

The effect of microbial and chemical corrosion on concrete structures operated in the conditions of chemical enterprises has been established that makes it possible to reliably predict the timing of their decommissioning in order to prevent industrial disasters. Even though the construction complies with all building codes, concrete structures eventually undergo chemical and biological corrosion.

The innovation proposed in this study implies investigating the depth and degree of damage to concrete at the microscopic level by the method of raster electron microscopy. In addition, the TPD-MS method has been suggested for determining the quantitative and qualitative state of the carbonate components of concrete and sulfur compounds.

This study has found that in concrete samples from the titanium dioxide production plant, the amount of carbon dioxide release is twice less than in control samples at $t=600\text{ }^{\circ}\text{C}$ while the level of sulfur dioxide, on the contrary, increases. This is due to the ability of thionic bacteria to accumulate sulfate acid that destroys the cementing component in concrete. The reported results confirm the impact of products of the activity of *Acidithiobacillus thiooxidans* microorganisms on corrosion processes in concrete.

In addition, when using the TPD-MS method, it was established in the storage room of the finished product that heating the control sample of concrete leads to a release of the significant amount of CO_2 at $t=580\text{--}600\text{ }^{\circ}\text{C}$. However, the experimental samples of concrete are almost lacking carbon compounds because the acid metabolites of microfungi interfere with its formation. Microscopic and REM studies revealed the localization of *Acidithiobacillus thiooxidans* and *Aspergillus fumigatus* in concrete.

This study has established patterns related to the mechanism that forms chemical compounds in concrete and the metabolism of microorganisms

Keywords: biochemical corrosion of concrete, sulfate acid, *Thiobacillus thiooxidans* bacterium, *Aspergillus fumigatus* micromycetes

UDC 614.48:631.223

DOI: 10.15587/1729-4061.2021.226587

DEFINING PATTERNS IN THE INFLUENCE EXERTED BY THE INTERRELATED BIOCHEMICAL CORROSION ON CONCRETE BUILDING STRUCTURES UNDER THE CONDITIONS OF A CHEMICAL ENTERPRISE

Oksana Shkromada

Doctor of Veterinary Sciences, Professor
Department of Obstetrics and Surgery**
E-mail: oshkromada@gmail.com

Viktoriia Ivchenko

PhD, Associate Professor
Department of Therapy, Pharmacology, Clinical Diagnostics and Chemistry**

Vadym Chivanov

Doctor of Agricultural Sciences, Associate Professor
Department of Radiation Biophysics
Institute of Applied Physics, National Academy of Sciences of Ukraine
Petropavlivska str., 58, Sumy, Ukraine, 40000

Liudmyla Tsyhanenko

PhD, Associate Professor*

Hennadii Tsyhanenko

Senior Lecturer*

Volodymir Moskalenko

Chief Engineer of Complex Installation
Department of Nuclear Physics Research
Institute of Applied Physics, National Academy of Sciences of Ukraine
Petropavlivska str., 58, Sumy, Ukraine, 40000

Iryna Kyrchata

PhD, Associate Professor***

Olena Shersheniuk

PhD, Associate Professor***

Yuliia Litsman

PhD, Associate Professor

Department of Theoretical and Applied Chemistry
Sumy State University
Rymskoho-Korsakova str., 2, Sumy, Ukraine, 40007

*Department of Building Structures**

**Sumy National Agrarian University

Herasyma Kondratiev str., 160, Sumy, Ukraine, 40021

***Department of Economics and Business

Kharkiv National Automobile and Highway University
Yaroslava Mudroho str., 25, Kharkiv, Ukraine, 61002

Received date 19.01.2021

Accepted date 11.03.2021

Published date 12.04.2021

How to Cite: Shkromada, O., Ivchenko, V., Chivanov, V., Tsyhanenko, L., Tsyhanenko, H., Moskalenko, V., Kyrchata, I., Shersheniuk, O.,

Litsman, Y. (2021). Defining patterns in the influence exerted by the interrelated biochemical corrosion on concrete building structures under the conditions of a chemical enterprise, 2 (6 (110)), 52–60. doi: <https://doi.org/10.15587/1729-4061.2021.226587>

1. Introduction

Most premises for industrial enterprises are made of concrete and reinforced concrete structures. Despite the reliability of the building material, there are certain factors of its destruction, which lead to a decrease in service life. Production of concrete structures remains popular and is constantly improving. Several issues related to the chemical and biological corrosion of concrete must be additionally addressed.

Concrete structures for chemical and livestock buildings, marine and sewerage structures, exposed to a specific chemical aggressive environment, suffer from the activity of microorganisms.

There are three main destructive principles for building structures: mechanical, assimilation, and dissimilative.

Violation of the integrity of the concrete surface, including due to chemical corrosion processes, creates favorable conditions for the development of specific microorganisms –

autotrophs that trigger the assimilation process. In turn, microorganisms are able to use concrete as a medium for life and nutrition (dissimilation). In the process of their activity, microorganisms can produce substances that enhance the mechanism of chemical corrosion.

Biological damage to concrete is closely related to chemical corrosion. At a chemical enterprise, in the titanium dioxide production plant, there is constant chemical corrosion due to the release of free sulfur and its oxides. In this environment, thionic bacteria grow well. Thiobacillus uses free oxygen for its activity and oxidizes sulfur. As a result of the dissimilation process, hydrogen ions and sulfate acid are formed. There is also a process that forms a large amount of gypsum, which creates pressure in the concrete, and cracks are formed. Thus, microbiological corrosion of concrete contributes to the further destruction of concrete structures. Chemical and biological factors of concrete corrosion penetrate very quickly through the cracks, which is difficult to stop. Micromycetes that use an already prepared environment for their existence also join this process.

The identification of patterns of influence of interrelated microbial and chemical corrosion of concrete building structures at a chemical enterprise requires determining the methods for studying corrosion processes in concrete on different surface layers at the microscopic level. This would make it possible to predict the service life of concrete structures and determine the degree of corrosion processes over time, which explains the relevance of related studies.

2. Literature review and problem statement

Concrete is used worldwide for the construction of roads, buildings, sewer communications, industrial and civil engineering structures. Many buildings have been shown to have suffered varying degrees of damage as a result of biologically induced destruction. Researchers determined the resistance of concrete to an aggressive environment and microorganisms. According to the results of experiments, antimicrobial agents were developed. At the same time, no attention was paid to the conditions of biological corrosion and chemical processes that took place in concrete. Many technological advances and experiments carried out in laboratory conditions do not take into consideration the environmental impact, which enhances the development of biological degradation of concrete [1].

Concrete structures of civilian infrastructure are essential for the social and economic development of most countries. In work [2], it is proposed to improve the resistance of concrete to corrosion due to using nanomaterials. However, the application of nanotechnology for concrete is under development. No careful study of its durability during operation in a specific aggressive environment, taking into consideration the biochemical processes that occur there, was carried out. Moreover, there is a danger related to the content of nanomaterials in concrete due to the impact on human health and the environment.

Agricultural enterprises also face the problem of biological corrosion of concrete enclosures (floor, states, machines). The main factors that contributed to the destruction of building materials were temperature, excessive moisture, weak ventilation system, the use of alkaline and acid disinfectants [3]. The researchers used an additive to concrete based on yellow iron oxide pigment, which exhibits antimicrobial

properties. However, the antimicrobial properties of the specified additive and environmental impact have not been determined [4].

In addition, the resistance of microorganisms to antimicrobial agents is not always taken into consideration. In the premises where people work or animals are kept, not all effective antimicrobial compounds can be used due to the release of some toxic agents during their operation [5].

Destruction of concrete in sewer communications, where there is a high concentration of hydrogen sulfide, is associated with the metabolism of the bacteria *A. thiooxidans* and *H. Neapolitanus*, which oxidize sulfur. The researchers conducted a number of experiments in laboratory conditions, imitating the environment in the sewer. As a result of the research, it was established in [6] that, in addition to weight, concrete in the process of destruction changes its structure and strength. However, artificially created laboratory conditions and the use of museum strains of microorganisms cannot accurately predict the duration of operation of concrete engineering structures of the sewerage system.

The causes and mechanism of damage to existing buildings by biochemical corrosion are usually determined visually and with the help of complex devices that do not give a complete picture of the processes occurring at the electrochemical level in concrete. The reason for this may be objective difficulties associated with studying already functioning concrete structures. Often, researchers predict the stability of concrete through the immersion of samples in a solution of hydrochloric acid. They also determine the degree of chemical corrosion by the depth of penetration of NaCl ions into concrete samples [7, 8].

Thus, they assessed the deterioration of the operational qualities of concrete, as well as the diffuse properties of corrosion substances in concrete. Scientists studied the progression of the development of the rate of corrosion of concrete under different natural conditions and developed a model for predicting the rate of propagation [9]. The cited study can assess the corrosion resistance of concrete mainly at the material level. However, there is no connection with strength at the microscopic level. Moreover, it is fundamentally impossible to trace the degree and depth of concrete corrosion over time by such methods as they are designed only for a short period of time, which makes relevant studies impractical. It is also difficult to determine the period of further operation of building structures and understand the possibilities of overcoming the destruction [10].

To study concrete during the operation of chemical enterprises, the use of programmable thermal mass spectrometry is proposed.

Temperature Programmed Desorption Mass Spectrometry (TPD MS) is used to investigate modified pyrogenic oxides. The researchers showed theoretical models to ensure the analytical processing of TPD MS data. The scientists developed formulae for the rate constant in the first, second, and third-order reactions. Thermal carbon breakup products can be observed and identified. Various variants of single- and bimolecular desorption with the help of temperature-programmed desorption mass spectrometry [11] are described.

The TPD MS method was proposed by scientists to develop a methodology for introducing gas for radiocarbon dating of natural calcium carbonates (corals, chalk, shells of anadary mollusks) and existing ancient buildings. The object for research was St. Sophia Cathedral (a monument of archi-

texture of the XI century) where the initial limit of the heating range for the release of carbon dioxide was 400 °C [12].

The concrete structure includes a solid phase and pores filled with gas and liquid. The strength of the concrete depends on the integrity of the frame, the pH of the liquid, the temperature range, and moisture. This approach is used in work [13], it is an important aspect of the study of the deformation of the microstructural level of cement stone for existing premises that have a long service life.

The researchers are encouraged to use raster electron microscopy to study the depth of damage and microstructure of concrete samples. The effect of biological and chemical corrosion on concrete structures in the premises and various infrastructure structures is often underestimated [14]. The role of microorganisms in the destruction of concrete on both surface and deeper layers of building structures is not sufficiently studied.

All this suggests that it is advisable to conduct a study into determining the causes and mechanism of development of interconnected biochemical corrosion over time in different layers of concrete structures using raster electron microscopy and temperature-programmed mass spectrometry.

3. The aim and objectives of the study

The purpose of this work was to determine the patterns of influence exerted by the biological and chemical corrosion processes on concrete in a shop where titanium dioxide is produced by sulfate method and in a storage facility for finished products, along various structural planes of building structures.

From a practical point of view, that could determine the extent of corrosion biochemical processes and predict the lifetime of concrete structure operation.

To accomplish the aim, the following tasks have been set:

- to investigate the causes of formation and the extent of concrete biochemical corrosion in a shop where titanium dioxide is produced by sulfate method;
- to determine the depth of the damage and a development mechanism of the biochemical corrosion of concrete structures in the facility for storing finished products.

4. Materials and methods to study the biochemical corrosion of concrete

The research was conducted at the Sumy Regional Laboratory of Veterinary Medicine of the Laboratory of Architecture and Engineering Solutions of Sumy National Agrarian University during 2019–2020 (Sumy, Ukraine).

Samples of concrete were received from a shop where titanium dioxide is produced by sulfate method and a facility for storing finished products, along various structural planes of building structures. Concrete samples were selected separately from another room as control (the enterprise's office). The samples from concrete building structures were received at different depths: surface; 0.5 cm; 1.0 cm.

4.1. Procedure to study concrete samples in order to determine their heat resistance using TPD MS

To study the heat resistance of concrete samples, we used a temperature-programmed desorption mass

spectrometry (TPD MS) installation, consisting of a high-temperature furnace and the gas mass spectrometer MH-7304 (VAT SELMI, Sumy, Ukraine). We heated concrete samples weighing 5–10 mg from 40 to 900 °C at a speed of 15 °C/min, accompanied by the simultaneous registration of the mass spectra of the mixture of gases released, in every minute. In the mass spectra, we identified the peaks of ions with molecular masses (m/z): 32 – O₂ oxygen; 18 – water; 44 – CO₂ carbon dioxide, 64 – sulfur dioxide SO₂. Technical details of the experiment are reported in work [15].

4.2. A method for the microbiological study of *Acidithiobacillus thiooxidans* and *Aspergillus fumigatus*

Samples for our microbiological study were received from the surface of the walls of a shop where titanium dioxide is produced and from a facility for storing finished products.

Acidithiobacillus thiooxidans were cultivated in the liquid nutrient environment WAKSMAN. The following components were added to the meat and peptone broth: (NH₄)₂SO₄ – 0.2 g; KH₂PO₄ – 3 g; MgSO₄·7H₂O – 0.5 g; CaCl₂·6H₂O – 0.25 g; FeSO₄·7 H₂O – 0.01 g; sulfur – 10 g; distilled water at pH=4 – 1 l. The medium pH was adjusted by adding 0.1 n of H₂SO₄ solution after sterilization of the medium [16].

The microscopic fungi *Aspergillus fumigatus* were cultivated in Petri dishes in the Chapek-Dox environment; they were kept in a thermostat at a temperature of 30 °C for 5 days [17].

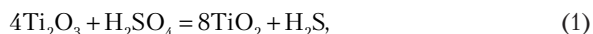
4.3. The procedure of scanning electron microscopy

We studied the microstructure of concrete samples by a scanning electron microscopy method using the device REM106i (VAT SELMI, Sumy, Ukraine). To establish corrosion changes in the microstructure of concrete, the samples were fixed on metal supports using two-sided carbon tape. To provide samples with electrical conductivity, spraying with silver was carried out. To study the bio-films of microorganisms, concrete samples were fixed with a 2.5 % glutaric aldehyde on a 0.2 M phosphate buffer solution, dehydrated in a series of ethyl alcohols of increasing concentration, and sprayed with silver [18]. We studied them in a raster electron microscope under the mode of secondary electrons in the range of electron-optic magnification from 200 to 5,000 times.

5. The results of studying the causes of biochemical corrosion of concrete in a shop where titanium dioxide is produced by sulfate method

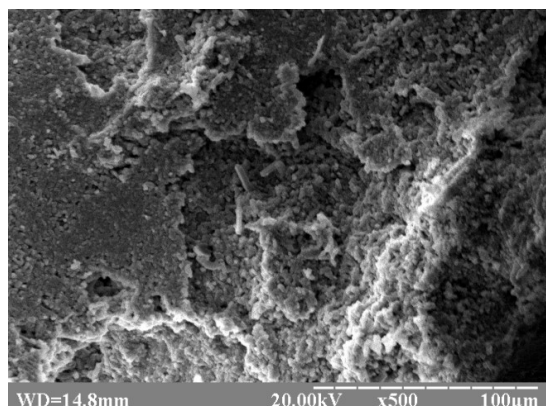
A shop where titanium dioxide is produced by the sulfate method was commissioned in 1975. The columns, coatings, and walls were made of precast reinforced concrete class not less than C20. The raft system is composed of metal frames from paired metal angles; the floor is paved with acid-resistant brick.

The TiO₂ technology implies the decomposition of titanium-containing raw materials under the influence of sulfate acid at a high temperature. Most of the oxides from raw materials turn into water-soluble salts, the rest forms solid slags. In the process of further decomposition of titanium-containing slags, hydrogen sulfide, SO₂ oxide, and free sulfur are released in accordance with reactions (1) to (3):

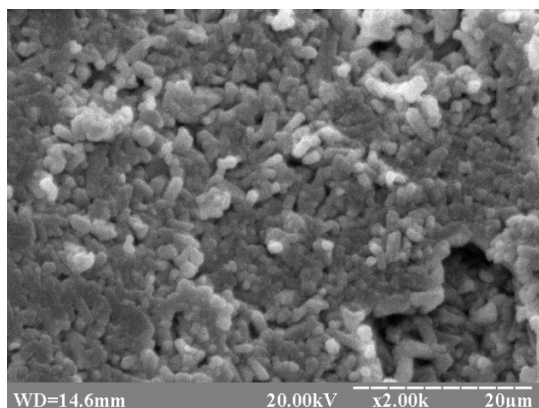


The release of elementary sulfur is observed in decomposition reactors in the form of yellow powdered plaque [19].

Microorganisms that form entire colonies and biofilms on the surface of concrete structures were found in the shop where titanium dioxide is produced (Fig. 1).



a



b

Fig. 1. REM images of *Acidithiobacillus thiooxidans*, formerly known as *Thiobacillus thiooxidans*, acquired from the surface of concrete structures in a shop where titanium dioxide is produced: a – magnification $\times 500$; b – magnification $\times 2000$

A. thiooxidans is an aerobe that uses sulfur in its life activity only in the presence of oxygen. Also important is the presence of a sufficient amount of moisture, at least 11.4. The intensity of biodegradation under the influence of chemically aggressive media is determined by the rate of chemical reactions both on the surface and by the diffusion of bacteria metabolism products deep into the concrete.

Confirmation of the destructive activity of the sulfate environment and the result of bacteria vital activity is the study of samples from different layers of concrete by the TPD MS method (Fig. 2).

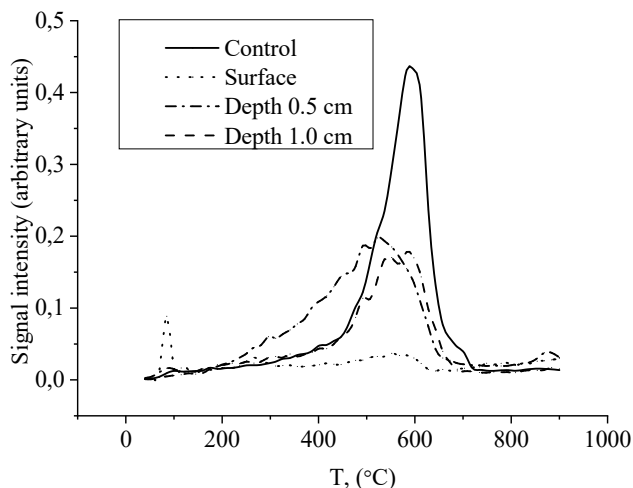
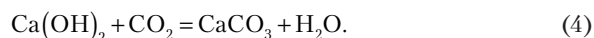


Fig. 2. Thermograms of CO_2 release ($m/z=44$) from the sample obtained from a shop where titanium dioxide is produced

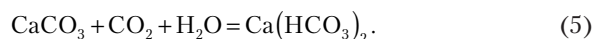
It was established that the control sample, the least affected by corrosion, produces a sharp peak at $t=600^\circ\text{C}$ on the chart, with a signal intensity of 0.45 (Fig. 2).

The sample of the surface, severely destroyed under the action of bacterial and chemical corrosion, is destroyed at a temperature of 100°C ; the signal intensity when carbonate is released is 0.1. At a depth of 0.5 cm, the concrete sample is less damaged than that at the surface, but the destruction t during CO_2 release is 500°C ; the signal intensity is 0.1. Building material from a depth of 1 cm is destroyed at a temperature of 500°C ; the signal intensity is 0.15.

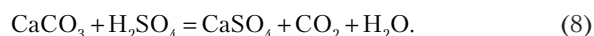
In the surface layers of concrete, in the process of carbonization of lime, water-soluble calcium carbonate is formed, which gradually accumulates in the pores and causes the formation of microcracks (4).



Under conditions of high humidity, calcium carbonate passes into soluble bicarbonate, which can be washed with water from the surface of a concrete structure (5):



Under conditions of high acidity, the destruction of carbonates and their transition to sulfates in accordance with reactions (6) to (8) is possible:



Thus, the larger the content of sulfates (SO_2) in concrete samples, the less the amount of carbonates (CO_2) (Fig. 2, 3).

Almost no sulfur was detected in the control sample. At the surface of the sample, the sulfur oxide is released at a temperature of 200°C for the first time with a signal intensity of 0.01. When the same sample is heated to 700°C , the signal intensity increases to 0.035. Moving deep, the

concrete has a stronger structure, and the level of sulfur dioxide release increases. Samples from a depth of 0.5 and 1 cm released SO₂ at $t=900\text{ }^{\circ}\text{C}$ with an intensity of up to 0.05.

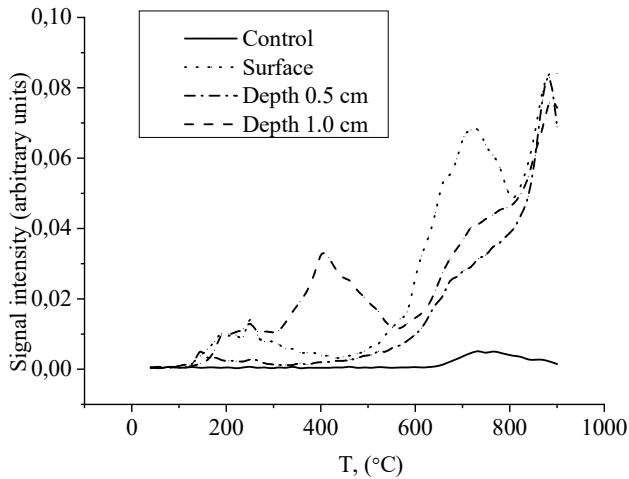


Fig. 3. Thermograms of SO₂ release ($m/z=64$) from the sample obtained from a shop where titanium dioxide is produced

The formation of sulfate acid by microorganisms destroys the cementing component in concrete and contributes to the formation of gypsum (Fig. 4) and ettringite, which have expansive properties. Gypsum acts as a protective coating for concrete, with the destruction of which corrosion of the concrete surface would accelerate. Also, aluminat of gypsum and calcium is formed in concrete – ettringite, which increases the internal pressure in the building material. As a result, cracks are formed through which microorganisms and moisture enter the concrete (Fig. 5).

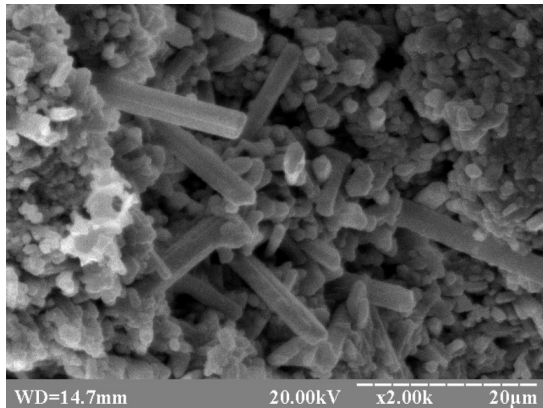


Fig. 4. REM images of gypsum crystals (CaSO₄·2H₂O) acquired from the surface of concrete structures in a shop where titanium dioxide is produced

Fig. 5 demonstrates the results of moisture evaporation from concrete samples when heated. The release of water when heating concrete samples occurs due to the decomposition of crystal hydrates, bicarbonates, lime, hydrosulfoaluminate, and organic components.

The control sample and a sample from the surface contained a minimum amount of moisture, which evaporated quickly at $t=100\text{ }^{\circ}\text{C}$ while the signal intensity was 0.5–0.6. Water evaporates over a longer time from samples taken

from the depth of 0.1-1 cm. This indicates the integrity of the frame and the chemical structure of concrete, which can retain moisture. The signal strength was 2.0.

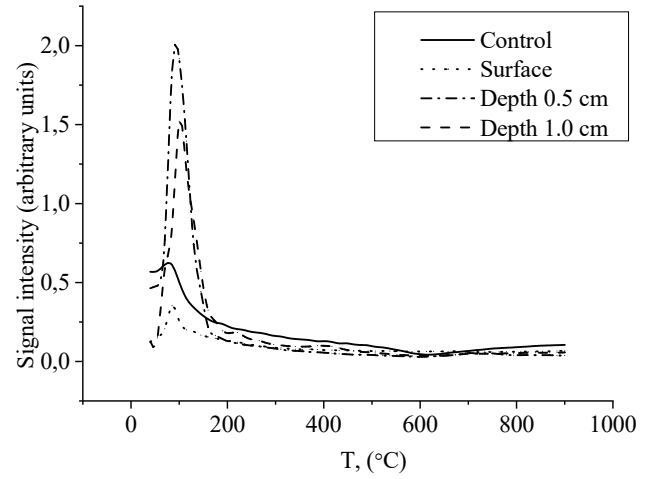


Fig. 5. Thermograms of H₂O release ($m/z=18$) from the sample obtained from a shop where titanium dioxide is produced

The loss of oxygen (Fig. 6), as well as the loss of water (Fig. 5), by the samples, occurred in a similar pattern.

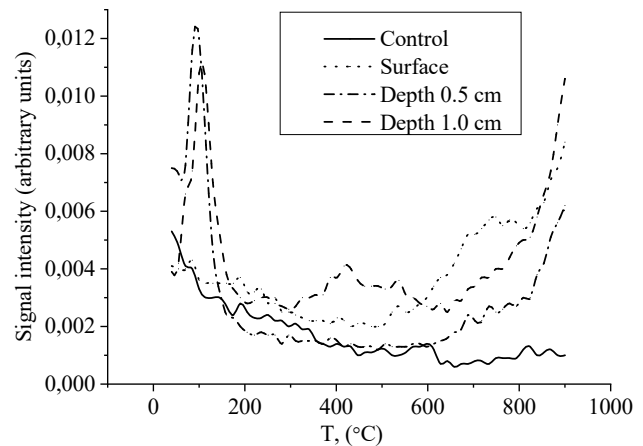


Fig. 6. Thermograms of O₂ release ($m/z=32$) from the sample obtained from a shop where titanium dioxide is produced

The highest signal intensity of up to 0.012 was observed in the sample from a depth of 0.5 cm, less than 0.010 – in a sample from a depth of 1 cm. In the control sample and from the surface, the O₂ release occurred almost at the beginning of heating, the signal intensity was 0.004–0.005.

It was established that the shop where titanium dioxide is produced is characterized by conditions that contribute to the growth of thionic bacteria, which are the cause of the biochemical corrosion of concrete structures.

6. The results of studying the depth of the damage and the mechanism of development of biochemical corrosion

We also performed a study at a facility for storing finished products, which was commissioned in 1975. Res-

toration work is currently underway. The foundation and basement are made from reinforced concrete; the frame is made of metal frame; coating – from a profiled sheet.

The fungus *Aspergillus fumigatus* was found at the surface of concrete structures at a facility for storing finished products (Fig. 7).



Fig. 7. *Aspergillus fumigatus*; washes taken from the concrete surface at a facility for storing finished products

In the process of their vital activity, micromycetes secrete a variety of organic acids. It is these acids that cause corrosion as a result of interaction with the alkaline components of concrete – lime and limestone. As a result, calcium passes into the form of calcium salts of organic acids, which are distinguished by a different ability to dissolve. Characteristic calcium citrate crystals on the surface of concrete samples affected by *Aspergillus fumigatus* were observed on REM (Fig. 8).

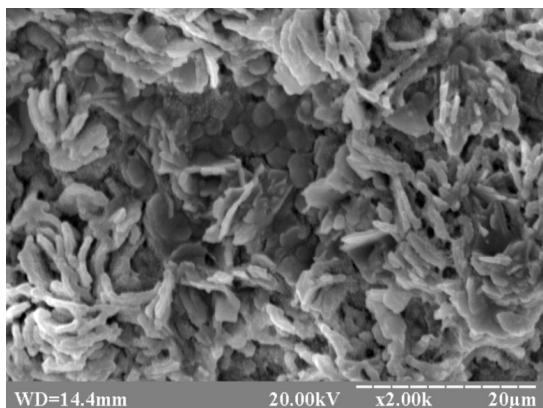


Fig. 8. REM image of calcium citrate crystals on the surface of concrete samples and the growth of *Aspergillus fumigatus* acquired from the concrete surface at a facility for storing finished products

Thus, organic acids interfere with the process of lime carbonization, as evidenced by the results of mass spectrometric analysis of CO₂ samples of concrete affected by *Aspergillus fumigatus* compared to control (Fig. 9).

The thermogram reflects the dynamics of CO₂ release when concrete samples are heated. When the control sample is heated, a clear and intense peak is formed, which corresponds to CO₂ at $t=580-600$ °C. This indicates the presence of limestone (calcium carbonate) in it. Which decomposes with the formation of CO₂ and CaO. In other samples of experimental samples of concrete from different depths, limestone is found in insignificant quantities. This is due to the fact that the acid metabolites *Aspergillus fumigatus* prevent the formation of limestone.

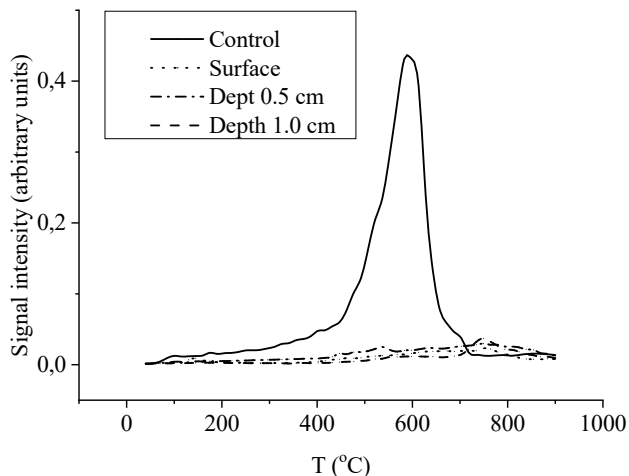


Fig. 9. Thermogram of CO₂ release ($m/z=44$) from the sample received at a facility for storing finished products

The thermogram in Fig. 10 shows the rate of evaporation of water from the samples of concrete when heated.

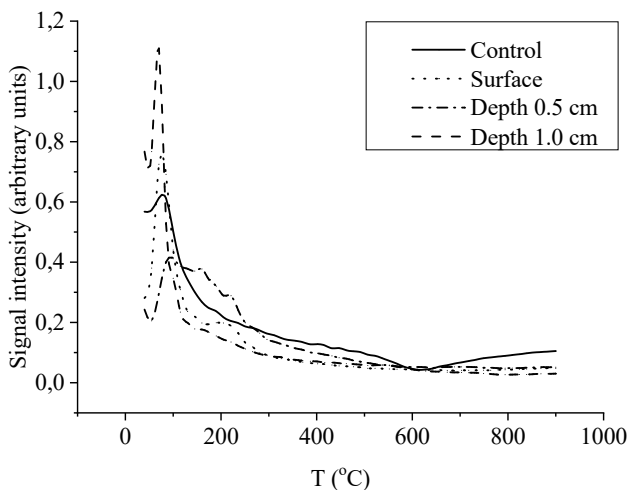


Fig. 10. Thermograms of H₂O release ($m/z=18$) from the sample received at a facility for storing finished products

Fig. 10 shows the results of moisture loss by concrete samples from different depths. Water evaporates gradually from the surface of the control sample, in proportion to the rate of destruction of concrete. In the experimental samples of concrete obtained from different layers, the structure is disturbed, and therefore, when heated to $t=100$ °C, water evaporation proceeds very quickly with the formation of peaks. The signal strength is 0.8–1.

Fig. 11 shows the intensity of oxygen loss by the concrete samples obtained from a shop where mineral fertilizers are produced, from different surface depths.

In control samples, oxygen evaporation occurs more slowly than from experimental ones with a signal intensity of 0.001–0.005. The intensity of O₂ release from concrete samples dynamically decreased when moving from the surface to deeper layers. Samples of concrete with a loose structure were more likely to be destroyed during heating. We receive additional confirmation that concrete corrosion began from the surface and gradually moved in the depths of building structures.

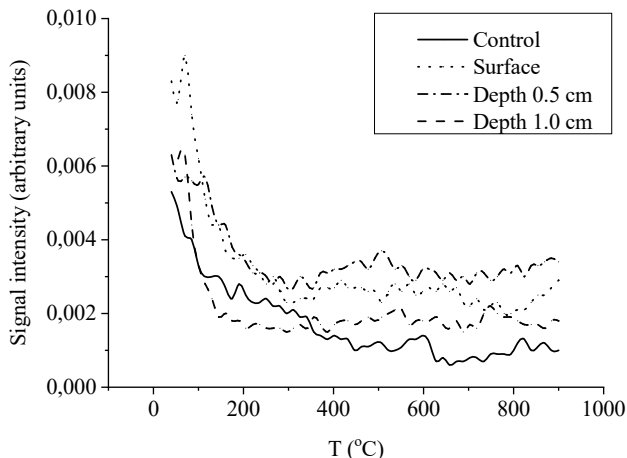


Fig. 11. Thermograms of O₂ release (*m/z*=32) from the sample received at a facility for storing finished products

Sulfur dioxide released from concrete samples is shown in Fig. 12. In the control samples of concrete, sulfur dioxide SO₂ was practically not detected.

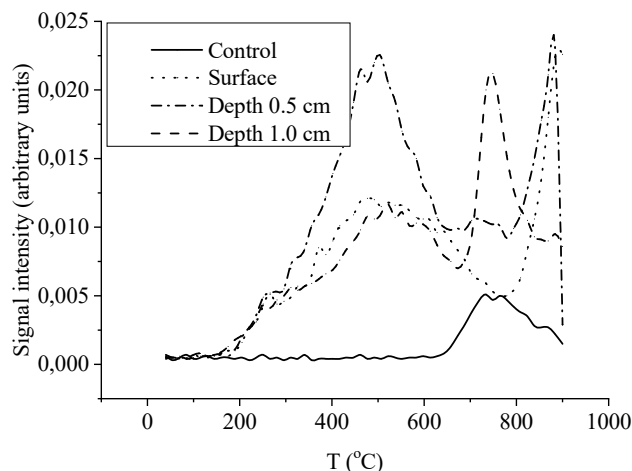


Fig. 12. Thermograms of SO₂ release (*m/z*=64) from the sample received at a facility for storing finished products

The two most intense peaks of sulfur dioxide release of 0.022 at a temperature of 500 °C and 900 °C were observed in samples obtained from a depth of 0.5 cm. In samples from the surface and from a depth of 1.0 cm sulfur dioxide at a temperature of 500 °C was released less intensively, 0.010. However, the destruction in the temperature range from 800 to 900 °C demonstrated the intensity of sulfur dioxide release of up to 0.022.

It has been experimentally proved that the titanium dioxide production shop and the mineral fertilizer storage facility undergo interrelated processes of chemical and biological corrosion of concrete structures, which poses a danger for the further operation of the structure.

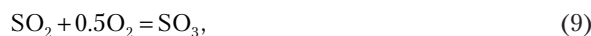
7. Discussion of results of studying the biochemical corrosion of concrete

We have experimentally established the growth of the thionic bacteria *A. thiooxidans* [20] on the surface of con-

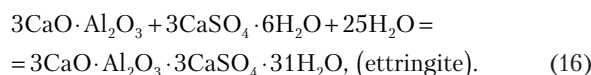
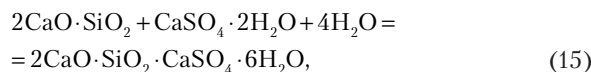
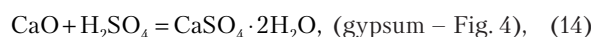
crete building structures. The microorganism uses sulfur, which is released into the environment when the sulfate method is used to produce titanium dioxide. *A. thiooxidans* is resistant to high acidity (pH 0.6 to 4.5). Also, in the process of its vital activity, the bacterium accumulates up to 7 % of sulfate acid [21].

Concrete structures of the titanium dioxide production shop, from ilmenite concentrate by using a sulfate technique – formulae (1) to (3), are exposed to an aggressive chemical environment that creates conditions for acid and sulfate chemical corrosion. As a result, either the washing of easily soluble compounds with water or the formation of fragile sediment [22] occurs.

The mechanism of sulfate corrosion that occurs in concrete begins with the transformation of oxidized sulfur compounds (SO₂ and SO₃) into sulfite (H₂SO₃) and sulfate (H₂SO₄) acids, by means of the following reactions (9) to (11):



Acids formed during reactions are promoted through microcracks in concrete and react with cement components. Expected are the reactions with SO₂, SO₃, water, sulfite and sulfate acids. There are also reactions with calcium hydroxide (Ca(OH)₂), calcium oxide (CaO), dicalcium silicate 2CaO·SiO₂, and tricalcium aluminate (3CaO·Al₂O₃). As a result of the interaction of tricalcium aluminate with calcium sulfate, ettringite crystals are formed, which are 5–30 times larger than the initial size of the spatial volume of concrete [23]. An increase in the volume of calcium hydrosulfoaluminate leads to the formation of large and micro-cracks, which cause further destruction and desegregation of concrete, according to the following reactions (12) to (16):



Experimentally, the causes of biochemical corrosion of concrete were established. With the help of laboratory microbiological studies, the bacterium *A. thiooxidans* was found. Also, the presence of bacterium growth on the surface of concrete structures has been proven by the use of REM (raster electron microscopy) (Fig. 1).

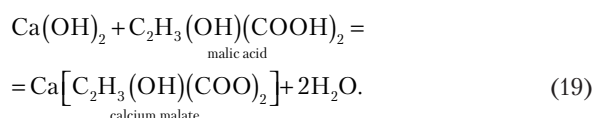
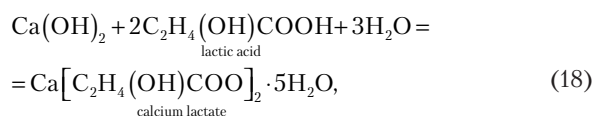
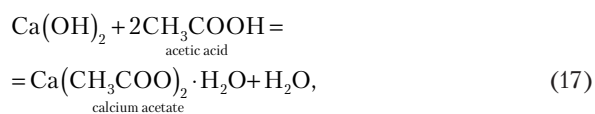
The method of studying the properties of building materials with the help of TPD MS was applied in the experiment. According to the results of temperature-programmed desorption mass spectrometry studies,

a comparative analysis of the relative number of ions of chemical compounds (O_2 ; H_2O ; CO_2 ; SO_2) in the experimental samples of concrete was performed (Fig. 2, 3, 5, 6). The mechanism of formation of chemical compounds in concrete compared to control samples was established and explained.

The disadvantage of the TPD MS method is that it shows the qualitative composition of the examined material rather than quantitative. Therefore, the comparative analysis method is always used in the experiment to the control sample.

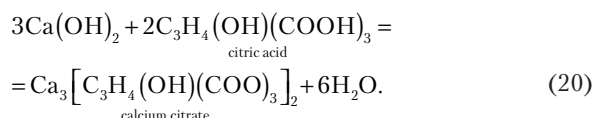
We studied the depth of the damage and the mechanism of development of biochemical corrosion of concrete structures in the premises for the production of mineral fertilizers. Microscopic fungus *Aspergillus fumigatus* was found at the surface of concrete structures, which is the cause of biological corrosion. *Aspergillus fumigatus* belongs to the species of mold fungi of the genus *Aspergillus*. Micromycetes are saprophytes that are pathogenic to humans and can cause aspergillosis (Fig. 7). In addition, *A. fumigatus*, which grew up on building materials, is able to form mycotoxin – gliotoxin [24].

Also, microscopic fungi in the process of their metabolism are able to form organic acids that react with the components of concrete (limestone). The greatest corrosion activity is demonstrated by lactic, acetic, and malonic acids. As a result, soluble calcium salts are formed, which are easily washed from the surface of the concrete (17) to (19):



The release of citrate acid is especially characteristic of *Aspergillus fumigatus* [25, 26].

During the interaction of lime concrete components with citrate acid, calcium citrates are formed, poorly soluble solid crystals (20):



In the mineral fertilizer production shop, the surface of concrete structures was infected by *Aspergillus fumigatus*. Electronic images (REM) of the samples demonstrated characteristic crystals of calcium citrate (Fig. 8).

In the experiment, concrete samples were obtained from a shop where titanium dioxide is produced and from a mineral fertilizer production shop at different depths from the surface.

Using a method of TPD-MS, it was established at a facility for storing finished products that when the control

sample is heated, a clear peak is formed, which corresponds to CO_2 at $t=580-600$ °C. This indicates the presence of limestone (calcium carbonate) in it. In the experimental samples of concrete from different depths, limestone is almost absent due to the fact that the acid metabolites *Aspergillus fumigatus* prevent the formation of limestone (Fig. 9). There is also a high evaporation intensity of H_2O and O_2 , in contrast to control, in proportion to their destruction (Fig. 10, 11).

One of the tasks was to establish the depth of distribution of biochemical corrosion of building structures. The solution to this problem was the use of laboratory microbiological studies and REM. However, during the experiment, samples were taken at different depths from different areas of concrete structures, where the damage due to biochemical corrosion could reach different distributions. Therefore, the experiment cannot be considered absolutely accurate but it gives an idea of the presence of destructive processes in concrete and the likely danger in the further operation of the premises.

The data above are acquired from chemical enterprises and characterize the destructive properties of interrelated chemical and biological corrosion of concrete, products that are formed as a result of these processes, the depth of damage to building material. Thus, it is possible to improve the methods of corrosion processes research in concrete construction structures exposed to the influence of specific aggressive environments.

The direction of further advancement is the development of integrated protective coatings to stop the biochemical corrosion of concrete at a chemical enterprise.

8. Conclusions

1. The possibility of establishing the quantitative and qualitative state of carbonate components of concrete and sulfur compounds in places of localization of thionic bacteria by the TPD-MS method has been proven. It was found that in concrete samples from a titanium dioxide production shop, the amount of carbon dioxide release is twice less than that in control samples at $t=600$ °C while the level of sulfur dioxide, on the contrary, increases. That relates to the ability of thionic bacteria to accumulate sulfate acid, which destroys the cementing component in concrete. The intensity of H_2O and O_2 release, when heated to 100 °C, grows with an intensity of 2.0 in experimental samples compared to the control sample of 0.5. Our results confirm the impact of life activity products of *Acidithiobacillus thiooxidans* microorganisms on corrosion processes in concrete.

2. TPD-MS method was used to establish that an insignificant amount of CO_2 is released in the experimental samples of concrete from a facility for storing finished products during heating. However, the high evaporation intensity of H_2O and O_2 in the experimental samples, unlike the control, indicates the destruction of the concrete structure and the accumulation of a significant amount of moisture in pores. Our microscopic and REM studies have revealed the localization of microfungi *Aspergillus fumigatus* in the concrete. The reported results testify to the established patterns in the influence of chemical and biological corrosion of concrete along the various structural planes of building structures.

References

1. Qiu, L., Dong, S., Ashour, A., Han, B. (2020). Antimicrobial concrete for smart and durable infrastructures: A review. *Construction and Building Materials*, 260, 120456. doi: <https://doi.org/10.1016/j.conbuildmat.2020.120456>
2. Noeiaghahi, T., Mukherjee, A., Dhama, N., Chae, S.-R. (2017). Biogenic deterioration of concrete and its mitigation technologies. *Construction and Building Materials*, 149, 575–586. doi: <https://doi.org/10.1016/j.conbuildmat.2017.05.144>
3. Shkromada, O., Skliar, O., Pikhtirova, A., Inessa, G. (2019). Pathogens transmission and cytological composition of cow's milk. *Acta Veterinaria Eurasia* 64, 73–79. doi: <https://doi.org/10.26650/actavet.2019.19004>
4. Shkromada, O., Paliy, A., Nechyporenko, O., Naumenko, O., Nechyporenko, V., Burlaka, O. et. al. (2019). Improvement of functional performance of concrete in livestock buildings through the use of complex admixtures. *Eastern-European Journal of Enterprise Technologies*, 5 (6 (101)), 14–23. doi: <https://doi.org/10.15587/1729-4061.2019.179177>
5. Shkromada, O., Paliy, A., Yurchenko, O., Khabot, N., Pikhtirova, A., Vysochin, I. et. al. (2020). Influence of fine additives and surfactants on the strength and permeability degree of concrete. *EUREKA: Physics and Engineering*, 2, 19–29. doi: <https://doi.org/10.21303/2461-4262.2020.001178>
6. Marquez-Peñaranda, J. F., Sanchez-Silva, M., Husserl, J., Bastidas-Arteaga, E. (2015). Effects of biodeterioration on the mechanical properties of concrete. *Materials and Structures*, 49 (10), 4085–4099. doi: <https://doi.org/10.1617/s11527-015-0774-4>
7. Petrov, A., Pavliuchenkov, M., Nanka, A., Paliy, A. (2019). Construction of an algorithm for the selection of rigid stops in steel concrete beams. *Eastern-European Journal of Enterprise Technologies*, 1 (7 (97)), 41–49. doi: <https://doi.org/10.15587/1729-4061.2019.155469>
8. Sun, C., Chen, J., Zhu, J., Zhang, M., Ye, J. (2013). A new diffusion model of sulfate ions in concrete. *Construction and Building Materials*, 39, 39–45. doi: <https://doi.org/10.1016/j.conbuildmat.2012.05.022>
9. Bonakdar, A., Mobasher, B., Chawla, N. (2012). Diffusivity and micro-hardness of blended cement materials exposed to external sulfate attack. *Cement and Concrete Composites*, 34 (1), 76–85. doi: <https://doi.org/10.1016/j.cemconcomp.2011.08.016>
10. Bastidas-Arteaga, E. (2018). Reliability of Reinforced Concrete Structures Subjected to Corrosion-Fatigue and Climate Change. *International Journal of Concrete Structures and Materials*, 12 (1). doi: <https://doi.org/10.1186/s40069-018-0235-x>
11. Bordunova, O. G., Loboda, V. B., Samokhina, Y. A., Chernenko, O. M., Dolbanosova, R. V., Chivanov, V. D. (2020). Study of the Correlations Between the Dynamics of Thermal Destruction and the Morphological Parameters of Biogenic Calcites by the Method of Thermoprogrammed Desorption Mass Spectrometry (TPD-MS). *Microstructure and Properties of Micro- and Nanoscale Materials, Films, and Coatings (NAP 2019)*, 37–50. doi: https://doi.org/10.1007/978-981-15-1742-6_5
12. Kuznetsov, V. N., Yanovska, A. A., Novikov, S. V., Starikov, V. V., Kalinichenko, T. G., Kochenko, A. V. et. al. (2015). Study of Thermal Activated CO₂ Extraction Processes from Carbonate Apatites Using Gas Chromatography. *Journal of Nano- and Electronic Physics*, 7 (3), 03034. Available at: https://jnep.sumdu.edu.ua/en/full_article/1557
13. Hilal, A. A. (2016). Microstructure of Concrete. *High Performance Concrete Technology and Applications*. doi: <https://doi.org/10.5772/64574>
14. Nnaji, C. C., Amadi, U. H., Molokwu, R. (2016). Investigative Study of Biodeterioration of External Sandcrete/Concrete Walls in Nigeria. *Research Journal of Environmental Toxicology*, 10 (2), 88–99. doi: <https://doi.org/10.3923/rjet.2016.88.99>
15. Pokrovskiy, V. A. (2000). Temperature-programmed Desorption Mass Spectrometry. *Journal of Thermal Analysis and Calorimetry*, 62, 407–415. doi: <https://doi.org/10.1023/A:1010177813557>
16. Waksman, S. A., Joffe, J. S. (1922). Microorganisms Concerned in the Oxidation of Sulfur in the Soil: II. *Thiobacillus Thiooxidans*, a New Sulfur-oxidizing Organism Isolated from the Soil. *Journal of Bacteriology*, 7 (2), 239–256. doi: <https://doi.org/10.1128/jb.7.2.239-256.1922>
17. Nieminen, S. M., Kärki, R., Auriola, S., Toivola, M., Laatsch, H., Laatikainen, R. et. al. (2002). Isolation and Identification of *Aspergillus fumigatus* Mycotoxins on Growth Medium and Some Building Materials. *Applied and Environmental Microbiology*, 68 (10), 4871–4875. doi: <https://doi.org/10.1128/aem.68.10.4871-4875.2002>
18. Wasik, A. (2007). *Electron Microscopy: Methods and Protocols*, by J. Kuo, ed. Humana Press 2007. 608 pp. ISSN 1064-3745. *Acta Biochimica Polonica*, 54 (4), 887–888. Available at: <https://ojs.ptbioch.edu.pl/index.php/abp/article/view/5078/4128>
19. Skomoroha, V. N., Zarechniy, V. G., Vorob'eva, I. P., Vakal, S. V.; Skomoroha, V. N. (Ed.) (2002). *Proizvodstvo dvoukisi titana pigmentnoy sul'fatnym sposobom*. Sumi: ATZT «Arsenal-Press», 204. Available at: <https://essuir.sumdu.edu.ua/handle/123456789/2527?locale=uk>
20. Yang, L., Zhao, D., Yang, J., Wang, W., Chen, P., Zhang, S., Yan, L. (2019). *Acidithiobacillus thiooxidans* and its potential application. *Applied Microbiology and Biotechnology*, 103 (19), 7819–7833. doi: <https://doi.org/10.1007/s00253-019-10098-5>
21. Justs, J., Bajare, D., Korjajins, A., Mezinskis, G., Locs, J., Bumanis, G. (2013). Microstructural Investigations of Ultra-High Performance Concrete Obtained by Pressure Application within the First 24 Hours of Hardening. *Construction Science*, 14. doi: <https://doi.org/10.2478/cons-2013-0008>
22. Wei, S., Jiang, Z., Liu, H., Zhou, D., Sanchez-Silva, M. (2013). Microbiologically induced deterioration of concrete: a review. *Brazilian Journal of Microbiology*, 44 (4), 1001–1007. doi: <https://doi.org/10.1590/s1517-83822014005000006>
23. Song, Y., Tian, Y., Li, X., Wei, J., Zhang, H., Bond, P. L. et. al. (2019). Distinct microbially induced concrete corrosion at the tidal region of reinforced concrete sewers. *Water Research*, 150, 392–402. doi: <https://doi.org/10.1016/j.watres.2018.11.083>
24. Van de Veerdonk, F. L., Gresnigt, M. S., Romani, L., Netea, M. G., Latgé, J.-P. (2017). *Aspergillus fumigatus* morphology and dynamic host interactions. *Nature Reviews Microbiology*, 15 (11), 661–674. doi: <https://doi.org/10.1038/nrmicro.2017.90>
25. Cwalina, B. (2008). Biodeterioration of concrete. *Architecture Civil Engineering Environment*, 1 (4), 133–140. Available at: <http://yadda.icm.edu.pl/yadda/element/bwmeta1.element.baztech-article-BSL2-0022-0118>
26. Yakovleva, G., Sagadeev, E., Stroganov, V., Kozlova, O., Okunev, R., Ilinskaya, O. (2018). Metabolic Activity of Micromycetes Affecting Urban Concrete Constructions. *The Scientific World Journal*, 2018, 1–9. doi: <https://doi.org/10.1155/2018/8360287>