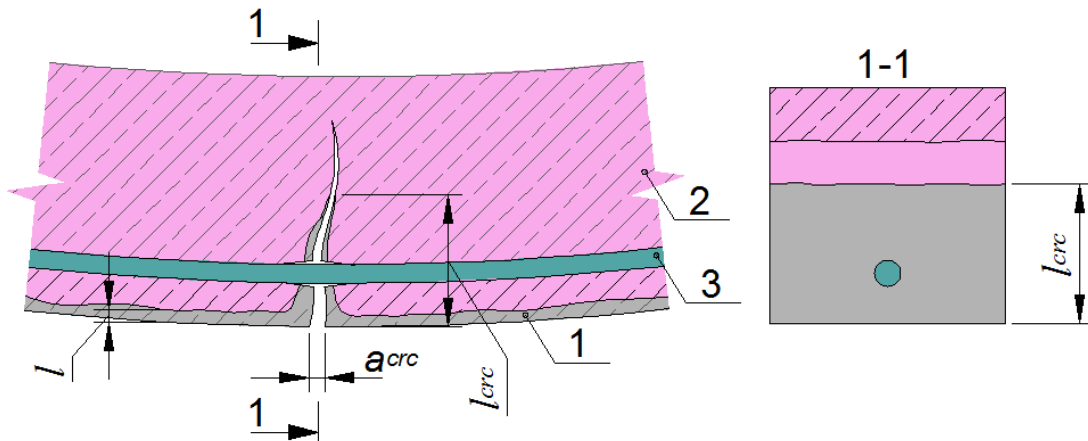
$$x = m_i m_5 \sqrt{at} \quad (8)$$

The numerical value of the coefficient  $m_5$  can be calculated by the empiric method determining the ratio of the depth of the carbonized concrete layer along the crack

to the depth of the carbonized concrete layer without the crack:

$$m_5 = \frac{l_{crc}}{l} \quad (9)$$

where  $l_{crc}$  is the depth of the carbonized concrete layer along the crack,  $l$  is the depth of the carbonized concrete layer without the crack (according to Figure-1).



**Figure-1.** A bent reinforced concrete element with a crack: 1 - carbonized layer; 2 - "healthy" concrete; 3 - reinforcement.

## METHODS

The experimental description of the coefficient  $m_5$  was made according to the accelerated method. The method of GOST 31383-2008 "Anti-corrosion protection of concrete and reinforced concrete structures. Testing methods" was taken as a base taking into account the recommendations specified in [17]. The tests were performed using the concrete samples-prisms, size 100×100×400 mm, reinforced by the metal rods along the lower active face.

Medium aluminate Portland cement of the brand TsEM II/A-Sh 32.5B (PTs400 D20) was used as a binder for concrete; the quartz stream sand with the fineness modulus M-2.5 was used as a fine filler; the crushed rock, fraction 5-10 mm was used as a large filler. The content of concrete was selected according to the requirements of the design strength - class B25 and workability with the cone slump CS=5 cm. The cement consumption was 380 kg/m<sup>3</sup>, and the water-cement ratio is 0.6. The plain reinforcing bars, diameter 6 mm, class A400, were used. The protection concrete layer was accepted 20 mm.

To form the required protection concrete layer, the reinforcement was supported from both ends by the steel plates that were removed after dismantling of the samples, and the ends of the bare reinforcing bars were coated with several layers of bitumen to prevent corrosion.

After reaching the design strength (28 days of natural hardening) before testing the samples by means of a special bending device according to the prototype specified in the works [16, 18], the cracks of various opening width were formed with their further fixation in the same position (Figure 2). The opening width of cracks

was measured by means of the microscope MIR-2 (range of measurement 0.015-6 mm) and in the program AutoCAD on the scaled image of the crack.

To exclude the impact of the fringe effects, all the edges except the low active face were coated with two layers of the waterborne polyacrylic paint and one layer of the airtight material (paraffin).

The tests were performed in the airtight unit with the relative humidity 75±3%, environment temperature 20±5 °C, concentration of carbon dioxide 2±0.1%.

The unit consisted of the following main parts: airtight chamber (V=0.2 m<sup>3</sup>) assembled in the form of aquarium made from the plexiglas sheets; a bulb filled with carbon dioxide, volume 10 L; a mechanical reducer; a solenoid valve, an automated gas-analyzer PKU-4 with an unified current output, a system of low speed fans along the perimeter of the chamber and an improved system of the overpressure relief in the form of a U-pipe filled with water. The supply of CO<sub>2</sub> into the chamber was performed automatically through the elbow installed on the end wall of the chamber. To prevent the point impact of the CO<sub>2</sub> flows on the samples, the flexible pipe with the bent end up was installed on the end of the elbow.

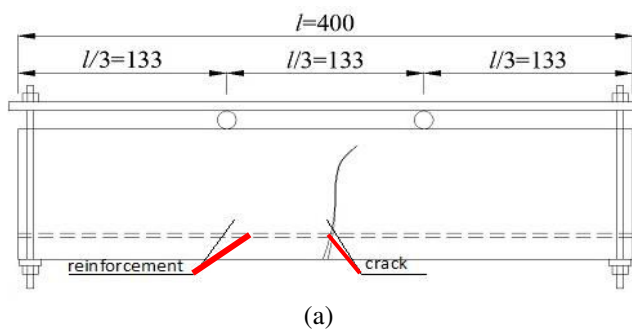
The relative humidity 75% in the chamber was provided by the saturated solution of sodium chloride. The change of the parameters of the temperature and humidity mode was made by means of the electronic hygrometer, brand Hygromaster and the autonomous register of temperature and humidity EClerk-USB-RHT.

24, 72, 120, 192, 264 and 300 hours since the beginning of carbon dioxide supply into the chamber the samples were taken out and a shear was performed along



the reinforcement of the sample perpendicular to the crack and a shear inside the crack itself (Figure-3). The area of the carbonated concrete was determined by the using of 1% alcohol phenolphthalein solution. Approximately in a minute, the shear treated by the indicator was photographed (macro survey). And the objective of the photo camera was installed strictly perpendicular to the axis of the sample to exclude the factor of image deformation. To provide this condition, the special support with a mechanic's level was used. The obtained image of the section was exported into the program AutoCAD and according to the actual sizes of the section was scaled.

The depth of the carbonated layer was determined according to the macro image of the shear in the crack and without the crack by choosing the area 40 mm. The data of the carbonation kinetics of the samples with the cracks, opening width 0.3 mm are shown in Table 1 and in Figure-4.



(b)



(c)



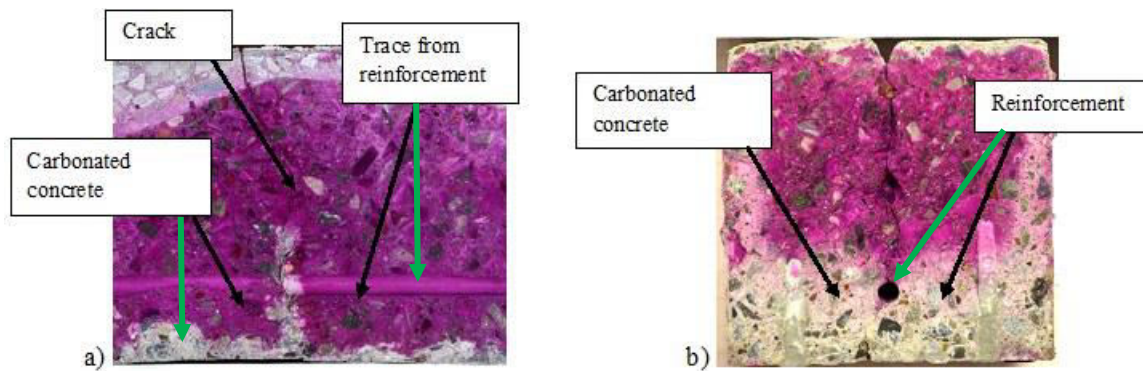
(d)

**Figure-2.** Crack formation: a) - a scheme of the bending mechanism; b) - a general view of the bending mechanism; c) - formation of holes along the crack; d) - caulking of holes by the cement solution for crack fixation.

## DISCUSSION AND RESULTS

It should be mentioned that the depth of the concrete carbonation in the crack is not clearly expressed as it is in the concrete without the crack (Figure-3). There is no such particular border between the "healthy" concrete coloured crimson and the uncoloured carbonated concrete. According to the different chemical reference books, the interval of the colour transition of the phenolphthalein indicator from the colourless to the crimson has different values and they are changing within the range from pH=8 to pH=10. Therefore, the measurement of the depth of the carbonated concrete layer in the crack was made along the two borders - where the concrete began to be coloured crimson and where the colour became more intensive. It is explained by the fact that the carbon dioxide concentration in the crack is changing depending upon the distance of the point along the crack from the concrete surface and consequently the insignificant amount of gas for the complete reaction of carbonation.





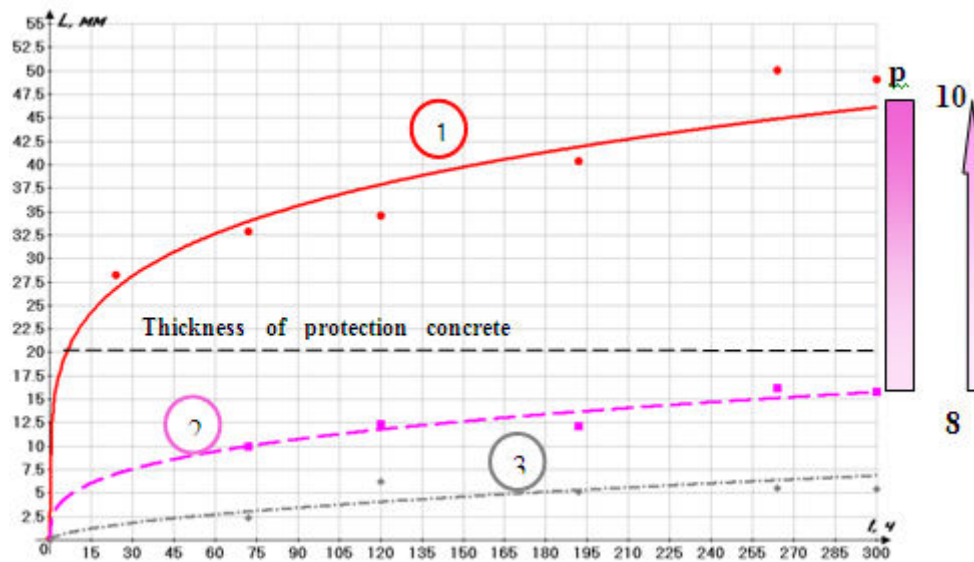
**Figure-3.** Sample shears:a) - along the reinforcement; b) - along the crack.

**Table-1.**Data of the depth of concrete carbonation.

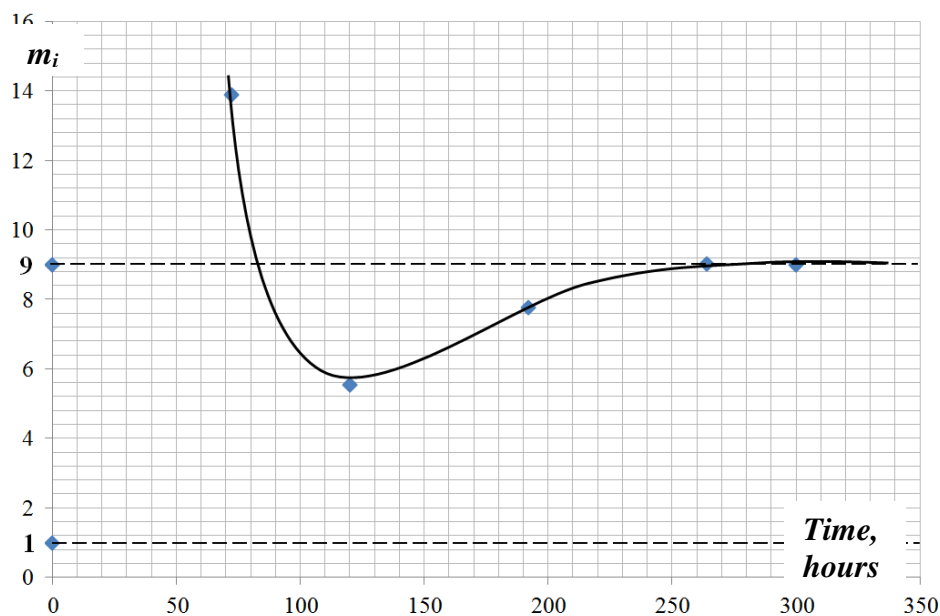
Time, hours	Equivalent time, year	Depth of concrete carbonation in crack, pH > 9, $l_1$ , mm	Depth of concrete carbonation in crack, pH < 7.5, $l_2$ , mm	Depth of concrete carbonation without crack, $l_3$ , mm	Ratio $l_1 / l_3 = m_5$
24	0.14	28.22	-	-	
72	0.41	32.92	10.02	2.37	13.89
120	0.68	34.58	12.35	6.23	5.55
192	1.1	40.35	12.19	5.18	7.79
264	1.5	50.02	16.24	5.54	9.04
300	1.71	49.08	15.75	5.45	9.00

The analysis of the obtained data shows that the coefficient  $m_5$  is not a constant value and it is changing with time that corresponds to the equations (4) and (5). For practical calculations, it is reasonable to accept the "steady

state" value of the coefficient  $m_5$ : for the concrete B25 and the opening width of the cracks 0.3 mm the value  $m_5 \approx 9$  is achieved 300 hours after the tests (Figure-5).



**Figure-4.** Dependence of the change of depth of concrete carbonation from time for the opening width of the crack 0.3 mm: 1 - depth of concrete carbonation along the crack, where  $\text{pH} > 10$ ; 2 - depth of concrete carbonation along the crack, where  $\text{pH} < 8$ ; depth of concrete carbonation without the crack.



**Figure-5.** Graph of change of coefficient  $m_5$  for the crack with the opening width 0.3 mm.

## MAIN RESULTS OF THE RESEARCH AND CONCLUSIONS

- the method of accelerated tests of the reinforced concrete samples under the impact of the carbon dioxide was improved taking into account the availability of cracks in the samples;

- the mechanism of concrete carbonation in the sample with the model crack was specified. Thus, at the opening width of crack 0.3 mm, the depth of the concrete neutralization B25 on the area without the crack formation has an approximately 9 times smaller value in comparison with the area with a crack;

- the method of recording of the impact of cracks when estimating the lifetime of concrete and reinforced concrete in the aggressive gas and air environments was offered, while calculating the "square root of time" according to the model, besides the coefficients of the working conditions taking into account the impact of the various parameters of the environment ( $\text{CO}_2$  concentration, humidity, temperature), an additional coefficient is introduced that takes into account the availability of cracks in the structures.



## ACKNOWLEDGEMENTS

The work was performed with the financial support from the Ministry of Education and Science of the Russian Federation within the framework of the basic part of the state assignment No. 2014/241, No. R&D 2093.

## REFERENCES

- [1] Migunov V.N. 2013. Eksperimental'no-teoreticheskoe issledovanie korrozii i dolgovechnost' zhelezobetonnnykh konstruktivov s treshchinami: monografiya [Experimental and Theoretical Study of Corrosion and Durability of the Reinforced Concrete Structures with Cracks] (Part 1). monography. Penza: PSUAC.
- [2] Dlugokencky E. & Tans P. 2016. Trends in Atmospheric Carbon Dioxide. Retrieved July 1, 2016, from <http://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>.
- [3] Czarnecki L. & Woyciechowski P. 2015. Modelling of Concrete Carbonation; Is It a Process Unlimited in Time and Restricted in Space? Bulletin of the Polish Academy of Sciences. Technical Sciences, 63(1), 43-54.
- [4] Papadakis V.G., Vayenas C.G., & Fardis M.N. 1991. Physical and Chemical Characteristics Affecting the Durability of Concrete. ACI Materials Journal, 9(2), 186-196.
- [5] Alekseev, S.N., & Rozental, N.K. 1976. Korroziionnayastoičnost' zhelezobetonnnykh konstruktivov v agressivnoipromyshlennoisrede [Corrosion Resistance of the Reinforced Concrete Structures in the Aggressive Industrial Environment]. Moscow: Stroiizdat.
- [6] Alekseev S.N., Ivanov F.M., Modry S. & Shissle P. 1990. Dolgovechnost' zhelezobetona v agressivnykh sredakh [Durability of Reinforced Concrete in the Aggressive Environment]. Moscow: Stroiizdat.
- [7] Polak A.F. 1982. Fiziko-khimicheskie osnovy korroziizhelezobetona [Physical and Chemical Foundations of the Reinforced Concrete Corrosion]. Ufa: UNI.
- [8] Fitzpatrick D. & Richardson M.G. 2015. Sequestration of Carbon Dioxide by Concrete Infrastructure: a Preliminary Investigation in Ireland. Journal of Sustainable Architecture and Civil Engineering, 1(10), 66-77.
- [9] Latypov V.M., Latypov T.V., Lutsyk E.V. & Fedorov P.A. 2014. Dolgovechnost' betona i zhelezobetona v prirodnykh agressivnykh sredakh: monografiya [Durability of Concrete in the Natural Aggressive Environments: Monograph] (2<sup>nd</sup> Ed., updated and revised). Ufa: RSC USSTU.
- [10] Richardson M.G. 2002. Fundamentals of Durable Reinforced Concrete. Boca Raton, FL: CRC Press.
- [11] Bob C. 1996. Probabilistic Assessment of Reinforcement Corrosion in Existing Structures. In: R.K. Dhir, and M.R. Jones (Eds.), Proceedings of the International Conference held at the University of Dundee Scotland, UK on 24-26 June 1996. London: E & FN Spon. pp. 17-28
- [12] Rozental N.K. 2004. Korroziionnayastoičnost' i osobonizkoipronitsaemosti: dis. dokt. tekhn. nauk [Corrosion Resistance of the Cement Concretes of Low and Extremely Low Permeability (Doctoral Thesis)]. Moscow: Research Institute of Concrete and Reinforced Concrete.
- [13] Novgorodskii V.I. 1984. O dopustimoishirine kratkovremennogo razkrytiya treshchiny [Allowable Width of Short-Term Opening of Cracks]. Beton i zhelezobeton, 7: 41-42.
- [14] Novgorodskii V.I. 2015. Osnovy dolgovechnost' zhelezobetonnnykh konstruktivov [Foundations of the Durability of Reinforced Concrete Structures]. Moscow: Sputnik+.
- [15] Migunov V.N. 2013. Eksperimental'no-teoreticheskoe issledovanie korrozii i dolgovechnost' zhelezobetonnnykh konstruktivov s treshchinami [Experimental and Theoretical Study of Corrosion and Durability of the Reinforced Concrete Structures with Cracks: Monograph]. Penza: PSUAC.
- [16] Talukdar S., Banthia N. & Grace J.R. 2012. The Effects of Structural Cracking on Carbonation Progress in Reinforced Concrete: Is Climate Change a Concern? In: B.J. Mage (Ed.), Proceedings of the 3<sup>rd</sup> International Conference on the Durability of Concrete Structures, Queen's University of Belfast, 17-19 September 2012. Belfast: Queen's University of Belfast.



- [17] Novgorodskii V.I., Ostrovskii A.B. & Migunov V.N. 1980.  
Metodopredeleniya effektivnosti inhibitorov korrozii stal  
i v treshchinakh betona.  
Metodicheskie rekomendatsii po issledovaniyu inhibitorov korrozii armatury v betone [Determination Method of Steel Corrosion Inhibitors Efficiency in the Concrete Cracks. Methodological Recommendations of Study of Corrosion Inhibitors of the Reinforcement in Concrete]. Moscow: Research Institute of Concrete and Reinforced Concrete.
- [18] Moskvina V.M., Podval'nyi A.M. & Ptitsyn O.A. 1962.  
Metody naturnykh issledovaniy na stende v  
Kol'skom zalive [Methods of Field Studies at the Stand in Kola Bay]. In Korroziya zhelezobetona i metody zashchity. Trudy instituta NIIZhB [Reinforced Concrete Corrosion and Protection Methods. Works of the Research Institute of Concrete and Reinforced Concrete] (Issue 28). Moscow: Gostroiizdat. pp. 178-187.