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SULFATE CORROSION OF CONCRETE CAUSED BY THIONIC BACTERIA

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The article deals with conditions for the occurrence of sulfate corrosion of concrete. It is noted that thionic bacteria, changing pH of the medium at the expense of formed sulfuric acid, are active corrosion agents. The activity of thionic bacteria leads to concrete corrosion of the second and the third type. It is shown that the intensity of biocorrosion destruction is determined by the rate of chemical reactions and microorganisms and internal diffusion of metabolic products in the concrete structure is determined by the rate of chemical reactions and internal diffusion microorganisms and products of their metabolism in the concrete structure. The article presents modern methods of protection from sulfate corrosion.

Concrete is the most common building material for the manufacture of structural elements of buildings and structures. Concrete and cement stone in environments is exposed to corrosive influences of various aggressive environments. One of the factors influencing the development and intensity of corrosion processes are microorganisms such as bacteria, fungi, algae, lichens and mosses. The products of microorganisms are organic and inorganic acids, sulfates, ammonia and other compounds which cause the destruction of concrete and the reinforcement in concrete structures. The degree of activity of the microorganisms causing corrosion of concrete depends on the temperature, humidity, pH, redox potential of the medium [1].

Biodegradation of concrete, mainly reduced to the violation of the clutch of cement stone and aggregate as a result of exposure to mineral or organic acids of microbial origin. The destruction of concrete structures is due to chemical reactions between cement stone and products of microorganisms. The most dangerous areas on the surface of concrete structures are cracks. Colonization of cracks leads to the penetration of microorganisms and their metabolic products in the mechanical damage increasing the internal pressure in the material.

According to conventional classification, corrosive effects of corrosive media on the concrete are divided into three main types:

- The first type includes corrosion processes occurring in the concrete when exposed to water with a low hardness when the components of the cement paste dissolve moving washed and entrained aqueous medium;

 Corrosion of the second type includes processes that develop in the concrete when exposed to liquids containing chemical substances that come into exchange reactions with components of the cement paste to form easily water-soluble or amorphous products, non-binding capacity of the masses in the zone reaction;

- Corrosion of the third type includes all processes of concrete corrosion by the activity of liquid corrosive media, the development of which in the pores, capillaries and other concrete voids is an accumulation of poorly soluble salts, the crystallization of which gives rise to considerable effort in the walls of the cement stone structure, limiting the growth of crystal formations.

One of the varieties of the third type is the corrosion of concrete in sulfate environments. Corrosion of concrete due to the activity of sulfates depends on the mineralogical composition of cement used and on the density and structure of concrete. Water containing more than 5000 mg / L of sulfates is aggressive even in relation to particularly dense concrete, a preparation of sulfate-resisting Portland cement [2]. It is also noted [3] that the concrete on the corrosion rate in sulfuric acid has a greater influence aggregate form, compared with cement views. Weight loss in the samples produced on calcareous aggregate was 4 times less than in the samples of quartzite aggregate. The layer of concrete destroyed disappeared much more slowly than the cement concrete stone grains of coarse aggregate of carbonate rocks, concerning the fracture surface of the concrete.

Thionic bacteria are active corrosion agents, forming a sulfate environment on the surface of concrete structures. Possessing a potent enzymatic apparatus of thionic bacteria by its oxidative activity can compete with chemical oxidation of metal sulfides, elemental sulfur, ferrous sulfate. The sulfuric acid microbiological aggression caused by thionic bacteria is the main cause of corrosion damage to the reinforced concrete drainage pipes, in addition to chemical corrosion processes [4].

The authors of [5] that thionic bacteria begin to develop at pH values of the surrounding environment below 8. The ageing of concrete and the interaction with the environment is a gradual acidification to the pH at which they are populated by bacteria. First, *Thiobacillusthioparus* start to develop which form elemental sulfur and reduce the pH to 5.0, followed by *Thiobacillusthiooxidans* already oxidized sulfur to sulfuric acid, the pH of the aqueous medium may be reduced to 2 or below. The relationship between pH and the number of bacteria in the acidification of the medium is linear. Exposure to microbiological and chemical factors leads to the destruction of concrete. Microscopic examination [5] sample surface of building materials exposed to corrosive changes

Architecture and Civil Engineering

showed that the cement structure is completely destroyed at the surface and burst sand. These results are also confirmed by X-ray phase analysis.

The mechanism of the activity of microorganisms on the concrete, according to B.Isachenko [6], can be represented as follows. When repairing, concrete is covered with a protective film formed by calcium carbonate $CaCO_3$. As long as the film is intact, it prevents the diffusion of water into the concrete masonry and protects concrete from destruction. Thionic bacteria settles on the surface of the carbonate layer, destroys it by changing the pH of water surrounding them which was formed by acids. In addition, thionic bacteria hamper the production of sulfate.

Sodium sulfate Na₂SO₄ initially reacts with Ca(OH)₂ according to the following scheme:

$$Ca(OH)_2 + Na_2SO_4 = CaSO_4 + 2NaOH$$
,

and then $CaSO_4$ – with mineral C_3A . $CaSO_4$ calcium sulfate reacts immediately with mineral C_3A under the scheme:

 $3CaO \cdot Al_2O_3 \cdot 6H_2O + CaSO_4 + (25-26)H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot (31-32)H_2O.$

Calcium sulfate has a higher solubility product than the starting material, and is leached from the concrete (corrosion of the second type). Crystalline three sulfate hydroaluminate (ettringite) due to the difference in coefficients of expansion (volume 2.8 times greater than the volume of the starting materials) causes cracking (the third type of corrosion).

It is known [7] that the reaction of calcium silicate and calcium hydroxide in the presence of carbonate ions results in the formation of thaumasite (calcium hydrated calcium sulfokarbosilicate). Crystal formation requires thaumasite sources – calcium silicates, sulfates, and carbonates. The source of calcium silicate is cement stone and sulfates – thionic bacteria carbonates contained in the lime constituents of cement stone, large or fine aggregate [8].

Thus, in microbiological effects thionic bacteria on concrete structures there is a significant removal of surface oxide and calcium relative accumulation of oxides of silicon, aluminum, potassium, sodium and sulfur.

The intensity of corrosion damage in the biodegradation proceeds similarly to the degradation of chemically aggressive media and is determined by the rate of chemical reactions on the surface of the material, internal diffusion of the microorganisms and their metabolic products in the structure of the material and the passage with chemical reactions.

Depending on the ratio of diffusion the rates of chemical interaction and failure occur in one of three areas [9]:

- external diffusion-kinetic, when the diffusion rate of the medium speed less than degradation and destruction of the material occurs in the surface layer (heterogeneous degradation);

- internal kinetic, when the diffusion rate of the medium exceeds the velocity of chemical reactions and the destruction of the entire volume of material is exposed (homogeneous degradation);

- internal diffusion-kinetic, when the chemical reaction rate commensurate with the rate of diffusion of destructive processes and accumulate over time (diffusion degradation).

The depth of concrete damage by chemical corrosion can be defined by the formula

$$a = K\sqrt{\tau} . \tag{1}$$

Where a - is the depth of corrosion;

 τ – is the exposure of the material in a hostile environment;

K – is coefficient of aggressiveness

Aggression factor is the determining criterion for assessing the chemical resistance of concrete and represents the ratio of the strength of concrete after exposure to aggressive environments (R_{τ}) or to original strength (R_0) [10]:

$$K = R_{\tau} / R_0. \tag{2}$$

When biocorrosion of normal kinematic equations of chemical corrosion is added to the equation of bacterial biomass, depending on the range of environmental conditions, it ensures the functioning of this type of microorganisms.

According to GOST 25881 [10], biochemical resistance of concrete is projected on the basis of the specific conditions of their operation in time for economically viable life of the structure (τ , the number of years),

Architecture and Civil Engineering

and it is assumed that under the influence of aggressive environment during this term allowable strength of reduction should correspond to the value for S. received the life of the chemical resistance of concrete products and structures It shall be provided on condition that:

$$K \ge 1 - C, \tag{3}$$

To determine the chemical stability of the coefficient K for the life of the adopted (with $\tau \ge 30$ days) use the relationship:

$$\lg K = a + b \cdot \lg \tau \,, \tag{4}$$

where $\lg K$, $\lg \tau - \log a$ ithm of the chemical resistance and received lifetime;

a and b – constant for a given type of concrete and the coefficients of the medium

Evaluation of resistance of concrete according to the following criteria: K > 0.8 – highly resistant; 0.5 < K < 0.8 – resistant; 0.3 < K < 0.5 – a relatively stable; $K \le 0.3$ – unstable [9].

Modern methods of protection from sulfate corrosion are [3]:

- Use of modern complex additives on the basis of dispersed silica and efficient water-reducing additives that reduce the permeability of the diffusion of concrete by 1–2 orders of magnitude;

- The suppression of life thionic bacteria through the use of biocide additives;

- Treatment by compositions of Ksaypeks, Penetron and Kalmatron that penetrate into the concrete and cause the pores and capillaries of the crystal growth, creating he so-called "crystallization barrier" that reduces the permeability of concrete;

- application of protective coatings made of polyethylene: smooth plastic film, polyethylene ribbed sheet, reinforced bearing precast concrete structures from total sectional elements with factory corrosion-resistant ribbed polyethylene coating.

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