



## Combined Effect of Carbonation and Chloride Aggression: Reliability and Safety of Reinforced Concrete Structures

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**Abstract:** Corrosion reinforcement marine hydraulic structures due to chloride aggression and carbonization of concrete leads to a sharp decrease in the safety of the structure. The steel reinforcement will be subjected to a so-called depassivation process, once the chloride concentration on surface exceeds a certain threshold concentration, or the pH value in the protective layer of concrete decreases to a threshold value due to carbonation. Electrochemical reactions begin to occur with the formation of corrosion products with the penetration of oxygen on the steel reinforcement surface. This leads to cracking of the protective layer of concrete. It should also be taken into account that, due to corrosion mechanisms, the cross-sectional area of the reinforcement also decreases. The article suggests a method for predicting the complex degradation of reinforced concrete structures, taking into account various mechanisms of corrosion wear, which will allow developing effective ways to improve the durability and maintainability of structures operated in the marine environment.

**Keywords:** structure, concrete, corrosion, carbonation, chloride aggression.

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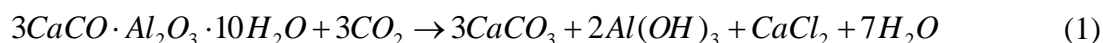
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**1. Review of researches.** Influence of the marine environment on intensity of corrosion demands additional researches since chloride aggression and carbonization of concrete considerably accelerate process of degradation [21]. The corrosion of fittings caused only by chloride is rather well studied and a number of models is available to modeling of this process. One models study the transport mechanism of ions of chloride from a surface of reinforced concrete elements others [4, 5-9] study influence of initial cracks in concrete [10-12] and influence of load of the transport mechanism of chlorides [18, 19].

In [16] numerical modeling of process of corrosion damage of concrete in which physical and electrochemical models are connected with mechanical model of formation of a crack was offered. Works on studying of joint factors of the environment are known: chloride aggression and carbonization [13-15]. It is noted that influence of carbonization on coefficient of diffusion of ions of chloride depends on types and proportions of mix of concrete. In [14-15] the variable test with chloride influence and carbonization where concentration of ions of chloride was maximum near the front of carbonization is described.

In spite of the fact that in the conditions of the marine environment at the same time there are a carbonization and chloride aggression, it should be noted that diffusion of ions of chloride goes much quicker, than carbonization process. Before carbonization concrete usually contains Friedel's

salt because of the chloride ion connected in concrete. When Friedel's salt reacts with carbon dioxide, ions of chloride are released in steam water [23]:



The released ions increase the concentration of free chloride much exceeding concentration of chloride ions which are transported from a surface on internal Wednesday. Therefore for the analysis and forecasting of the combined action of carbonization and penetration of chlorides it is necessary to model as carbonization interacts with chloride transfer without carbonization. Authors have offered complex model of the combined action of carbonization and chloride aggression which is compared to chloride transfer without carbonization and is checked experimentally.

**2. Carbonization model.** The effect of carbonization consists in reduction of alkalinity of the porous environment in concrete that allows to destroy a passive film on fittings and by that to initiate corrosion, leading to chips of a protective layer of concrete and decrease in durability. Thus, carbonization of concrete represents difficult physicochemical process. The differential equation of the first law of A. Fick is the cornerstone of the description of this process [4]:

$$J = -D \frac{dc}{dx} \quad (1)$$

If we consider carbonization as the steady continuous process described by this law, then the deterministic model of depth of passing of the front of carbonization for a construction, registers as follows [4]:

$$x_c(t) = \sqrt{\frac{2D(t)}{a} \int_1^t f_T(t) \cdot f_w(t) \cdot k \cdot C_{CO_2}(t) dt \cdot \left(\frac{t_0}{t}\right)^n} \quad (2)$$

where  $t$  – time of operation advanced in years;  $t_0 = 1$  year;  $n$  – age factor age factor;  $k$  – the coefficient considering the increased content of carbon dioxide in big cities;  $f_T(t)$  and  $f_w(t)$  functions of change of temperature and humidity in time respectively;  $C_{CO_2}(t)$  – concentration change function  $C_{CO_2}$  in time;  $D(t)$  – coefficient of diffusion of carbon dioxide in concrete, as function of time;  $a$  – quantity  $C_{CO_2}$  necessary for transformation of all capable to be carbonated hydration products, is determined by a formula [1]:

$$a = 0,75 \cdot CaO \cdot b \cdot a_H \cdot \frac{M_{CO_2}}{M_{CaO}} \quad (3)$$

where  $CaO$  – content of oxide of calcium in cement;  $b$  – amount of cement;  $M_{CO_2}$  – molar mass of carbon dioxide;  $M_{CaO}$  – molar mass of oxide of calcium;  $a_H$  – extent of hydration of cement.

On the offered model calculations of depth of carbonization of a protective layer of concrete of a reinforced concrete shelf construction remote from coastal line at distance of 10 m and flooded only in the period of storm are carried out. The design is operated in the south of the island of Sakhalin, is made of reinforced concrete. A class of B22,5 concrete with a consumption of cement of 350 kg/m<sup>3</sup> and the water knitting relation 0,4. The design term of operation of a design – 50 years.

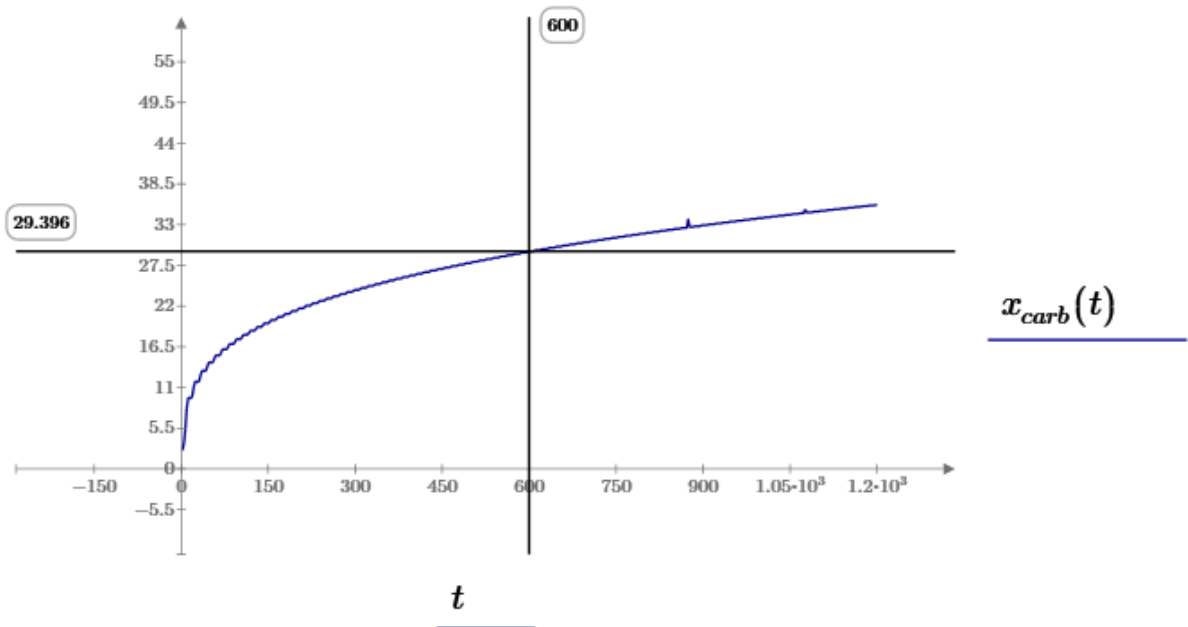
Basic data of model are given in table 1.

Table 1 – Basic data

Parameter	Value
Average temperature of the warmest month $T_{\max}$	17,7 °C
Average temperature of the coldest month $T_{\min}$	2,4 °C
Average humidity of the most damp month $W_{\max}$	0,85

Average humidity of the driest month $W_{\min}$	0,71
The water knitting relation w/b	0,4
Cement consumption b	350 кг/м <sup>3</sup>

The model (2) paid off in the Mathcad program. Results of modeling are given in fig. 1.



$T$  – time, month,  $x_{carb}(t)$  – carbonization depth

**Figure 1** – Schedule of change of depth of carbonization of concrete of a protective layer in time. From the schedule it is visible that in 50 years (600 months) of operation depth of carbonization of concrete will be 30 mm or 60%. Extent of carbonization in this case  $a_c=0,6$ .

**3. Model of diffusion of chlorides.** In a protective layer of concrete the equation of the second law of Fick is the cornerstone of the description of process of diffusion of chlorides [4]:

$$\frac{dc}{dx} = D \frac{d^2c}{dx^2} \quad (4)$$

When accounting of the connecting ability the equation of diffusion (4) takes a form [4]:

$$\frac{dC_f}{dt} = \frac{D_{cl}}{1 + \left( \frac{1}{w_e} \right) \cdot \left( \frac{\partial C_b}{\partial C_f} \right)} \frac{d^2C_f}{dx^2} \quad (5)$$

where  $C_f$  – concentration of free chlorides in concrete;  $C_b$  – concentration of the connected chlorides in concrete;  $D_{cl}$  – effective coefficient of diffusion of chlorides in concrete;  $w_e$  – free steam moisture;  $\frac{\partial C_b}{\partial C_f}$  – the connecting ability of concrete.

The connecting ability of not aerated concrete often is defined by an inclination of a binding isotherm. In this research the model of an isotherm Lengmyur is used [4]:

$$\frac{\partial C_b}{\partial C_f} = \frac{\alpha_L}{\left(1 + \beta_L \cdot \frac{C_f}{b}\right)^2} \quad (6)$$

The effective coefficient of diffusion of chlorides pays off as [23]:

$$D_{Cl} = D_{Cl,0} \cdot f_T(t) \cdot f_w(t) \cdot f_i(t) \quad (7)$$

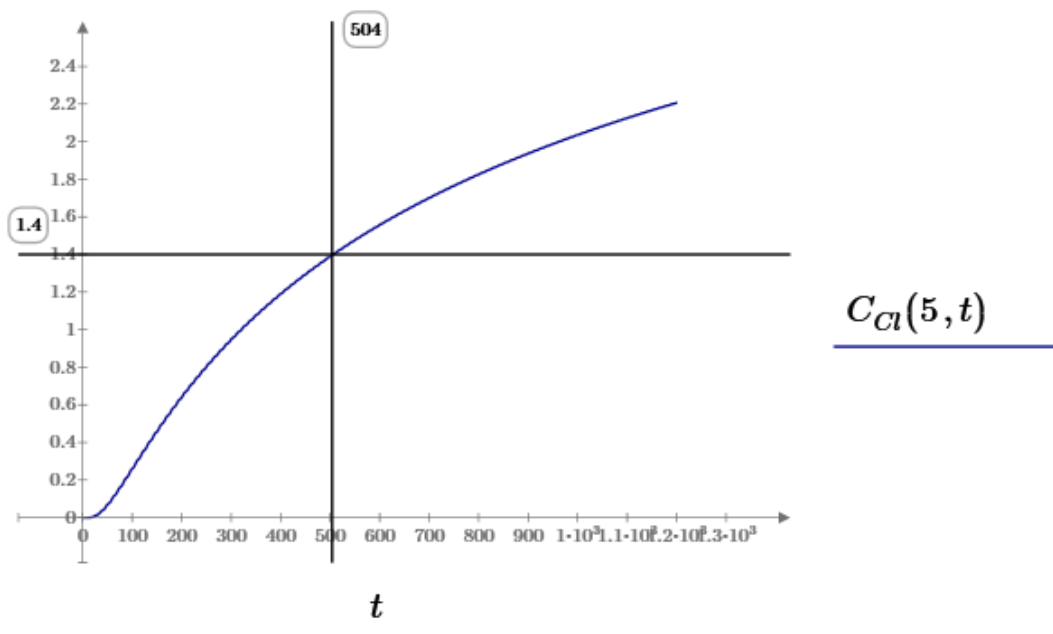
where  $f_T(t)$ ,  $f_w(t)$ ,  $f_i(t)$  – according to function of influence of temperature, humidity and time for diffusion coefficient;  $D_{Cl,0}$  – initial coefficient of diffusion of chlorides..

Substituting the equations (6) and (7) in the equation (5) defining the equation of diffusion it is modified as follows [4]:

$$\frac{d}{dt} C_{Cl} = \frac{D_{Cl,0} \cdot f_T(t) \cdot f_w(t) \cdot f_i(t)}{1 + \left(\frac{1}{w_e}\right) \cdot \left(\frac{\alpha_L}{\left(1 + \beta_L \cdot \frac{C_{Cl}}{b}\right)^2}\right)} \frac{d^2}{dx^2} C_{Cl} \quad (8)$$

On the offered model calculation of concentration of chlorides at a depth of a protective layer of concrete of a reinforced concrete shelf construction remote from coastal line at distance of 10 m and flooded only in the period of storm is carried out. The design is operated in the south of the island of Sakhalin, is made of reinforced concrete. A class of B22,5 concrete with a consumption of cement of 350 kg/m<sup>3</sup> and the water knitting relation 0,4. The design term of operation of a design – 50 years. Basic data are presented in table 1.

The model (8) also paid off in the Mathcad program (fig. 2)



$C_{Cl}(x;t)$ - concentration of ions of chloride at a depth of protective layer Of  $X$  see depending on time of  $t$ , kg/m<sup>3</sup>. Critical concentration of chlorides is accepted 0,4% or 1.4 kg/m<sup>3</sup> on the mass of knitting

**Figure 2** – The schedule of change of chlorides in time (months) without carbonization at a depth of protective layer of 5 cm

From the schedule in fig. 2 it is visible that the level of content of chlorides in a priarmaturny zone will reach critical concentration in 504 months of operation or about 42 years.

**3. Model of the combined impact of carbonization and chloride aggression.** It is supposed that the equation of transfer of ions of chloride after carbonization still corresponds to the second law of diffusion of Fick (5). The total of chloride in unit of volume of concrete consists of free chloride in steam solution and the connected chloride (Friedel's salt) [23]:

$$C_{Cl,card} = w_e C_{fc} + C_{bc} \quad (9)$$

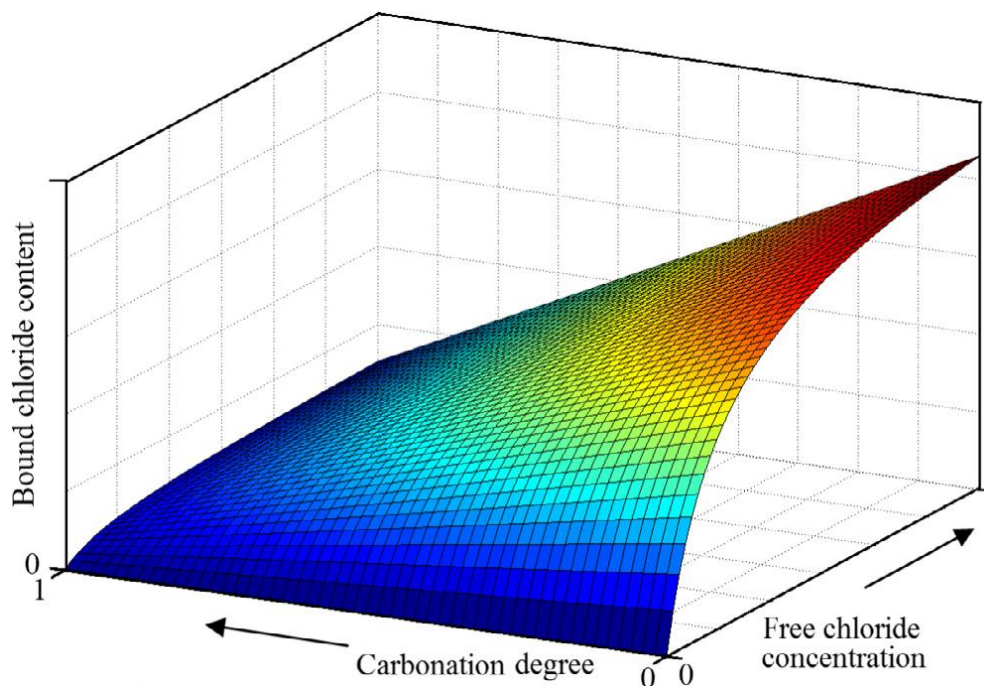
where  $C_{Cl,card}$  – the general concentration of chloride taking into account carbonization;  $C_{fc}$  – content of free chlorides in concrete;  $C_{bc}$  – content of coherent chlorides in concrete,  $w_e$  – steam moisture.

As in a concrete case interaction of concrete with the environment is followed not only by penetration of ions of chloride but also carbonization, the residual connecting ability of concrete after carbonization decreases.

On the basis of pilot studies [23], the amount of the connected chloride depends not only on concentration of free chloride in steam solution, but also on extent of carbonization, as shown in fig. 3 therefore it is offered to replace  $\alpha_L$  to  $\alpha_{Lc}$  for concrete after full carbonization [23]:

$$\alpha_{Lc} = \alpha_L (1 - d \cdot a_c) \quad (10)$$

where  $d$  – the coefficient of reduction of the connecting ability of ions of chloride due to carbonization accepted equal 0,88 on the basis of researches [23].



**Figure 3** – Change of content of the connected chloride depending on concentration of free chloride and extent of carbonization [23]

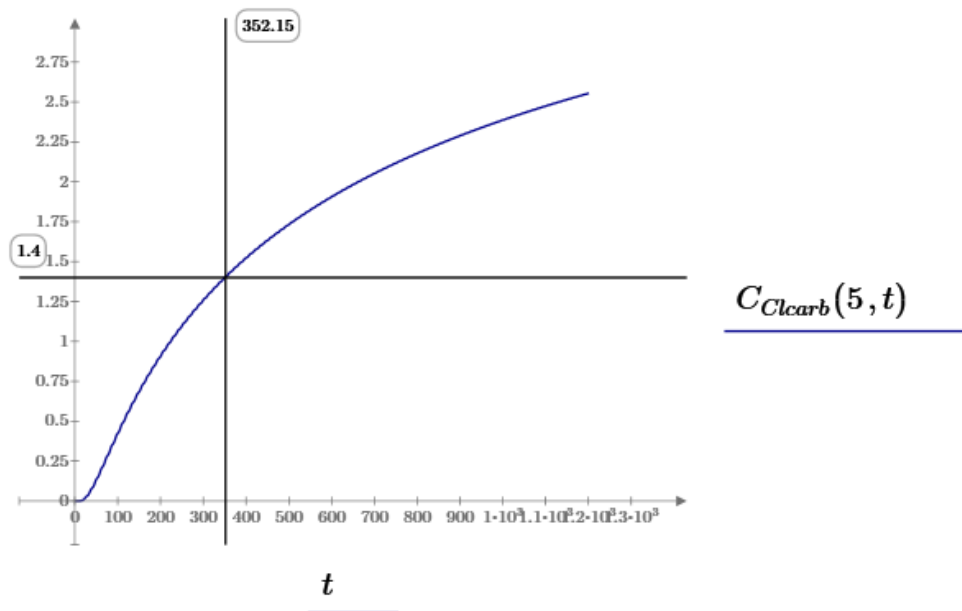
In view of the equation (10), the law Lengmyura (6) taking into account carbonization looks as follows:

$$\frac{\partial C_b}{\partial C_f} = \frac{\alpha_L(1-d \cdot a_c)}{\left(1 + \beta_L \frac{C_f}{b}\right)^2} \quad (11)$$

Then the defining equation of diffusion is modified as follows:

$$\frac{d}{dt} C_{Cl} = \frac{D_{Cl,0} \cdot f_T(t) \cdot f_w(t) \cdot f_i(t)}{1 + \left(\frac{1}{w_e}\right) \cdot \left(\frac{\alpha_L(1-d \cdot a_c)}{\left(1 + \beta_L \cdot \frac{C_{Cl}}{b}\right)^2}\right)} \frac{d^2}{dx^2} C_{Cl} \quad (12)$$

As well as in the previous case, by means of the Mathcad program for the offered model calculation of concentration of chlorides at a depth of a protective layer of concrete of a reinforced concrete shelf construction remote from coastal line at distance of 10 m and flooded only in the period of storm is carried out. The design is operated in the south of the island of Sakhalin, is made of reinforced concrete. A class of B22,5 concrete with a consumption of cement of 350 kg/m<sup>3</sup> and the water knitting relation 0,4. The design term of operation of a design – 50 years. Basic data are presented in table 1. Results of modeling are given in the figure 4.



*t* - time (months).  $C_{Clcarb}(x; t)$  - concentration of ions of chloride at a depth of protective layer of  $X$  see depending on time of  $t$ , kg/m<sup>3</sup>. Critical concentration of chlorides is accepted 0,4% or 1.4 kg/m<sup>3</sup> on the mass of knitting

**Figure 4** – The schedule of change of chlorides in time (months) with accounting of carbonization at a depth of protective layer of 5 cm

Apparently from the schedule on fig. 4, level of content of chlorides in a priarmaturny zone will reach critical concentration in 352 months of operation or approximately in 29 years that strikingly differs from a case without carbonization where critical concentration was reached in 42 years.

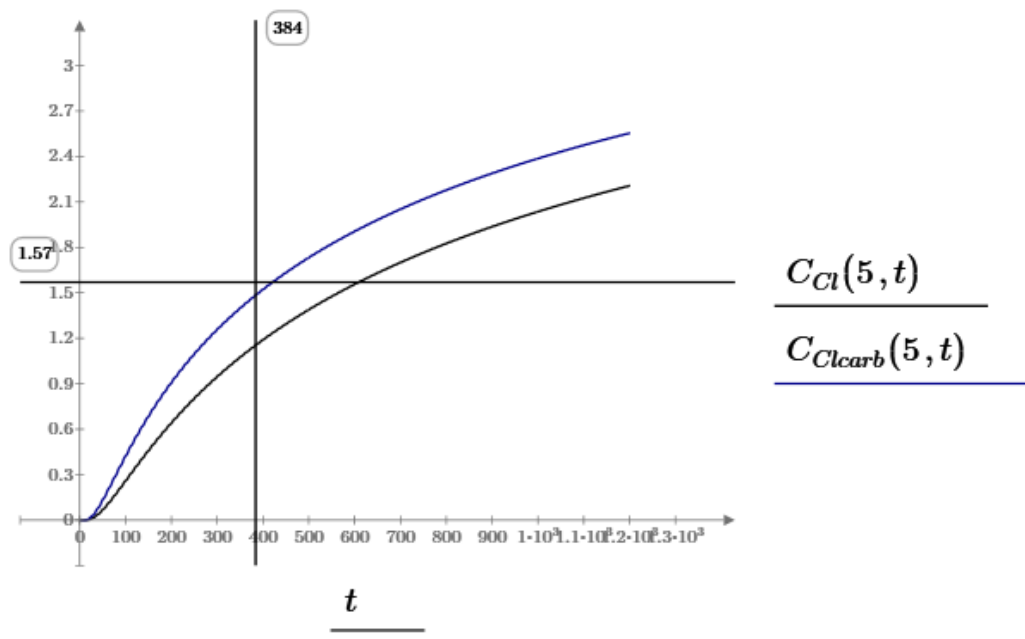
**4. Verification of model of joint action of carbonization and chloride aggression.** For assessment of results of model of joint action of carbonization and chloride aggression, in 2016 on-site investigation of port constructions in the south of the island of Sakhalin is conducted. The combined effect of chlorides and carbon dioxide was most well traced in a structure of the

pedestrian bridge of Holmsky sea trade port (fig. 5). On the basis of the passport of a construction the pedestrian bridge has been entered into operation in 1984 i.e. at the time of inspection the term of his operation was 32 years. The design settles down in 10 meters from coastal line, is in a zone of splashes and periodically floods during storm.



**Figure 5** – Flight of the pedestrian bridge of Holmsky sea trade port

Results of measurement of depth of carbonization, by fenolftaleinovoy test have shown that depth of carbonization is about 25 mm. Level of concentration of chlorides at a depth of a protective layer of concrete in this case was  $1,57 \text{ kg/m}^3$  on the mass of knitting.



$t$  - time (months) of.  $C_{Cl}(x; t)$  - concentration of ions of chloride at a depth of protective layer of  $X$  see depending on  $t$  time without carbonization,  $\text{kg/m}^3$ .  $C_{Clcarb}(x; t)$  - concentration of ions of chloride at a depth of protective layer of  $X$  see depending on  $t$  time for concrete in a consequence of the combined action of carbonization and chloride aggression,  $\text{kg/m}^3$ . Critical concentration of chlorides is accepted 0,4% or  $1.4 \text{ kg/m}^3$  on the mass of knitting

**Figure 6** – The schedule of comparison of change of chlorides in time (months) with account and without carbonization at a depth of protective layer of 5 cm

In the figure 6 comparison of results of modeling of change of chlorides in time taking into account and without carbonization with natural tests is shown. Apparently from the schedule, for a structure of the pedestrian bridge the curve of joint action is closest to operation term 384 months (or 32 years) that confirms adequacy to the offered model.

### Conclusion:

1. The analysis of the mechanism of corrosion destruction of shelf designs is made, the limit state for chemical reaction of chloride in a protective layer of concrete of shelf designs is formulated.
2. The model of degradation of a protective layer of concrete of coastal constructions from joint action of carbonization and chloride aggression is offered.
3. Verification of model on port constructions of Sakhalin Island is carried out. The executed field measurements of penetration of chlorides into concrete have shown that with a depth of 50 mm, in a zone of splashes, concentration of chlorides exceeds 0,4% of weight of cement (a corrosion threshold) at age of a design about 30 years.
4. Inspection in the port of Kholmsk has confirmed that locally, in certain cases, in a protective layer of concrete there are areas where simultaneous action and carbonizations and chloride aggression is observed. In these local areas the maximum concentration of chlorides is reached and there is a corrosion of fittings. Service life of the surveyed constructions didn't reach design service life.
5. Modeling of concentration of ions of chlorine in concrete of a protective layer according to the accepted models depending on service life, climatic conditions and depth of reinforcing, has allowed to compare the content of chloride at some depth when calculating taking into account and without joint impact of carbonization and chloride aggression.
6. Results of modeling well correspond to natural researches that will allow to develop further effective ways of increase in durability and maintainability of the designs operated in the marine environment.

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