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# Forecasting the Durability of Composite Materials Products under the Combined Action of Mechanical Loads and Chemically Aggressive Media

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**ABSTRACT**

Structures made of composite materials with a complex structure during operation are subjected to the combined effects of mechanical loads and aggressive media, which initiate the accumulation of damage in the material. As a result, premature destruction of structures, buildings, structures are possible. To prevent emergencies, it is necessary to be able to assess the resource of structures at any time. The article analyzes the previously proposed methodology of mathematical modeling of degradation processes, calculation and prediction of durability, resource structures, based on the application of the fundamental laws of mechanics of deformable solids and physico-chemical kinetics. The mechanisms of degradation of composites, methods of experimental determination of the main degradation parameters, conditions for calculating the durability of two groups of limit states are considered.

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Building materials and structures throughout the entire life cycle are exposed to the damaging effects of various aggressive environments. In accordance with the second law of thermodynamics, the process of degradation of a highly ordered structured system is irreversible and develops for the worse - from order to disorder [1]. In the case of uncontrolled accumulation of damage, this leads to premature onset of limit states. Therefore, in order to prevent emergency situations, it is necessary to be able to evaluate the resource of structures at any time. To date, this problem is nontrivial and has no analytical solution. The results of numerous studies confirm the complexity and nonlinearity of degradation processes, as a result of which the color, average density, structure, strength, chemical and elemental compositions of the material change [2-13].

The field of research into the problems of reliability and durability of building materials and structures has been especially relevant for the past few decades. This fact is confirmed by a large number of scientific papers on this topic, on the basis of which representatives of various scientific centers, institutes, international committees and associations (FIB, ISO) develop and annually improve the regulatory framework. Among the documents regulating the principles of designing the life cycle of structures, the main one is the ISO 16204:2012 standard introduced in 2012 "Durability. Calculation of the service life of concrete structures. It is designed to determine the durability of structures, as well as to assess their residual life [14-16].

However, despite the great work done in the area under study, there is still no unanimous decision on the widespread introduction into practice of designing computational models of the degradation of building structures during their operation in aggressive environments. Among the numerous approaches proposed by researchers in related fields, the most developed in assessing the durability of building materials and structures are methods based on: methods of probability theory [17,18]. analysis of changes in the elemental and chemical compositions of the material and filtrate [11,19]. application of calculation schemes of the classical theory of the resistance of materials and the laws of thermodynamics [20-22]. The most accurate, perfect and experimentally substantiated method is the method of estimating the chemical resistance of building materials and structures using degradation functions. Degradation functions describe the kinetics of the interaction of the product material with an aggressive environment and its effect on the stiffness and load-bearing capacity of the elements. This method was developed in detail in, where the authors carried out a deep analysis of various mathematical models [11, 23-26].

**Mathematical Models of Degradation**

Mathematical modeling of complex degradation processes is based on the analysis of experimental data: the distribution of microhardness within the cross-sectional area of the samples; changes in the strength of the composite of the outer contact layers; depth of structural damage. It is proposed, regardless of the type of energy, the nature of the destructive effect on the material of the structure, to distinguish three degradation mechanisms: heterogeneous; homogeneous; diffusion [27].

The degradation model is based on the analysis of experimental data: distribution of microhardness within the cross-sectional area changes in the strength of the material of the outer contact layers depth of structural damage.

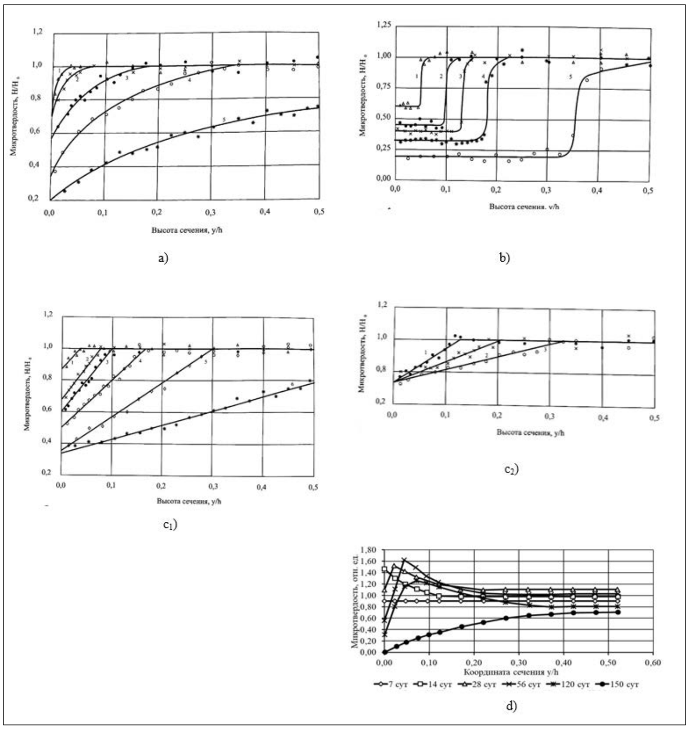


**Figure 1:** Change in microhardness along the height of the cross section of specimens from composites:
**a)** polyester in 10% $H_2SO_4$ solution
**b)** polyester in 20% NaOH solution
**c1)** polyester in water (exposure time per day: 1-15; 2-30; 3-45; 4-175; 5-265; 6-400.)
**c2)** polyester in water (exposure time per day: 1-65; 2-165; 3-260.)
**d)** cement in 2% $H_2SO_4$ solution

Figure 1 shows the experimental data on the distribution of microhardness along the height of the cross section of specimens made of polyester, epoxy, cement composites soaked in water and an aqueous solution of NaOH, $H_2SO_4$. The characteristic features for the graphs shown in Figure 1 are: the microhardness on the surface (in the contact zone) of the samples decreases rapidly during exposure; degradation isochrones can be linear, stepwise, non-linear; the coordinate of the front of violation of the structure of the material (depth indicator) depends on the duration of exposure [11].

Taking into account the experimental data, the degradation model can be represented by plots in the "y – E" coordinates, where y is the coordinate of the height of the sample cross section; E is the coordinate denoting the value of the physical characteristics of the material (microhardness, strength, deformation modulus) (Fig. 2).

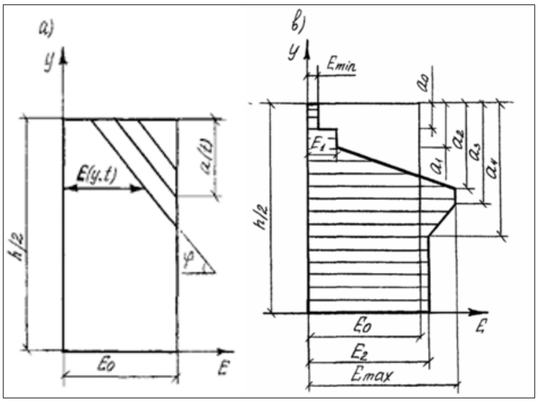


**Figure 2:** Experimental Degradation Models

In Figure 2, on the basis of experimental data, degradation models are built, the main characteristics of which are: depth indicator (a); property value in the contact zone - Emin; type and nature of the location of degradation isochrones - linear, non-linear (φ). If φ = 0, then we have a heterogeneous degradation mechanism; φ = 90 - homogeneous;
0 < φ < 90 – diffusion; φ = const is a linear model.
Each degradation mechanism corresponds to certain models and degradation functions, for example, stiffness F(W) or bearing capacity F(N). A relationship can be established between various degradation functions, which makes it possible to deal with only one function, the definition of which is most convenient [11]. In general, it can be represented by the expression:

$$F = B(t)/B(0) = f(t,T,\tau,\sigma,C,h,a,\beta), \quad (1)$$

where t is the current time; T is temperature; τ is the age of concrete; σ is stress; C is the concentration of the aggressive medium; h is a geometric characteristic; a - depth indicator; β is the index of chemical resistance; B(t),B(0) - one of the characteristics of the structural element - rigidity, bearing capacity at time t and $t_0$=0.

In some cases, the degradation function of stiffness is the basis. This function is characterized by the law of change in the deformation modulus over the section of the element, which can be linear (Fig. 3, a) or non-linear (Fig. 3, b).

For example, for a bending element with a rectangular shape (b x h) of the cross section, the stiffness degradation function can be determined by the formula:

$$F(W_u) = \iint E(t,y,x)y^2dxdy/\iint E(t_0,y,x)\,y^2dxdy\,, \quad (2)$$

For a linear model (Fig. 2) we can write:

$$= 1 - 4\left(\frac{a^2}{h^2}\right)\left[0{,}5\left(\frac{a^2}{h^2}\right) - \left(\frac{a}{h}\right) + 0{,}75\right]\left(\frac{E(t)}{E(t_0)}\right)/\left(1 - \frac{2a}{h}\right);\quad (3)$$

$$0 < \varphi < 90°\,,$$

where a(t) is the depth (kinetic) index; β=E(t)/E(t_0) is a kinetic characteristic that characterizes the rate of change in the properties of the contact layers (on the product surface).
E(t),E($t_0$) – deformation modules taking into account the duration t of the action of the medium, $t_0$=0.

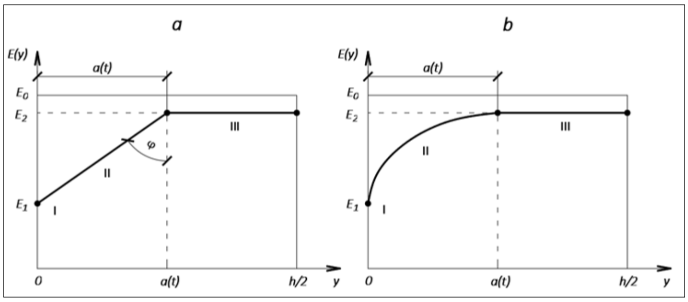


**Figure 3:** Idealized (phenomenological) models of element cross section degradation: a – linear, b – non-linear

Given the geometric and physical heterogeneity of the composite material, the degradation model can be represented in an idealized form (Fig. 3).

On the presented degradation models (Fig. 2, 3), three characteristic areas can be distinguished: I - zone (destruction) of direct contact of the material with the environment; II - the zone of simultaneous occurrence of mass transfer processes, chemical interaction, the release of neoplasms in the solid phase (latent degradation); III - zone not subject to corrosive effects of the environment (natural hardening).

Modern non-destructive methods for determining the elastic-strength characteristics of building materials make it possible to determine with high accuracy the numerical values of microhardness within the cross-sectional area of the sample, which are directly proportional to the values of the modulus of deformation. Consequently, the laws of their distribution over the cross section are identical, and the nature of the curves mainly depends on the structure of the material, the type of aggressive medium and the operating time. Such graphs are usually called degradation isochrones. The position of the degradation isochrones is characterized by three parameters: the coordinate of the destruction front is the depth indicator (a); linearity characteristic of the degradation mechanism - (φ) (Figure. 2, 3); β is the relative change in the mechanical properties of the material in the contact zone ($k_{xc}$) is the coefficient of chemical resistance.

**Static Model**

The static force model in general is based on the fundamental laws of the mechanics of a deformable solid body, which determine the relationship between: internal and external forces (L. Navier's equations); deformations and displacements (O. Cauchy's equations); stresses and strains (R. Hooke's law) [27].

To solve engineering problems, it is possible to use the method of limit states, according to which the calculation of bending elements for the first group of limit states consists in checking the strength of normal and inclined sections. Therefore, the mathematical model can be represented by a system of static (4, 5), geometric (6) and physical equations (7):

$$M(q,p,l,k,\gamma_i) \le M_{ult}\left(R_b, R_s, b, h, E_b, A_{s,}\gamma_i, \gamma_k, a, \beta\right); \quad (4)$$

$$Q(q,p,l,k,\gamma_i) \le Q_{ult}\left(R_{bt}, R_s, R_{sw}, b, h, E_b, A_{s,} A_{sw,}\gamma_i, \gamma_k, a, \beta\right); \quad (5)$$

$$\frac{1}{\rho}=\frac{\varepsilon}{y};\ \varepsilon=\varepsilon_e+\varepsilon_p+\varepsilon_{ep}; \quad (6)$$

$$\sigma(t)=\varepsilon(t,t_0)E_{\text{пр}}(\eta,t,t_0)\ \text{или}\ \sigma=E_b\varepsilon(\sigma_{bu},\varepsilon_{bu}) \quad (7)$$

where $\varepsilon_e$, $\varepsilon_p$, $\varepsilon_{ep}$ are relative elastic, plastic deformations of elastic consequences.

Designations in formulas (4-7) are adopted in accordance with the norms of SP 63.13330.2018 "SNiP 52-01-2003 Concrete and reinforced concrete structures. Basic Provisions".

In equations (4) and (5), on the right side of the inequality, the presented characteristics will change in time under the influence of an aggressive environment.

**Kinetic Model of the Interaction of Concrete with an Aggressive Environment**

A kinetic model that describes the process of interaction of a structural material with an aggressive environment is formed on the basis of the laws of physical chemistry by a system of kinetic equations:

- transfer and distribution over the volume of the product of a chemically active liquid (A. Fick's equations):

$$J=-D_m grad(\omega);\ \frac{\partial\omega}{\partial t}=D_m\frac{\partial^2\omega}{\partial x^2}; \quad (8)$$

- actions of the masses (K. Guldberg - P. Waage):

$$\frac{\partial\omega}{\partial t}=-k\omega_1^n\omega_2^m\omega_3^0; \quad (9)$$

- sorption (I. Langmuir):

$$\omega=\frac{\omega_0 t}{t_{0,5}+t}, \quad (10)$$

where J is the substance flow density; $D_m$ is the effective diffusion coefficient; ωi is the concentration of chemically active components in the material; $\omega_0$ – limiting sorption capacity at $t\to\infty$; $t_{0.5}$ is a characteristic of sorption kinetics.

**Determination of Degradation Model Parameters from experimental sorption curves**

From the solution of equations (8), knowing the limiting value of the sorption capacity or the constant t0.5, one can determine the diffusion coefficient D_m by the formulas:

$$D_m=\left[ln\frac{8}{\pi}-ln\frac{\omega_0-\omega(t)}{\omega_0}\right]\frac{4R^2}{\pi^2 t};\ D_m=k(\xi)\frac{R^2}{t_{0,5}}, \quad (11)$$

*R* – geometric characteristic of the sample.

Then the coordinate of the front (region boundaries) of degradation (depth indicator) can be determined by the formula:

$$a=k(\xi)\sqrt{D_m\,t}, \quad (12)$$

where $k(\xi)$ is a coefficient, the value of which depends on the instrumental accuracy of determining the value of a and in the first approximation is equal to 0.1.

Describing the process of degradation in strength, hardness by the Guldberg-Waage kinetic law, it can be argued that the rate of change in the number of operable bonds in the upper layers of the product material will be described by equation (9), from the solution of which, at $\omega=\omega_0$ (that is, in the contact zone, the concentration of the medium in material is close to the limiting sorption capacity), we obtain an equation for determining the coefficient of chemical resistance:

$$\beta = k_{x.c.} = \frac{C_b(t)}{C_b(0)} = \frac{R_b(t)}{R_b(0)} = \frac{H(t)}{H(0)} = \frac{E(t)}{E(0)} = exp\{-k\omega_0 t\}. \quad (13)$$

**Probabilistic Model**

Probabilistic approaches to the calculation of building structures have received a deep justification in the works of N S Streletsky, V V Bolotin, A R Rzhanitsyn, V P Chirkov, AP Kudzisa [10,28-33].

The development of probabilistic methods for calculating building structures, taking into account the action of aggressive media, is presented in the works of V P Chirkov, A P Kudzis, L M Puhonto, V P Selyaev, which the probability of destruction is considered taking into account the model of A.R. Rzhanitsyn [10,14,27-29,32,33]. It is assumed: all calculated ($q_i$) product parameters, loads, external influences are random and obey a normal distribution; the indestructibility function ($\Psi=M_u - M>0$) is a linear function of the calculated parameters and is represented by the difference between the forces perceived by the product, Mu, and those created by external influences, M.

If the distributions $M_u$ and M are normal, then Ψ will also obey the normal distribution law. Considering that $M_u$ and M are independent random variables, it is proposed to determine the center and variance of the function Ψ using the formulas:

$$\mathrm{M}(\Psi) = \bar{\mathrm{M}}_u - \bar{M};\ S^2(\Psi) = S^2(M_u) + S^2(M), \quad (14)$$

$M(\Psi), \bar{M}_u, \bar{M}$ – mathematical expectations, average values;

$S^2(\Psi), S^2(M_u), S^2(M)$ – dispersions of random variables.

Taking into account formulas (14), the indicator γ is introduced - the reliability index (according to Streletsky) or the safety characteristic (according to A.R. Rzhanitsyn), equal to:

$$\gamma = \frac{\bar{M}_u - \bar{M}}{\sqrt{S^2(M_u) + S^2(M)}}. \quad (15)$$

If we accept γ=3, then the reliability of the product will be P=0.9987.

The safety characteristic γ can be determined through the safety factor ξ according to the formula of the form:

$$\gamma = \frac{\xi - 1}{\sqrt{\mathrm{A}_R^2\xi^2 + \mathrm{A}_Q^2}}. \quad (16)$$

$$\xi = \bar{M}_u - \bar{M};\ \mathrm{A}_R^2 = S^2(M_u)/\bar{M}_u^2;\ \mathrm{A}_Q^2 = S^2(M)/\bar{M}^2.$$

The values $A_R$ and $A_Q$ are the variability of the values $M_u$ and M, equal to the ratio of the standard of the corresponding value to its center.

If the dependence of the function Ψ on the calculated parameters is not linear, then it can be linearized by expanding in a Taylor series in the vicinity of the center of the distribution of random variables and discarding the nonlinear terms of the expansion. This technique is called the method of statistical linearization.

So, function $\bar{M}_u = M(\bar{R}_s, \bar{R}_в, \bar{h}_0, \bar{a})$ can be expressed approximately as:

$$\tilde{M}\,(\tilde{R}_s, \tilde{R}_в, \tilde{h}_0, \tilde{a}) \approx M(\bar{R}_s, \bar{R}_в, \bar{h}_0) + \frac{\partial M}{\partial R_s} R_s, R_в, h_0, a)\,(\tilde{R}_s - \bar{R}_s) + $$
$$+ \frac{\partial M}{\partial R_в}(R_s, R_в, h_0, a)(\tilde{R}_в - \bar{R}_в) + \frac{\partial M}{\partial h_0}(R_s, R_в, h_0, a)(\tilde{h}_0 - \bar{h}_0) \times$$
$$\times \frac{\partial M}{\partial a}(R_s, R_в, h_0, a)\,(\tilde{a} - \bar{a}). \quad (17)$$

Denoting the derivatives by the ordinal number of the sum term $A_2$, $A_3$, $A_4$, $A_5$, we get:

$$\tilde{M} \approx M_0 + A_2(\tilde{R}_S - \bar{R}_S) + A_3(\tilde{R}_в - \bar{R}_в) + A_u(\tilde{h}_0 - \bar{h}_0) + A_5(\tilde{a} - \bar{a}). \quad (18)$$

Then we find the approximate values of the center and variance of the random variable $\tilde{M}$:

$$\tilde{\mathrm{M}} \approx M_0;\ S^2(M) \approx \mathrm{A}_2^2 S^2(R_3) + A_3^2 S^2(R_в) + A_4^2 S^2(h_0) + A_5^2 S^2(a). \quad (19)$$

We propose to determine the influence of an aggressive environment on a change in the reliability of a building structure by the method of degradation functions.

To do this, we write the reliability index taking into account the degradation of concrete in the following form:

$$\gamma = \frac{\bar{M}_u(t) - \bar{M}}{\sqrt{S^2(M_u) + S^2(M)}}, \quad (20)$$

$\bar{M}_u(t)$ bearing capacity of a reinforced concrete element, determined by the formula:

$$\bar{M}_u(t) = \bar{M}_u(0)D(t). \quad (21)$$

Consider a reinforced concrete bending element, which is operated in an environment that is aggressive towards concrete. Adopted single-span hinged beam of rectangular section (b=10 cm, h=25 cm, l= 6 m), made of class B25 concrete, reinforced 2Ø12 AIII ($A_s$= 226 mm2, a= 2 cm, $h_0$= 22.4 cm). A uniformly distributed load q is applied to the beam along the entire length.

Consider a linear degradation model according to the classification given in [27].

$\bar{\mathrm{M}}_u(0)$ – the bearing capacity of a bent element in terms of the strength of a normal section is determined by the formula:

$$M_u(0) = R_s A_s h_0 \left(1 - 0{,}5\frac{R_s}{R_в}\mu\right). \quad (22)$$

In the first approximation, D(t) has the form:

$$D(t) = 1 - \frac{0{,}5\frac{\delta}{h_0}(1 - k_{xc})}{1 - 0{,}5\frac{R_s}{R_в}\mu}. \quad (23)$$

Experimental and theoretical methods have established [27] that the change in the depth of penetration of an aggressive medium into concrete (depth indicator δ) is preferably determined by the formula of the form:

$$\delta = k(\xi)\sqrt{Dt}\,. \quad (24)$$

It is proposed [27] to determine the change in the strength of concrete of the outer layers in contact with an aggressive environment by the formula:

$$k_{xc} = exp\{-kt\}\,. \quad (25)$$

Then the change in time of the moment perceived by the cross section of the beam can be described by a function of the form:

$$M_u(t) = M_u(0)\cdot D(t) = R_s A_s h_0\left(1 - 0{,}5\frac{R_s}{R_в}\mu\right) - R_s A_s h_0 \times$$

$$\times\left[0{,}5\frac{k(\xi)\sqrt{Dt}}{h_0}(1 - exp\{-kt\})\right]. \quad (26)$$

In the above formulas, random variables are $\bar{R}_S$ – ultimate strength of reinforcement; $R_в$ – ultimate strength of concrete; $\bar{h}\,0$ – is the height of the cross section of the beam; $\bar{q}$ uniformly distributed load; $k_{xc}$ – is the coefficient of chemical resistance; $\delta$ depth indicator.

Let's define partial derivatives:

$$\frac{\partial M_u}{\partial R_S} = A_1; \frac{\partial M_u}{\partial A_S} = A_2; \frac{\partial M_u}{\partial h_0} = A_3; \frac{\partial M_u}{\partial \delta} = A_4; \frac{\partial M_u}{\partial k_{xc}} = A_5; \frac{\partial M_u}{\partial q} = A_6\,. \quad (27)$$

Then the approximate values of the center (mathematical

expectation) $\bar{M}_u$ and dispersion $S^2$ ($M_u$) determined by the formulas:

$$\bar{M}_u = \bar{M}_u(0)D(t)\,; \quad (28)$$

$$S^2(M_u) = A_1^2 S^2(R_s) + A_2^2 S^2(A_s) + A_3^2 S^2(h_0) +$$

$$A_4^2 S^2(\delta) + A_5^2 S^2(k_{xc})\,; \quad (29)$$

$$\bar{M} = \bar{q}\frac{\bar{\ell}^2}{8};\ S^2(M) = A_6^2 S^2(M)\,. \quad (30)$$

Substituting the obtained values into formula (20), we find the reliability index γ.
The graph of the change in time of the index γ is shown in Figure 4.

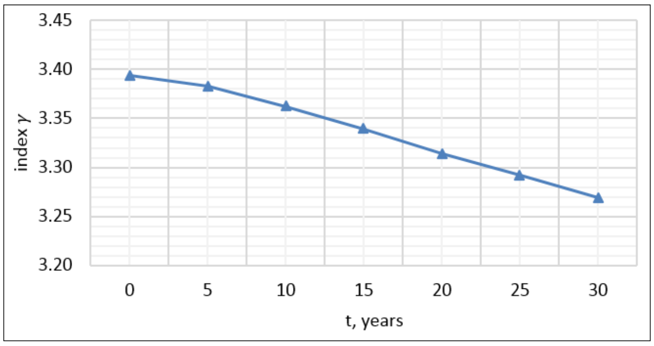


**Figure 4:** Change of reliability index γ over time

If we take the index γ=3.25 as the limiting value, then it can be argued that after 30 years of operation, the structure must be examined and solutions should be proposed to restore (increase) its bearing capacity.

## Conclusions

Analyzing the experimental data [11,13]. It can be argued that the process of interaction of an aggressive environment with the product material can be described using mathematical models, the main degradation parameters of which will be: depth index - a; chemical resistance coefficient - $k_{(h.s.)}$ ; chemical resistance of reinforcement - $A_s$ (t), $A_{sw}$ (t); sorption capacity - $\omega_0$; effective conductivity coefficient - $D_m$; taking into account the theory of degradation, the durability of the product can be determined by probabilistic methods from the conditions of limit states in terms of bearing capacity and deformability, which for a bending element (beam) can be written as:

$$M_q \le M_{ult}\cdot D(N)\,; f_q \le f_{ult}\cdot D(W)\,, \quad (31)$$

where M_q is the moment from the external load; M_ult is the limiting moment perceived by the bending element at the initial moment of time (duration of the action of the medium t=0); f_q - deflection from external load; f_ult - maximum allowable deflection; D(N) and D(W) are the degradation functions of the bearing capacity and cross-section stiffness, respectively.

The results of experimental studies confirm the adequacy of the obtained solutions.

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