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Reinforced Concrete under the Action of Carbonization and Chloride Aggression: a Probabilistic Model for Service Life Prediction

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Abstract. Reinforcement corrosion of marine and coastal hydraulic structures due to chloride aggression and concrete carbonization leads to a sharp decrease in structure safety. The reinforcement is subjected to a depassivation process as soon as a chloride concentration on its surface exceeds a certain threshold concentration, or the pH value in a concrete protective layer is decreased to a threshold value due to carbonation. Electrochemical reactions are realized with formation of corrosion products due to penetration of oxygen up to reinforcement surface. This leads to cracking of the concrete protective layer and decrease in reinforcement cross-section. The paper proposes a method for predicting a complex degradation of reinforced concrete structures with due account of various mechanisms of corrosion wear that allows to develop efficient methods for improvement of structure durability and maintainability which are operated in the marine environment. A methodology for forecasting of reinforced concrete service life prediction has been developed under a combined effect of carbonization and chloride aggression while using finite-difference and probability models. The paper takes into account initiation periods of reinforcement corrosion and propagation periods for conditions of Sakhalin shelf zone. Field surveys of Kholmsk and Korsakov port facilities are presented in the paper. Carbonization front and chloride content have been estimated according to depth of the concrete protective layer. The paper proposes a model that allows to determine an average period prior to repair while taking into account rate of concrete protective layer degradation caused by simultaneous action of two corrosion processes: carbonization and chloride aggression.

Keywords: reinforced concrete, carbonization, chloride aggression, service life prediction, probabilistic model

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Железобетон при воздействии карбонизации и хлоридной агрессии: вероятностная модель расчета-прогноза срока службы

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Реферат. Коррозия арматуры морских и прибрежных гидротехнических сооружений вследствие хлоридной агрессии и карбонизации бетона ведет к резкому снижению безопасности сооружения. Арматура подвергается процессу депассивации как только концентрация хлорида на ее поверхности превысит пороговую либо значение pH в защитном слое бетона уменьшится до порогового значения в результате карбонизации. При проникновении кислорода до поверхности арматуры реализуются электрохимические реакции с образованием продуктов коррозии. Это приводит к растрескиванию защитного слоя бетона, уменьшению площади сечения арматуры. В статье предложен метод прогнози-

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рования комплексной деградации железобетонных конструкций прибрежных сооружений с учетом различных механизмов коррозионного износа, что позволяет разработать эффективные способы повышения долговечности и ремонтпригодности конструкций, эксплуатируемых в морской среде. Разработана методика прогнозирования долговечности железобетонных конструкций при совместном воздействии карбонизации и хлоридной агрессии с использованием конечно-разностной и вероятностной моделей. Учтены периоды инициирования и распространения коррозии арматуры для условий шельфовой зоны острова Сахалин. Выполнены полевые исследования сооружений портов Холмск и Корсаков. Произведена оценка фронта карбонизации и содержания хлоридов по глубине защитного слоя бетона. Предложена модель, позволяющая определить средний период до ремонта с учетом скорости деградации защитного слоя бетона от одновременного воздействия двух коррозионных процессов: карбонизации и хлоридной агрессии.

Ключевые слова: армированный бетон, карбонизация, хлоридная агрессия, прогнозирование срока службы, вероятностная модель

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State of the Issue and Research Objectives

Existing models do not allow to take into due consideration possible changes in operating conditions, a combination of several factors of an aggressive environment. Complex modeling of various factors makes it possible to take into account the stochastic nature of the processes of carbonization and chloride aggression, changes in operating conditions of structures or requirements imposed on them.

The purpose of the study: to develop a methodology for calculating of reinforced concrete structures durability for the climatic conditions of the coastal Far East seas zone from the complex effects of carbonization and chloride aggression.

Objectives of the study: analyze the results of studies on the complex effects of carbonization and chloride aggression on marine concrete; to improve the theoretical models of carbonization and chloride aggression, taking into account the crack formation and propagation in the protective layer of concrete; to develop a probabilistic method for predicting the service life of reinforced concrete port structures, taking into account the complex effects of carbonization and chloride aggression; experimentally investigate the technical condition of the reinforced concrete elements of the port facilities in exploitation, and identify the specific features of their degradation in the marine environment, including taking into account technological factors.

Verification of a deterministic model for calculating the combined effect of carbonization and chloride aggression

The deterministic model for calculating the combined effect of carbonization and chloride ag-

gression on marine concrete based on the 2nd Fick Law was verified.

A model for solving the differential diffusion equation, J. Crank has been adopted, taking into account the effect of carbonization on the transport of chlorine ions in concrete. The basic equation has the Cl form:

$$\frac{\partial C_{Cl}}{\partial t} = \frac{D_{Cl}^*}{1 + \left(\frac{1}{w_e}\right) \cdot \left[\frac{\alpha_L (1 - da_c)}{\left(1 + \beta_L \frac{C_f}{b}\right)^2} \right]} \frac{\partial^2 C_f}{\partial x^2}, \quad (1)$$

where α_L , β_L – empirical constants; a_c – empirical constants; d – coefficient of decrease in the connecting ability of chloride due to carbonization; C_{Cl} – general content of chloride in concrete; C_f – content of free chloride in concrete; t – operation time; b – mass of knitting; x – depth of a protective layer.

Extent of carbonization of concrete is defined from a proportion:

$$\%X_c - 100 \% a_c;$$

$$\%KC - x \% a_c,$$

where X_c – extreme size of carbonization; KC – carbonate component

$$KC = \frac{m_{CaCO_3}}{m_H} \cdot 100 \% ; \quad (2)$$

m_{CaCO_3} – mass of a carbonate component; m_H – the mass of a hinge plate of test, is defined experimentally.

Extreme size of carbonization is determined by a formula

$$X_c(t) = \sqrt{\frac{2D_{CO_2}}{a_c} \int_1^t f_T(t)f_W(t)C_{CO_2}(t)dt \left(\frac{t_0}{t}\right)^{0,12}}, \quad (3)$$

where $f_T(t)$, $f_W(t)$, $C_{CO_2}(t)$ – funktion of influence of temperature, humidity and concentration CO₂ on diffusion coefficient; a_c – the coefficient defining quantity CO₂, necessary for transformation of all capable to be carbonated hydration products; D_{CO_2} – initial coefficient of diffusion of carbon dioxide in concrete.

For taking note CO₂ assessment of content of carbon dioxide in air taking into account service life of reinforced concrete structures is executed, according to data of Keeling a curve. As concentration of chlorides in the marine environment changes depending on weather conditions, the model of sea water impact on constructions is modified by input of dependence on distance between a construction and the coast [1–4].

For verification of model of joint action of carbonization and chloride aggression reinforced concrete structures of the classes XC4 and XS3 under the terms of operation with average values of parameters of concrete mix according to EN 206:2013 and the minimum thickness of concrete protective layer on the joint venture 28.13330.2012 are taken. According to the offered technique, calculations for these tab. 1 are carried out.

Table 1

Basic data of final and differential model

Parameter, unit-ism.	Site of Sakhalin Island		
	Northern	Central	Southern
$T_{max}, ^\circ C$	18,3	20,5	17,7
$T_{min}, ^\circ C$	-7,3	-6,2	-2,4
$W_{max}, \%$	86	81	85
$W_{min}, \%$	74	76	71
w/b	0,4	0,4	0,4
$b, kg/m^3$	350	350	350
Carbonization			
g_e	2,5	2,5	2,5
f_e	5	5	5
$E, kJ/mol$	40	40	40
$R, kJ/K$	$8,314 \cdot 10^{-3}$	$8,314 \cdot 10^{-3}$	$8,314 \cdot 10^{-3}$
$C_s, kg/m^3$	$3,890 \cdot 10^{-4}$	$3,890 \cdot 10^{-4}$	$3,890 \cdot 10^{-4}$
$D_{CO_2}, sm^2/s$	$3,399 \cdot 10^{-4}$	$3,399 \cdot 10^{-4}$	$3,399 \cdot 10^{-4}$
n_m	0,12	0,12	0,12
Chloride aggression			
$E, kJ/mol$	41,8	41,8	41,8
$R, kJ/K$	$8,314 \cdot 10^{-3}$	$8,314 \cdot 10^{-3}$	$8,314 \cdot 10^{-3}$
α_L	0,1185	0,1185	0,1185
β_L	0,09	0,09	0,09
$W_{ref}, \%$	65	65	65
$C_{env}(L), kg/m^3$	6,2	6,2	6,2
m	0,4	0,4	0,4
$t_0, days (years)$	28 (0,0767)	28 (0,0767)	28 (0,0767)
$t, year$	50	50	50

For modeling the program in Mathcad (authors D. Shestovitsky and E. Karapetov) executed on the basis of final and differential approach is used and modified (fig. 1, tab. 2).

Table 2

Results of modeling

Parameter, unit-ism.	Place of operation		
	Northern	Central	Southern
Front of carbonization ($t = 50$ of years), mm	30,80	29,60	29,40
Extent of carbonization	0,61	0,60	0,60
Concentration of chlorides on fittings depth without carbonization (at $t = 50$ of years), %	0,55	0,65	0,44
Too taking into account carbonization (at $t = 50$ of years), %	0,65	0,60	0,54
Time of initiation of chloride corrosion without carbonization, year	50	40	43
Too taking into account carbonization, year	45	35	30

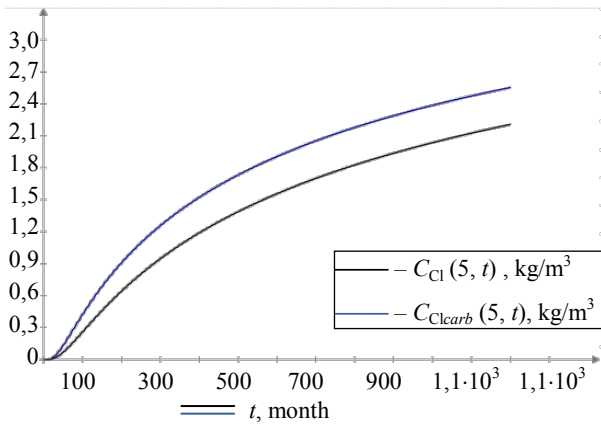


Fig. 1. Change of concentration of chlorides in protective concrete layer taking into account and without carbonization (the southern site): $C_{Cl}(x, t)$ – concentration of chloride ions in protective layer without carbonization; $C_{Clcarb}(x, t)$ – concentration of chloride ions in protective layer with carbonization. Critical concentration of chlorides – 0,4 % or 1,4 kg/m³

Results have shown, that carbonization has led to release of chloride ions in pore’s solution, in the investigation of what, service life of structures decreases.

Technique of probabilistic calculation of joint action of carbonization and chloride aggression

The technique of probabilistic calculation of joint impact of carbonization and chloride aggression on concrete is developed. The equation of probability of refusal is the cornerstone:

$$P_f = P(R - S \leq 0) \leq P, \tag{4}$$

where P_f – rejection probability; P – admissible probability of approach of a limit state; S – loading function; R – function of resistance of a structures.

For chloride corrosion, in probabilistic statement, represents value of concentration of chlorides $C_{Cl}(x, t)$. C_{crit} – parameter of critical (threshold) concentration of chloride at the level of bedding of fittings, which excess leads to corrosion initiation. In this case probability of no-failure operation:

$$P_f = P(\{C_{crit} - C(x, t)\} \leq 0) \leq P. \tag{5}$$

$C_{Cl}(x, t)$ decides on use of model, which is based on the decision of the 2nd law of diffusion of A. Fick by means of function of a mistake of C. Andrade:

$$C_1(x, t) = C_0 \sum_{n=0}^{\infty} a^n \left[\operatorname{erfc} \left(\frac{2ne + x}{2\sqrt{D_1(t) \cdot t}} \right) - \right.$$

$$\left. - a \cdot \operatorname{erfc} \left(\frac{(2n + 2)e - x}{2\sqrt{D_1(t) \cdot t}} \right) \right]; \tag{6}$$

$$C_2(x, t) = \frac{2kC_0}{k + 1} \sum_{n=0}^{\infty} a^n \operatorname{erfc} \left[\left(\frac{(2n + 1)e + kx}{2\sqrt{D_1(t)}} \right) \right]; \tag{7}$$

$$a = \frac{1 - k}{1 + k}; \tag{8}$$

$$k = \sqrt{\frac{D_1}{D_2}}, \tag{9}$$

where $D_1 = D_{Cl,cb}$ – coefficient of diffusion of chlorides of carbonized concrete; $D_2 = D_{Cl,ucb}$ – coefficient of diffusion of chlorides of not carbonized concrete.

The model is based on difference of coefficients of diffusion in one cut (“skin-effect”), that results or repair restoration of a protective layer of concrete, or at action of a set of aggressive factors of the external environment on a structure. In a case of joint action of carbonization and chloride aggression, formulas (6) and (7) will be transformed to a type:

$$C_{Cl,cb}(x, t) = C_S \sum_{n=0}^{\infty} a^n \left[\operatorname{erfc} \left(\frac{2nX_c + x}{2\sqrt{D_{Cl,cb}(t) \cdot t}} \right) - \right. \tag{10}$$

$$\left. - a \cdot \operatorname{erfc} \left(\frac{(2n + 2)X_c - x}{2\sqrt{D_{Cl,cb}(t) \cdot t}} \right) \right];$$

$$C_{Cl,ucb}(x, t) = \frac{2kC_S}{k + 1} \times \sum_{n=0}^{\infty} a^n \operatorname{erfc} \left[\left(\frac{(2n + 1)x + k(x - X_c)}{2\sqrt{D_{Cl,cb} \cdot t}} \right) \right], \tag{11}$$

where C_S – superficial concentration of chlorides, %; x – thickness of a protective layer of concrete, mm; (x) – inverse function of mistakes of Gauss; $X_c = X_c(t)$ – depth of carbonization of concrete, mm; t – time, years; k – coefficients from formulas (8) and (9).

In a research resistance between layers, which results from a difference of coefficients of diffusion in one cut is also considered

$$C_{Cl,cb}(x, t) = \frac{2kC_S R}{k + 1} \sum_{n=0}^{\infty} a^n \operatorname{erfc} \times \left[\left(\frac{(2n + 1)x + k(x - X_c)}{2\sqrt{D_{Cl,cb} \cdot t}} \right) \right], \tag{12}$$

where R – resistance between layers.

$C(x, t)$ calculates taking into account action of carbonization how system from formulas (10) and (12).

A row of basis variables enters estimated model of combined action of carbonization and chloride aggression. Recommendations about mean values of these variables and their types of distribution are offered. For the southern part of Sakhalin Island in tab. 3 their mean values, a standard deviation and type of distribution are this.

Table 3

The concentration of chlorides for probable simulation

Parameter, unit-ism.	Southern part of Sakhalin Island		
	Distribution type	Average value	Standard deviation
$C_s, \%$	Const	2,5	–
x, mm	Const	Vector from a set {0–50}	–
$D_{ck,cb}^0, \text{m}^2/\text{s}$	Normal	$11,689 \cdot 10^{-12}$	$1,2 \cdot 10^{-12}$
$D_{cl,ucb}^0$	Normal	$2,387 \cdot 10^{-12}$	$1,2 \cdot 10^{-12}$
k_e	Normal	0,67	0,05
K	Normal	–	–
K	Const	273	–
k_t	Normal	0,80	0,05
k_c	Normal	1	0,125
t_0, year	Const	0,0767	–
t, year	Const	Vector from a set $\{t_0-50\}$	–
ncl	Beta	0,3	$a = 0; b = 1$
$C_{crit}, \%$	Normal	0,4	0,063

For the analytical solution of a direct problem of determination of probability of resource refusal and the return problem of definition of a percentage resource of structures imitating modeling with calculation of necessary functionalities, for example, of the content of chlorides at the set depth, service life, etc. is used.

For computer realization in the Matlab program the calculation code for model of penetration of chlorides taking into account effect of carbonization is written. Result of calculation of the program – probabilities of resource refusal of a structure and indexes of reliability during service life for various values of thickness of a concrete protective layer. At the first stage the program determines depths of carbonization and change of concentration of chlorides by depth (fig. 2–4).

The Probability refusal of construction and index of reliability are presented in fig. 5, 6 and tab. 4.

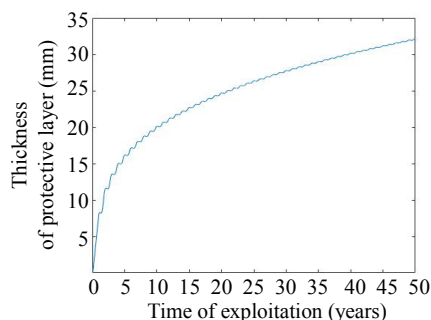


Fig. 2. Growth of depth of carbonization eventually

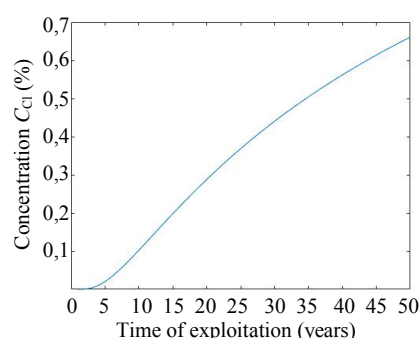


Fig. 3. Change of concentration of chlorides in a zone near reinforcement for all term of an exploitation

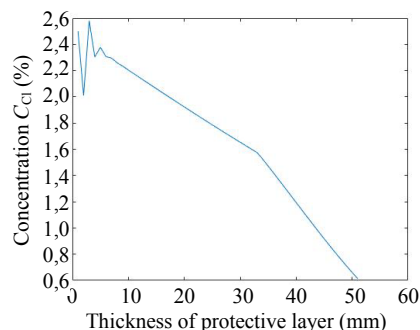


Fig. 4. Profile of concentration of chlorides in zone near reinforcement in the last year of exploitation (50 years)

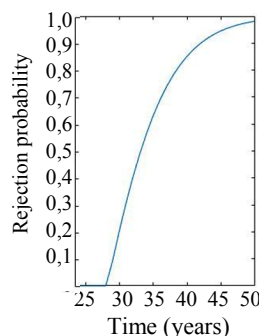


Fig. 5. Probability refusal of construction

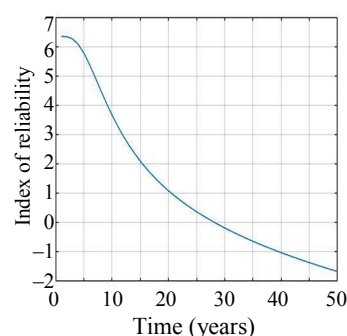


Fig. 6. Index of reliability of a construction

Table 4
Probability of refusal and the index of reliability of reinforced concrete constructions, depending on exploitation term for the southern site of Sakhalin Island

Operation term	Probability of refusal p_f	Index of reliability β
10	0,0001	3,688
20	0,005	1,102
30	0,190	-0,173
40	0,849	-1,020
50	0,981	-1,660

Results of natural researche

The executed natural researches: visual survey, determination of critical elements and areas, determination of strength and thickness of a concrete protective layer, the choice of test zones by results of measurements.

In test zones are carried out: visual survey for the choice of places of testing and sampling, check of concrete protective layer depth, the choice of places of sampling in "the worst places" of construction, determination of carbonization depth by phenol-phtalein test (6 and more places); selection of plates for chloride profiles (at least six plates in each test zone of the minimum size of 70×70 mm and minimum depth of 50 mm).

The laboratory is defined: by means of an ion-selective electrode value of concentration of chlo-

rides on depth of samples, phenol-phtalein test – carbonization depth.

Results of modeling of joint action of carbonization and chloride aggression and their comparison with experimental data (tab. 5).

The good convergence with probabilistic model and satisfactory with final and differential is received (the last doesn't consider "skin-effect"). The diffusion coefficient in final and differential model is constant at all depth of a protective layer, i. e. there is no breakdown on 2 layers with different diffusion and there is no resistance between these layers therefore concentration of chlorides in a zone near reinforcement it is overestimated. However, this model can be applicable for calculation of joint action of carbonization and chloride aggression with a small depth of carbonization when "skin-effect" doesn't exert considerable impact on concentration of chlorides in a zone near reinforcement.

Thus, with an insignificant depth of carbonization (up to 8 mm) calculation can be conducted on final and differential model, at considerable – values are overestimated and calculation should be conducted on probabilistic model. In practice with a depth of carbonization up to 8 mm the effect of joint action of carbonization and chloride aggression isn't considered, and the DuraCrete model is used. Thus, the most exact model – probabilistic.

Table 5

Comparison of computational and experimental results

Type	The place of selection of test	Age of a coonstruction	Depth of a protective layer, mm	The measured concentration of Cl, %	The measured concentration of Cl, %	Concentration of Cl, % on probabilistic model
Holmsk sea trade port						
X4	Reinforced concrete column of the bridge	33	10	2,24	2,80	2,20
			20	1,97	2,20	1,90
			30	1,64	1,81	1,62
			40	1,10	1,20	1,03
			50	0,51	0,58	0,49
X5	Reinforced concrete beam of the bridge	33	10	2,25	2,28	2,21
			20	1,98	2,21	1,94
			30	1,68	1,82	1,62
			40	1,10	1,20	1,03
			50	0,50	0,58	0,49
Korsakov sea trade port						
K4	The base under the sign SNO	44	10	2,32	2,76	2,13
			20	1,81	2,19	1,77
			30	1,46	1,77	1,44
			40	1,10	1,17	1,07
			50	0,55	0,63	0,53
K5	Reinforced concrete foundation under pipes.	46	10	2,32	2,79	2,15
			20	1,81	1,22	1,80
			30	1,48	1,81	1,50
			40	1,10	1,23	1,10
			50	0,55	0,65	0,55

Probabilistic model for determination of parameters for repair of a concrete protective layer

It is supposed that the irreversible consequences leading to chloride corrosion of fittings in carbonized concrete can begin already at concentration of ions of chloride of 0,2 %. Using this value as critical at which it is necessary to make repairs of a concrete protective layer, and also using model for the double environment formulas (10) and (12), the program of calculation of average time and depth of repair of the damaged protective layer which also allows to predict construction ser-

vice life, but already taking into account repair is developed (tab. 6, fig. 7). As material for repair the solution similar to initial composition of concrete is chosen. Probability of refusal and the index of reliability are represented in tab. 7 and fig. 8, 9.

After 50 years of operation in the most adverse region of Sakhalin Island under the terms of operation, the probability of refusal was $p_f = 58\%$. Thus, repair of a construction by the method of replacement of a carbonized layer new with similar characteristics increases strength. For example, in a construction, in which corrosion after 29 years of operation was initiated the modern times of initiation are 45 years.

Table 6

Service life of a reinforced concrete construction, taking into account repair of a concrete protective layer

Parameter, measuring	Place of operation, Southern part Sakhalin Island
Time of initiation of chloride corrosion without replacement of a carbonized layer, year	29
Design service life without replacement of a carbonized layer, year	33
Average time of replacement of a carbonized layer, year	16
Average depth of replacement of a carbonized layer, mm	24.5
Time of chloride corrosion initiation, taking into account replacement of a carbonized layer, year	45
Design service life, taking into account replacement of a carbonized layer, year	49

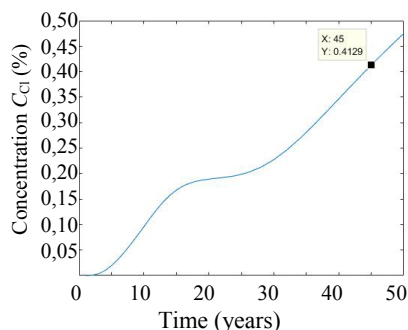


Fig. 7. Change of Concentration of Chlorides in zone near reinforcement for all term of an exploitation taking into account repair

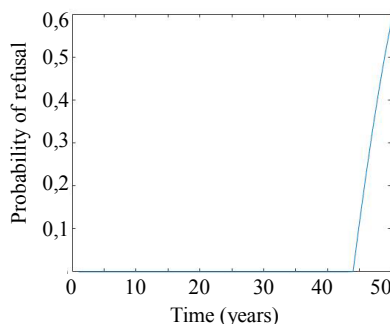


Fig. 8. Probability of refusal of the repaired construction

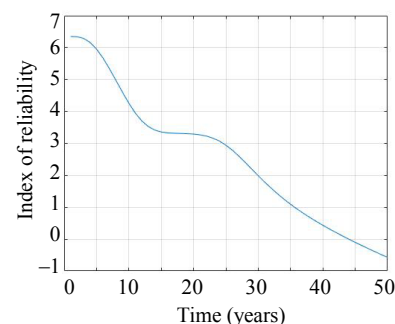


Fig. 9. The index of reliability of the repaired construction

Table 7

Probability of refusal and the index of reliability of the repaired reinforced concrete construction, depending on operation term for the most adverse region of Sakhalin Island under the terms of exploitation

Operation term	Probability of refusal p_f	Index of reliability β
10	0,0001	4,27
20	0,0008	3,29
30	0,0120	2,00
40	0,1090	0,44
50	0,5820	-0,57

CONCLUSIONS

1. On the basis of the analysis of models of joint action of carbonization and chloride aggression of a concrete protective layer and verification with experimental data the model for assessment of durability of sea reinforced concrete constructions considering the following factors is defined: thickness of a concrete protective layer; coefficients of diffusion of chlorides in carbonized and not carbonized concrete; critical content and superficial content of chlorides, superficial amount of CO_2 ,

their time of influence; sea conditions; front of carbonization, etc.

2. The technique of determination of repair term of a constructions and depth of concrete protective layer repair of constructions is developed.

3. The technique of forecasting of durability of reinforced concrete constructions at influence of the hostile marine environment, taking into account repair of a constructions is developed and with use of probabilistic model of calculation.

4. Verification of results of probability calculations of refusal of reinforced concrete elements for the offered probabilistic model is executed.

Recommendations about practical use of results

The developed models allow to count the carbonization depth, concentration of ions of chloride at the set depth, the term of exploitation of a construction, time of possible repair and depth of possible restoration of a concrete protective layer for a coastal and shelf zone of the Far East.

The developed technique of forecasting of durability of reinforced concrete constructions at joint impact of carbonization and chloride aggression with use of final and differential calculation model is offered to be used with a depth of carbonization up to 8 mm.

The developed technique of forecasting of durability of reinforced concrete constructions at joint impact of carbonization and chloride aggression with use of probabilistic model of calculation can be used:

- at assessment of operational suitability (safety) at inspection of reinforced concrete constructions of coastal and shelf constructions;
- when forecasting service life of again projected reinforced concrete designs;
- when calculating necessary thickness of a concrete protective layer of the projected reinforced concrete constructions at the set service life and service conditions;
- when calculating service life of concrete in specific conditions of exploitation;
- when forecasting term of repair of the operated constructions.

The received results can be used in design of new constructions and/or repair (reconstruction) of the existing constructions, operated in aggressive conditions of the marine environment and also in educational process.

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