Forecasting the durability of reinforced concrete under conditions of microbiological corrosion

Konstantin Strokin[1], *Denis* Novikov[1], and *Viktoriya* Konovalova[2*[0000-0003-4088-8318]]

[1]Sakhalin State University, 693000 Yuzhno-Sakhalinsk, Russia
[2]Ivanovo State Polytechnic University, 153000 Ivanovo, Russia

Abstract. The article presents data on the study of the kinetics of liquid corrosion of cement concrete infected with microorganisms Bacillus subtilis and Aspergillus niger. The equilibrium concentrations of calcium cations during fungal and bacterial corrosion of cement concrete in an aqueous medium are established. According to the profiles of calcium hydroxide concentrations in the thickness of cement concrete during fungal and bacterial corrosion, it was found that during fungal corrosion of concrete, the intensity of interaction of calcium hydroxide with the products of the vital activity of microorganisms is higher than during bacterial corrosion. In case of fungal corrosion under conditions of Aspergillus niger infection, citric acid has the greatest impact on concrete since its amount in the products of the vital activity of microorganisms is maximum. Profiles of concentrations of aggressive substances by the thickness of the concrete sample show that bacterial corrosion proceeds more slowly than fungal corrosion and allow us to calculate the time to reach the maximum concentration of aggressive substances at the surface of steel reinforcement in concrete. Corrosion of reinforcement in concrete with fungal corrosion will begin in 2.5 years after infection, with bacterial corrosion after 5.5 years.
Keywords. Liquid corrosion, concrete corrosion, microbially induced, corrosion, fungal corrosion, bacterial corrosion, durability of reinforced concrete.

1 Introduction

The rate of concrete damage in structures depends on the type of aggressive environment affecting the concrete. Aggressive substances from the environment enter the concrete components and react with them.

Microorganisms grow mainly attached to the surfaces of solid materials. Localized biofilms (microcolonies) can have a serious harmful effect on materials [1].

The growth of microorganisms is influenced and sometimes limited by several chemical and physical factors [2]. Water is a necessary condition for the life and growth of microorganisms. Microorganisms vary significantly in the amount of water needed [3]. In particular, fungi are able to live in extremely dry conditions. Lichens, due to the symbiosis of a photosynthetic partner (algae or cyanobacteria) with fungi, may resemble fungi in their need for water. All other microorganisms are extremely sensitive to water scarcity. In porous

*Corresponding author: kotprotiv@yandex.ru

systems, such as soil or concrete, water activity is reduced due to capillary bonds in pores of small diameter (less than 10 microns) [4].

Another important factor is the concentration of hydrogen ions. Microorganisms can be distinguished by their ability to grow in acidic, neutral, or alkaline conditions. Therefore, they are called acidophiles, neutrophils, or alkalophiles [5]. The bacterium A thiooxidans was found in samples with a negative pH value, whereas in soda lakes life was found at pH values of 12 and higher. Fungi can grow in a large range of pH values. Moldy fungi were found at pH values from 2 to 12. Most microorganisms, however, develop in the neutral pH range from 6 to 8 [6, 7].

During the vital activity of microorganisms, carbon dioxide is released as the final product of metabolism. It reacts with water to form carbon dioxide, which can be dissolved, for example, in carbonates, forming soluble bicarbonates. In this way, the concrete binder, lime, can be dissolved [8, 9].

In the process of their metabolism, microorganisms secrete organic acids, such as oxalic, citric, malic, lactic or acetic acids, amino acids, uronic acids, etc. [10, 11]. Organic acids are usually available temporarily. However, their presence could cause transformations in the crystal lattice of the exposed material [12-15]. Organic acids can be released by almost all bacteria, cyanobacteria, algae, lichens, and fungi.

Biogenic reactions occurring under the influence of microorganisms lead to the formation and the accumulation (except for the aquatic environment) of salts as reaction products. Since the salts are hydrophilic, they are usually hydrated, which leads to an increase in the water content of the porous material [16]. In addition, salt crystals may form during drying, causing the surface removal of layers of material [17]. Another harmful effect of salts is associated with the formation of large crystals that cause swelling [18, 19]. A well-known example is the formation of ettringite from gypsum crystals that destroy concrete and brick.

Microbiological corrosion is a widespread phenomenon, but the involvement of microorganisms and their significance are not fully understood. The physical and chemical transformations occurring in concrete under the influence of microorganisms are complex, they can be modified and slowed down, but they cannot be completely suppressed [20-22]. A thorough knowledge of all the processes involved will significantly increase the service life of the materials.

2 Materials and methods

The study of corrosion resistance was carried out on samples of concrete made of Portland cement of the CEM I 42.5N brand with a water-cement ratio W/C = 0.3. Samples of a cubic shape with an edge length of 3 cm were made up of tightly fitted plates with a size of 1×3×3 cm. The side faces of the plates, as well as the end face of the lower plate, were covered with a layer of cold-cured bitumen-polymer mastic to isolate them from the aggressive environment. Thus, only one face of the sample was in contact with the liquid medium. The tests were carried out on samples after gaining strength for 28 days in air with a relative humidity of 65-70 % at a temperature of 20±2 °C.

Samples were infected with suspensions of microorganisms Aspergillus niger van Tieghem to study fungal corrosion of concrete and Bacillus subtilis to study bacterial corrosion of concrete. Medium for transferring the bacterial strain: meat water – 1000 ml (500 g of skimmed minced meat pour 1000 ml of tap water, extract at 37-39 °C for 2 hours, squeeze through cheesecloth, then boil for 30 minutes, filter through cotton wool and bring the volume to 1000 ml); NaCl – 5.0 g/l; pepton – 10.0 g/l; agar (if necessary) – 20.0 g/l; pH = 6.8-7.0. Sterilization at a pressure of 1 atm for 30 minutes. Optimal growth temperature: 30-37 °C. Medium for transferring strains of micromycetes (fungi): malt extract – 30.0 g/l, peptone – 1.0 g/l, agar – 20.0 g/l, distilled water – 1000 ml. A suspension of spores in distilled

water is prepared immediately before testing. Before conducting the experiment, the culture medium is sterilized with saturated steam under pressure. The surface of the samples is infected with an aqueous suspension of spores of microorganisms by uniform spraying or applying drops, preventing their fusion. Infected samples are dried in a box at a temperature of 25 °C and a relative humidity of 70 to 90 % until the drops dry, but not more than 60 minutes. Petri dishes with samples infected with spores of microorganisms will be placed in a desiccator, at the bottom of which distilled water is poured to create a high humidity of the air environment necessary for the development of microorganisms. The tests are carried out at a temperature of (29±2) °C and a relative humidity of more than 90 %. The duration of the tests is 28 days. Every 7 days the caps of the desiccators are opened for 3 minutes for air access. Control Petri dishes are examined after 5 days. If the growth of microorganisms is not observed on the nutrient medium, then they are considered non-viable.

The samples were placed in vessels with an aqueous medium with a volume of 1000 cm^3, from which samples of the solution with a volume of 10 cm^3 were taken at intervals of 14 days. Distilled water (pH = 6.6) was used as the reaction medium for studying the process of microbiological corrosion. The content of calcium cations in the analyte was determined by complexometric volumetric titration with trilon B in the presence of a black chromogen indicator.

Determination of the calcium content in the sample was carried out using the derivatograms obtained by analyzing crushed cement stone samples on the derivatograph. For the derivatographic analysis, the sample was disassembled into plates, and a piece was extracted from the center of each plate for grinding.

Determination of the composition of corrosion products after exposure to concrete fungi Aspergillus niger van Tieghem and bacteria Bacillus subtilis was carried out on a chromatograph. To do this, scraping was performed from the surface of the samples.

3 Results

During the experiment, it was found that the state close to the equilibrium concentration of calcium cations in solutions with samples infected with Bacillus subtilis and Aspergillus niger is reached after 80 days of the sample's stay in a corrosive environment, whereas for non-infected samples, the equilibrium state occurs after 70 days [23]. However, the equilibrium value of the concentration of Ca^{2+} ions in solutions differ greatly. In an aqueous environment with uninfected concrete samples, the change in the concentration of Ca^{2+} ions stopped when the value reached 22 mg/l, for samples infected with Bacillus subtilis, this value was 28 mg/l, and for samples infected with Aspergillus niger it was 33 mg/l, which is 1.5 times more than with uninfected concrete.

The results of the derivatographic analysis of cement stone samples after exposure to the water environment and microorganisms for 70 days are presented in Table 1.

The result of the analysis of the experimental data was to obtain the values of the concentrations of "free" calcium hydroxide over the thickness of the concrete sample at different points in time. Based on the numerical values obtained by differential thermal analysis, concentration profiles are constructed (Fig. 1) for cement stone samples exposed to the aquatic environment and microorganisms.

Corrosion products from the surface of cement samples infected with Bacillus subtilis and Aspergillus niger were studied by gas-liquid chromatography. As a result of the vital activity of fungal microorganisms, organic acids accumulate on the concrete surface : citric acid (57.5 wt. %), oxalic acid (27 wt. %), dairy (8 wt. %), apple (6 wt. %), wine (1.5 wt. %).

Based on the obtained profiles of calcium ion concentrations, the concentration profiles of citric acid (Fig. 2) and carbonate ions (Fig. 3) were calculated for the thickness of concrete samples in the case of fungal and bacterial corrosion.

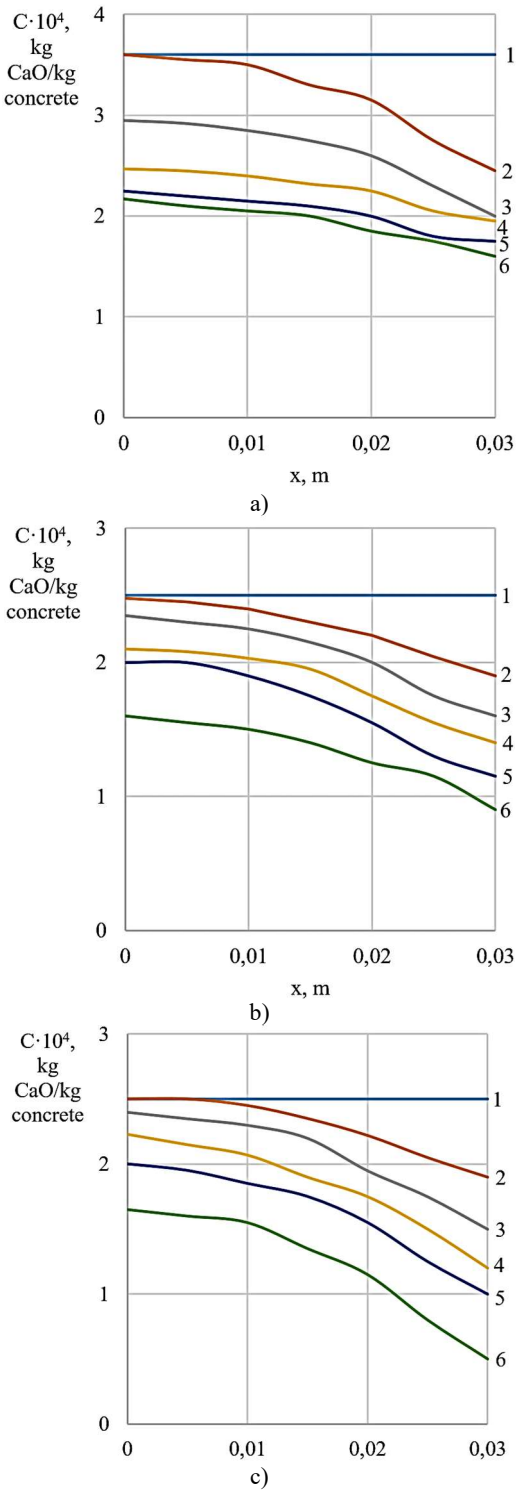

Fig. 1. Profiles of $Ca(OH)_2$ concentrations by the thickness of the cement stone sample at different time intervals (at τ : 1 – 0 days ; 2 – 14 days ; 3 – 28 days ; 4 – 42 days ; 5 – 56 days ; 6 – 70 days) : a) for corrosion in water ; b) for bacterial corrosion ; c) for fungal corrosion.

Table 1. Changes in the mass and energy of cement stone samples.

t, °C	The nature of the effect	The process that causes the effect	Change in mass before exposure, %	Change in mass after exposure, %
After exposure to water and bacteria Bacillus subtilis				
100-130	Endothermic	Removing physically bound water	6.2	7.7
430-480	Endothermic	Dehydration of calcium hydroxide $Ca(OH)_2 \rightarrow CaO + H_2O$	1.8	0.9
550-650	Endothermic	Polymorphic transformations of quartz $\alpha\text{-}SiO_2 \rightarrow \beta\text{-}SiO_2$	7.9	5.0
780-815	Endothermic	Decarbonization $CaCO_3 \rightarrow CaO + CO_2$	4.4	3.2
Total mass change:			20.3	16.8
After influence of water environment and Aspergillus niger fungi				
100-130	Endothermic	Removing physically bound water	6.2	11.7
430-480	Endothermic	Dehydration of calcium hydroxide $Ca(OH)_2 \rightarrow CaO + H_2O$	1.8	0.8
550-650	Endothermic	Polymorphic transformations of quartz $\alpha\text{-}SiO_2 \rightarrow \beta\text{-}SiO_2$	7.9	1.1
650-815	Endothermic	Decarbonization $CaCO_3 \rightarrow CaO + CO_2$	4.4	6.8
Total mass change:			20.3	20.4

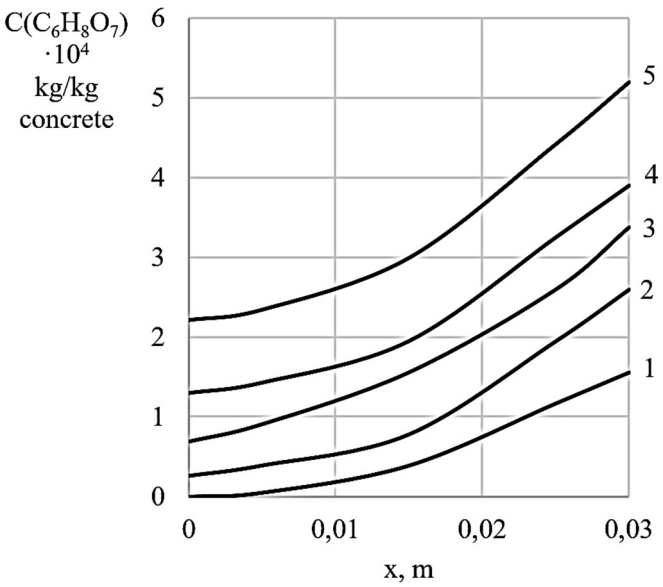

Fig. 2. The profiles of the citric acid $C_6H_8O_7$ concentrations by the thickness of cement stone samples under fungal corrosion (Aspergillus niger) at τ (days): 1 – 14; 2 – 28; 3 – 42; 4 – 56; 5 – 70.

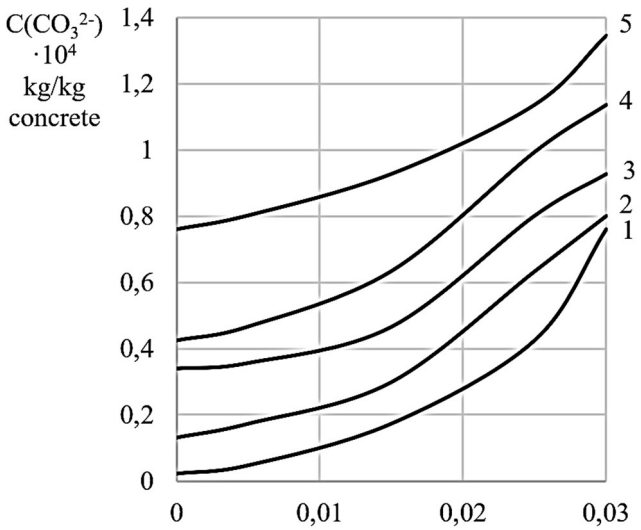

Fig. 3. The profiles of the carbonate ion concentrations by the thickness of cement stone samples under bacterial corrosion (Bacillus subtilis) at τ (days): 1 – 14; 2 – 28; 3 – 42; 4 – 56; 5 – 70.

4 Discussion

In the case of fungal corrosion of concrete, the flow rate of the mass of the substance is higher than in the case of bacterial corrosion. The aggressiveness of micromycetes against cement concretes is higher than that of bacteria.

The aggressiveness of organic acids for concrete is determined by the solubility of their calcium salts according to SP 28.13330.2017 «Protection against corrosion of construction». The most soluble is calcium lactate (54 g/l), so lactic acid is extremely aggressive. Malic acid is also extremely aggressive for concrete, since the solubility of calcium malate is 2.83 g/l. If calcium salts have a solubility of 0.002-2 g/l, then organic acids are medium-aggressive: citric acid (solubility of calcium citrate 0.95 g/l), tartaric acid (solubility of calcium tartrate 0.045 g/l), oxalic acid (solubility of calcium oxalate 0.006 g/l).

It should be assumed that since the content of extremely aggressive organic acids in the waste products of Aspergillus niger fungi is small, the positive effect of concrete corrosion is due to the leaching of calcium under the influence of citric acid.

After exposure to Bacillus subtilis bacteria, calcium carbonate was found in the surface layer of concrete, which is formed as a result of the impact of carbonic acid on the concrete, which is a product of the vital activity of bacteria due to the processing of carbon dioxide. Traces of pectolic enzymes were also found in small amounts.

The acids accumulated in the waste products of microorganisms penetrate deep into the pore structure of the concrete and gradually penetrate into the surface of the steel reinforcement. Oxalic, citric and lactic acids cause corrosion of steel only at high concentrations. Organic acids cause pitting corrosion of steel, which leads to local dissolution of the metal surface and point thinning of the reinforcing bar [22]. When carbonic acid enters the pore liquid of concrete, hydroxide, carbonate, and bicarbonate ions appear in it. Their interaction with iron ions formed during the dissolution of steel is accompanied by the formation of poorly soluble iron hydroxide and carbonate and well-soluble iron bicarbonate. The latter mainly appears on the surface areas washed by an environment with an excess of carbon dioxide (carbonic acid). With an increase in the pH value of the medium, the probability of the formation of poorly soluble corrosion products increases. The corrosion of

the steel surface is ulcerative in nature. The corrosion of steel in the combined presence of carbonic acid and oxygen in the liquid proceeds almost without slowing down due to the instability of the resulting oxide films [24].

Obviously, bacterial corrosion is slower than fungal corrosion. This is because when carbon dioxide corrosion occurs in the pores of concrete, insoluble calcium carbonate $CaCO_3$ is formed. This salt accumulates and clogs the pores, thereby preventing further penetration of the aggressive environment deep into the concrete.

According to the results of the derivatographic analysis of cement stone, four main endothermic effects were recorded: (-)130 °C, (-)455 °C, (-)550 °C, (-)800 °C for bacterial damage; (-)130 °C, (-)450 °C, (-)550 °C, (-)700 °C, (-)790 °C for fungal damage, which determine the dehydration of the corresponding hydrate compounds. In all samples, a change in the content of calcium hydroxide by the endothermic effect was recorded at a temperature of 430-480 °C (Table 1). In the samples exposed to microorganisms, the effect area, which characterizes the dehydration of calcium hydroxide, decreased. This corresponds to a decrease in the amount of $Ca(OH)_2$. A decrease in the amount of portlantide indicates that the risk of ettringitis and thaumacitis is reduced. For samples exposed to microbiological effects, a decrease in the final dehydration temperatures of hydrate compounds to 790-800 °C was recorded, which indicates the presence of a small amount of calcium carbonate in the cement stone.

Concentration profiles allow us to estimate the flow density of the transported components by the thickness of the concrete and calculate the periods of the beginning of corrosion damage in reinforced concrete.

For concrete and steel reinforcement, the concentration of citric acid above 0.05 g/l is aggressive [22]. This value of the citric acid concentration at the reinforcement surface occurs 964 days (2.5 years) after the concrete surface is infected with the Aspergillus niger. After that, pitting corrosion begins in the places of destruction of the passive film on the steel.

The concentration of dissolved carbon dioxide in the pore liquid of concrete more than 2000 mg/m^3 is aggressive in relation to steel reinforcement. It will take 2057 days (5.5 years) to reach such a concentration at the surface of steel reinforcement in concrete during bacterial corrosion under the influence of Bacillus subtilis. After that, local corrosion processes will begin on the surface of the steel due to a decrease in the pH of the concrete at the surface of the reinforcement below 9 and the cessation of the passivating effect of the concrete alkalis.

5 Conclusion

The resource of safe operation of structures made of concrete exposed to microorganisms in a liquid environment directly depends on the speed of mass transfer processes in the system.

The mechanism of corrosion of concrete under the influence of microorganisms combines the I and II types of corrosion (according to professor Moskvin), since at the initial stage there is a leaching of calcium under the influence of water, then due to the multiplication of microorganisms on the surface of concrete and the accumulation of their waste products, acid corrosion occurs, and the formation of calcium carbonate in the pores of concrete leads to clogging of pores and an increase in internal stress.

Irreversible processes of corrosion destruction in reinforced concrete under conditions of fungal corrosion will begin in 2.5 years, in conditions of bacterial corrosion – in 5.5 years.

References

1. M.I. Ansari, K. Schiwon, A. Malik, E. Grohmann. Environ. Prot. Strateg. Sustain. Dev., (2012).
2. T. Verdier, M. Coutand, A. Bertron, C. Roques. Build. Environ. **80**, 136 (2014).

3. C.H. Posten, C.L. Cooney. Biotechnol. Second. Complet. Revis. Ed., (2008).
4. A.E. Charola, E. Wendler. Restor. Build. Monum. **21**, (2016).
5. U. Moral, P. Nagar, S. Maan, K. Kaur. Int. J. Curr. Microbiol. Appl. Sci. **6**, (2017).
6. H. Horn, S. Lackner. Adv. Biochem. Eng. Biotechnol. **146**, (2014).
7. M.C.M. Van Loosdrecht, J.J. Heijnen, H. Eberl, J. Kreft, C. Picioreanu. Antonie van Leeuwenhoek. Int. J. Gen. Mol. Microbiol. **81**, (2002).
8. I.V. Stolbikhin, S.V. Fedorov. Water Ecol. **2017**, (2017).
9. B. Dubravka, S. Marijana, C. Igor. *Kuei Suan Jen Hsueh Pao*, Journal Chinese Ceram. Soc. **38**, (2010).
10. P. Marcus. Corrosion Mechanisms in Theory and Practice: Third Edition, (2011).
11. M. Fomina, E.P. Burford, G.M. Gadd. *Fungi Biogeochem*, Cycles, (2006).
12. M. Fiertak, E. Stanaszek-Tomal. Brittle Matrix Compos, **11** Proc. 11th Int. Symp. Brittle Matrix Compos. BMC, (2015).
13. M.E. Bazhanova, D.A. Svetlov, T.A. Saltanova, O.P. Grigorkina. IOP Conf. Ser. Mater. Sci. Eng., (2020).
14. D. Svetlov, A. Kachalov. Russ. J. Transp. Eng. **6**, (2019).
15. V.V. Strokova, V.V. Nelubova, M.D. Rykunova. Mag. Civ. Eng. **90**, (2019).
16. M. Sato, T. Hattanji. Prog. Earth Planet. Sci. **5**, (2018).
17. I.M. P.Q. Delgado, A.S. Guimarães, V.P. De Freitas, I. Antepara, V. Kočí, R. Černý. Adv. Mater. Sci. Eng. **2016**, (2016).
18. T. Stryszewska, S. Kańka. Procedia Eng., (2017).
19. V. Erofeev, V. Kalashnikov, D. Emelyanov, E. Balathanova, I. Erofeeva, O. Smirnova, I. Tretiakov, A. Matvievskiy. Solid State Phenom., (2016).
20. O. Wanner. Biofouling **10**, (1996).
21. A.R. Erbektas, O.B. Isgor, W.J. Weiss. RILEM Tech. Lett. **4**, (2019).
22. D. Svetlov, A. Kachalov. Russ. J. Transp. Eng. **6**, (2019).
23. S.V. Fedosov, V.E. Rumyantseva, I.V. Krasilnikov, V.S. Konovalova, I.V. Karavaev. Izv. Vyss. Uchebnykh Zaved. Seriya Teknol. Tekst. Promyshlennosti **372**, 268 (2017).
24. N.A. Khudhair, A.M.A. Al-Sammarraie, Baghdad Sci. J. **17**, (2020).