The object of this study is the regularity of changes in the biogenic destructive effect of microorganisms on the concrete structural elements of livestock facilities due to the use of the original liquid phase mixture of disinfectant based on aldehyde and surfactant.

Microorganisms use construction materials as a substrate for growth and nutrition; they produce citric acid, which leads to a change in the composition and morphology of hydrated cement new formations.

The composition of the microflora of the pigsty has been determined, and the minimum concentration of disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride was found. By the TPD MS method, a decrease in the intensity of carbon dioxide (CO_2) release in concrete samples during the heating of the sample to 900 °C was proved, compared to the control intact corrosion sample. Electron microscopy of concrete samples shows the presence of destructive changes and colonies of micromycetes. It was established that calcite was intensively released in the control sample of concrete, which retained its integrity and was not subjected to corrosion when heated to a temperature of 600 °C. Electron microscopy confirms the preservation of the homogeneous structure of concrete.

The use of a disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride at a concentration of 1 % destroys colonies of micromycetes, 2 % – the shell of microorganisms, and 3 % – biofilm. Treatment of concrete with a disinfectant at a concentration of 3 % destroys microorganisms Aspergillus fumigatus and Penicillium oxalicum, inhibits the process of biological corrosion of concrete, and strengthens the structure of concrete.

The results of the experiment can be applied to inhibit the corrosion of concrete and extend the life of building structures made of concrete through the use of a disinfectant based on aldehyde and didecyl dimethyl ammonium chloride at a concentration of 3 %

Keywords: biodestruction of construction materials, thermoprogrammed mass spectrometry, micromicents, carbonates, calcium citrate

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REDUCING THE BIOGENIC CORROSION OF CONCRETE IN A PIGSTY BY USING DISINFECTANTS

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1. Introduction

Scientific studies that address the issues of chemical and biological interrelated corrosion of concrete are very important. Microbial-induced corrosion is considered as a process in which microorganisms change the properties of construction materials and lead to destruction [1, 2].

During the fermentation of silage and milk, lactic acid ($CH_3CHOHCOOH$) is formed, which reduces the pH to 5 [3]. Bacterial and fungal corrosion leads to a significant

increase in water absorption and a decrease in the density of concrete [4]. The proposed solutions for the cessation of biological corrosion of concrete for this problem are quite limited [5]. In [6], it was established that under the action of corrosion, the physicochemical properties of the concrete material change significantly, which leads to a decrease in the corresponding resistance stresses to the spread of cracks.

In addition, each construction site has a different degree of aggressive environmental impact and service life. The results of such studies are needed in practice because the assimilation of construction materials by microorganisms leads to the destruction of building structures made of concrete.

To protect concrete structures, disinfectants from existing groups are most suitable for having an approximate to neutral pH and high efficiency. The representative of these types of disinfectants is quaternary ammonium compounds (QAC) [7]. The quaternary element nitrogen is found naturally in living systems, where it plays an important role in biological processes. QACs are used in the food and medical industry, animal husbandry for cleaning and surface disinfecting. They are characterized by low toxicity [8] and a wide range of antimicrobial action.

QACs are cationic detergents (surfactants) that can reduce surface tension and form micelles, which makes it possible to disperse in a liquid. They have hydrophobic membrane activity. Didecyl dimethyl ammonium chloride interacts with the cytoplasmic membrane of bacteria, and the plasma membrane of microscopic fungi and viruses. QACs also interact with intracellular targets and bind to DNA [9].

In addition, an effective component for the disinfectant can be glutaraldehyde. Glutaraldehyde has the formula of $C_5H_8O_2$, a molar weight of 100.12 g/mol, and is used to destroy microflora on the surface of building structures and in the air [10]. The drug belongs to the group of aldehydes and contains an active substance of at least 25 %. Single freezing (to –8 °C) does not change its physicochemical and disinfectant properties. Glutaraldehyde molecules are small enough to easily penetrate the pores of concrete. The mechanism of action on microorganisms is the denaturation of membrane proteins. Aldehyde is used to fix a sample intended for microscopy, in order to preserve as much as possible their structures in a constant state. It is also used in the leather industry and for impregnation of textile materials to give materials rigidity, reduce contamination, shrinkability, wear resistance, and hydrophobicity.

The relevance of the related studies is the need to determine the microbiological corrosion of concrete caused by microscopic fungi and find a way to destroy them.

2. Literature review and problem statement

The main task is the study of biological corrosion of concrete, which is caused by microorganisms, and the search for a way to inhibit it. Paper [11] proposed additives to concrete mix based on organic and inorganic antimicrobial compounds to prevent microbial corrosion of concrete. However, the disadvantage of this proposal is the need to completely replace the existing concrete structures with new ones with the addition of an anti-corrosion component. Thus, in the study of concrete by the TPD MS method, each sample will have excellent results, due to the degree of damage to the structure by corrosion and proliferation of microorganisms.

In [12], it was proved that due to the development of biogenic corrosion, dissolved and ionized calcium penetrated pores and washed out of concrete. Laboratory studies with concrete samples built on the reproduction of natural conditions take much less time compared to the actual corrosion process on site. However, the researchers faced the problem of reproducing real conditions in the laboratory. experiments at the site of biological corrosion development were described, but the researchers could not reproduce a sufficient period of exposure to biogenic corrosion on concrete. To solve the problem, experiments at the site of the development of biological corrosion are described in [13], however, the researchers could not reproduce a sufficient time period of the impact of biogenic corrosion on concrete. Biological corrosion, which is formed at a particular object, is specific due to many factors, and it is practically impossible to reproduce it under laboratory conditions.

Therefore, it is interesting and promising to study existing concrete building structures and determine the technique of stopping the further development of biological corrosion.

In addition, the presence of constant moisture in the room, which impregnates the pore space of concrete, impairs its strength characteristics [14]. Even with a slight load, cracks appear in the concrete. The researchers determined the degree of destruction of the structure of the facility but the physical and chemical changes that occurred in the concrete were not taken into consideration.

To protect concrete structures, disinfectants from existing groups are most suitable for having an approximate to neutral pH and high efficiency. The representative of these types of disinfectants is quaternary ammonium compounds (QAC). However, the mechanisms of destruction of the membranes of microorganisms by QAC have not yet been clarified [15].

In [16], the sensitivity of five different types of bacteria and microscopic fungus was proved – *Trichophyton mentagrophytes* to 2 % of glutaraldehyde, and 0.4 % of a quaternary ammonium compound. The disadvantage of the study is that the experiment was carried out in a laboratory, and disinfection took place on smooth surfaces. Concrete has a porous structure, so the studies carried out do not provide accurate data on how disinfectants would destroy microorganisms on a heterogeneous surface and when penetrating into the structures of the material. Therefore, one of the tasks of the research was to determine the effectiveness of the disinfection of concrete with a surface-active substance and to determine with the help of electron microscopy the changes that occur in microorganisms when they interact with the agent.

In addition, a determining factor is the concentration of the disinfectant. Usually, biocides are used in the concentrations specified in the instructions for use. In [17], it is reported about the often-acquired resistance of microorganisms to the agents of QAC. However, laboratory and production studies have been carried out only on work surfaces that have a smooth structure, such as glass, plastic, and tile. No studies have been conducted on the resistance of microorganisms in materials that have a porous structure, such as concrete, brick, wood, or plaster.

Didecyl dimethyl ammonium chloride (D_4) refers to QACs and is used in the disinfection of premises, has hydrophobic membrane activity. It was established that the activity of QAC can decrease in the presence of cellulose and organic residues (manure, milk, skin epithelium), and it

also does not affect spores of microorganisms and enveloped viruses [18]. The use of one product for high-quality disinfection of concrete may not be enough as it has limitations in the spectrum of action. In addition, there are no data on the effectiveness of its action in concrete and the impact on its structure. Therefore, another disinfectant from another group of biocides and a mechanism of action on microorganisms was chosen for the study.

The authors of [19] tested the glutaraldehyde destruction of microflora on the surface of building structures and in the air on the farm. Despite the positive effect, the minimum effective bactericidal concentration for disinfecting concrete and its effect on the structure remains unclear.

Based on the analysis of previous experiments, it became necessary to study the microbial corrosion of concrete at livestock facilities, which progresses over time. In addition, studies should cover the choice of a disinfectant that is not aggressive to concrete but effective for the destruction of microorganisms. When choosing disinfectants, attention was paid to the spectrum of antimicrobial action. We also selected components that had a different mechanism of action on the microbial cell to maximize the coverage of antimicrobial properties. When calculating the effective concentration of each component of the disinfectant, the possibility of reducing its antimicrobial properties in the presence of organic animal residues was taken into consideration. In addition, we took into consideration the degree of possible corrosion effect on the building structures of the pigsty.

The use of an experimental complex liquid disinfectant for the destruction of microorganisms in concrete is justified to prevent the destruction of building structures of livestock facilities.

3. The aim and objectives of the study

The aim of this study is to determine the influence of microorganisms on the formation of structural changes in the concrete of livestock facilities, which lead to their destruction. This will determine ways to reduce the biogenic effect on concrete using disinfectants.

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

– to determine the presence and intensity of structural changes in concrete under the conditions of action of an aggressive environment created with the participation of microorganisms using thermoprogrammed mass spectrometry and electron microscopy;

– to investigate the composition of the circulating microflora in the pigsty room and determine the effective concentration of the disinfectant in relation to isolated microorganisms;

– to determine the antimicrobial activity of the disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride in different concentrations in samples of concrete affected by microorganisms using electron microscopy.

4. The study materials and methods

4. 1. The object and conditions of the study

Laboratory tests were performed in the laboratory of veterinary pharmacy and electron microscopy at the Faculty of Veterinary Medicine, Sumy National Agrarian University; Laboratories of the Department of Radiation Biophysics at the Institute of Applied Physics of the National Academy of Sciences of Ukraine (Sumy, Ukraine).

The object of this study is concrete (cement-sand mortar) in the pigsty room.

The subject of the study is the regularities of changes in the biogenic destructive effect of microorganisms on the concrete structural elements of livestock facilities.

The main hypothesis of the study assumed that based on determining the structural changes in concrete under the action of microorganisms, it is possible to reasonably choose original liquid-phase mixtures of disinfectant based on aldehyde and surfactant, which would minimize the destructive effect of microorganisms.

Production studies were carried out at the pig farm of Sumypostachfond LLC, Sumy district, Sumy oblast in the period of 2021–2022. Studies were performed in the pig fattening workshop. The four-row pigsty for 1200 heads of pigs was commissioned in 1975. The facility is built of reinforced concrete trusses, the floor is concrete.

For disinfection, we used a complex liquid disinfectant containing active ingredients (%): glutaraldehyde – 60.0; didecyl dimethyl ammonium chloride – 40.0. Solutions of 1–3 % solution of experimental disinfectant were used. The disinfectant solution was prepared before use at a temperature of 18–20 °C and applied by spraying.

4. 2. Procedure for studying circulating microflora

Washouts were carried out from the surfaces of the building structures of the farm (walls, machines, feeders, floor). Cultivation of microorganisms was performed on elective media, taking into consideration species. The cultivation of microscopic fungi was carried out on the apek-Dox medium [20].

4. 3. Procedure for determining the antimicrobial action of disinfectants

The method of diffusion into agar holes in Petri dishes was used [21]. Complex disinfectant in different concentrations (1–3 %) was poured into the wells of meat-peptone agar with cultures of isolated microorganisms. Petri dishes were placed in a thermostat for 48 hours after which we determined the zone of delayed growth of microorganisms around the holes with a disinfectant.

Concrete samples, which were taken from the pigsty, were also treated with various solutions of experimental complex disinfectant (1 %, 2 %, and 3 %). The result of the destruction of microorganisms was determined using electron microscopy and TPD MS.

4. 4. Procedure for studying concrete samples using TPD MS

Concrete samples were obtained from the walls and floor of the pigsty, measuring 0.2–0.5 cm^2, selecting the most corrosive-affected areas. A thermally programmed mass spectrometry (TPD MS) plant was used to study concrete samples. Concrete samples weighing 5–10 mg were heated at temperatures from 40 to 900 °C. At the same time, fixation of the mixture of gases took place using the mass spectrum, which was separated during heating. Gases were identified by molecular masses (m/z): H_2O – 18 a.o.m., CO – 28 a.o.m., CO_2 – 44 a.o.m. [22]. The intensity of peaks of ions in mass spectra was given in arbitrary units (a.u.). The basic principles of identification of chemical compounds by their molecular weight are given in detail in the procedures from [23].

4. 5. Scanning electron microscopy procedure for concrete samples

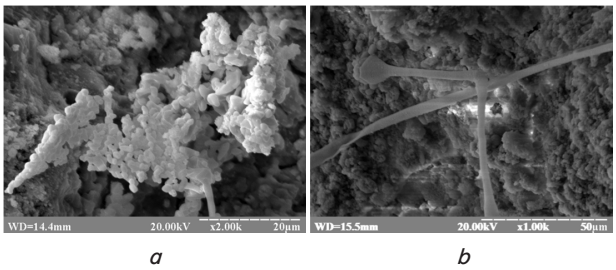
The microscopic structure of concrete samples was examined by scanning electron microscopy using the device REM 106 and (VAT SELMI, Sumy, Ukraine). A raster electron microscope with a mode of secondary electrons in the range of electron-optical magnifications from 200 to 5,000 times was used for research. To study the biofilms of microorganisms, concrete samples were fixed with 2.5 % glutaraldehyde on 0.2M phosphate buffer solution, dehydrated in a series of ethyl alcohols of increasing concentration, and sprayed with silver [24].

5. The results of studying the biological corrosion of concrete and determining the effectiveness of the experimental disinfectant

5. 1. The results of studying the presence and intensity of structural changes in concrete under the conditions of action of an aggressive environment created with the participation of microorganisms using thermoprogrammed mass spectrometry and electron microscopy

Concrete samples were taken in the pigsty room (control – unchanged, and experimental – with signs of corrosion). All concrete samples were examined using electron microscopy and thermoprogrammed mass spectrometry.

In the premises of the pigsty, micromycetes of the genus *Penicillium oxalicum* (Fig. 1, *a*) and *Aspergillus fumigatus* (Fig. 1, *b*) were isolated through microbiological studies of the premises and using raster electron microscopy of concrete samples. Hyphae of the fungus grow in concrete, in which smaller hyphae rise at the ends, which end with spherical cells – conidia.

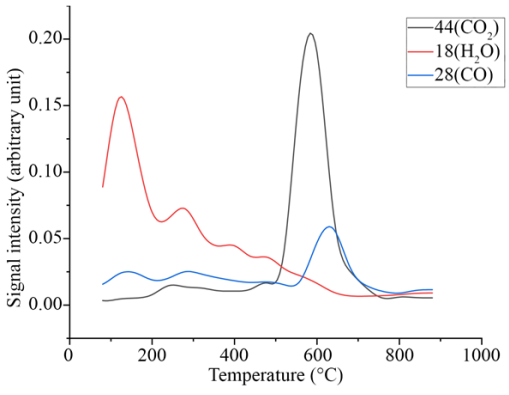


a *b*

Fig. 1. Raster electron microscopic image of microorganisms in concrete: a – *Penicillium oxalicum*; *b* – *Aspergillus fumigatus* (hyphae and conidia)

Microscopic fungi assimilating concrete lead to the formation of calcium citrate crystals. The reason for the formation of these crystals is the interaction of the alkaline medium of concrete with organic acids that are secreted by micromycetes. Thus, interrelated microbiological and chemical corrosion of construction materials occurs. Depending on the degree of damage to concrete by fungi, characteristic formations of crystals can be seen over a large area of construction materials (Fig. 3, *b*).

To determine the constituent components of concrete and structural changes, a thermoprogrammed mass spectrometry was carried out on those control samples that were not damaged and had no signs of biological corrosion (Fig. 2).



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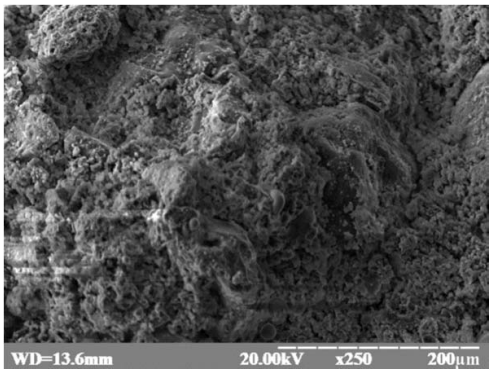


b

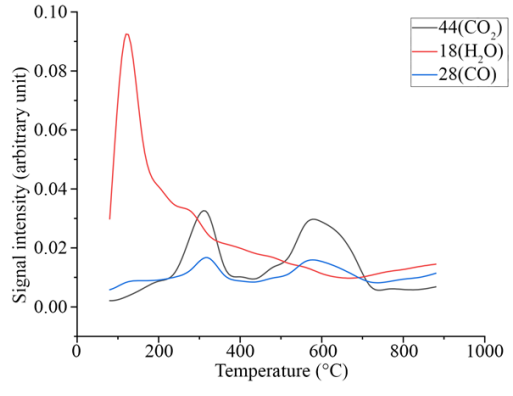
Fig. 2. Structural changes in concrete: *a* – thermograms of H_2O release (m/z=18), CO release (m/z=28), CO_2 (m/z=44) release from the control sample of concrete; *b* – raster electron microscopic image of a concrete sample with a preserved structure

The thermoprogrammed mass spectrometry showed that when the sample was heated (Fig. 2, *a*) to a temperature of 100 °C, water was released (H_2O (m/z=18) with an intensity of up to 0.16 arbitrary units (a.u.). When heated to a temperature of 600 °C, gas-phase carbon oxides were released more intensively due to the thermal destruction of carbonates (mainly calcium), namely: CO_2 (m/z=44) with an intensity of 0.2 a.u. and CO (m/z=28) with an intensity of 0.06 a.u. The intense peak of carbon dioxide release indicates the preservation of the pristine integrity of the concrete structure, one of the components of which is calcium carbonate ($CaCO_3$).

In a subsequent study, a sample of concrete most affected by microorganisms and subjected to corrosion was analyzed (Fig. 3).

According to the results of the study, it can be noted that water began to be released at a temperature of 100 °C and then gradually evaporated when heated to 1000 °C. The intensity of carbonate release is low, the peaks are not clear. The first peak of CO_2 release corresponds to a low intensity – 0.03 a.u. (85 %), compared with control, within the temperature regime of 200–300 °C, which appears due to the burnout of organic substances – in our case, mainly microorganisms. The second peak of CO_2 is in the temperature range of 500–600 °C with 0.23 a.u. (88.5 %), asymmetric, with low intensity, associated with an insufficient amount of calcium carbonate and the loss of its original micro- and macrostructure. The process occurs when acids interact, secreted by microscopic fungi into car-

bonates. Therefore, in this concrete sample, there is a shortage of $CaCO_3$ and, as a result, partial destruction of the concrete structure and the formation of insoluble salts. A similar situation with CO release with an intensity of –0.010 a.u. (83.3 %), in comparison with the control sample, according to the first peak in the range of 200–300 °C, during the destruction of microorganisms. The second peak also has a low CO release intensity of 0.008 a.u. (86.6 %), compared to the control. In addition, under the condition of even an approximate estimated analysis of the shape of the peak corresponding to CO_2, it is clearly seen that it consists of a lesser than two components – the first peak is located in the range of 420–530 °C, and the second



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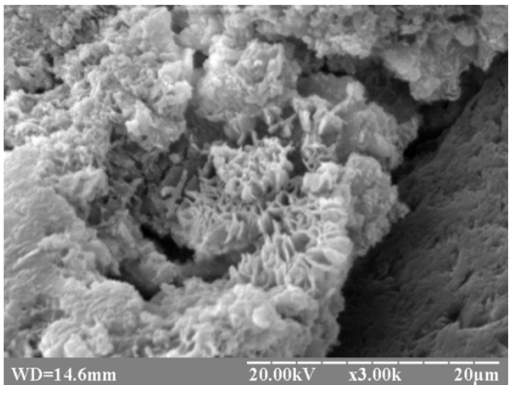
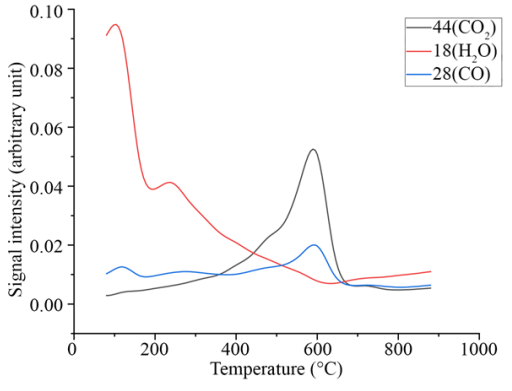


b

Fig. 3. Structural changes in concrete: *a* – thermograms of H_2O release (m/z=18), CO release (m/z=28), CO_2 release (m/z=44) from a concrete sample that is most susceptible to corrosion; *b* – raster electron microscopic image of calcium citrate crystals in concrete samples obtained in the pigsty room

A more powerful peak of CO_2 in the range of 450–750 °C originates from the internal component of carbonate structures, which still retains its original integrity and has not undergone the destructive effects of acids and other secondary metabolites of microflora.

After determining the effective concentration of a two-component disinfectant that corresponded to 3 %, the concrete sample was treated and dried. Subsequently, thermoprogrammed mass spectrometry of the treated concrete sample was carried out (Fig. 4, *a*), which showed differences in comparison with the control and the most destroyed untreated samples.



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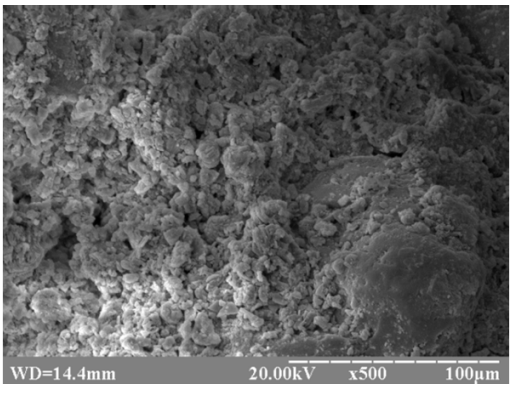


b

Fig. 4. Structural changes in concrete: *a* – thermograms of H_2O release (m/z=18), CO release (m/z=28), CO_2 release (m/z=44) from a concrete sample; *b* – raster electron microscopic image of concrete moderately affected by corrosion, treated with a 3 % concentration of disinfectant

There is a certain pattern in the reported studies; the more concrete is affected by microorganisms and has a destroyed loose structure, the faster it undergoes destruction when heated at lower temperatures with a low intensity of release of dioxide and carbon monoxide within wider temperature limits – 450–750 °C. This testifies in favor of the fact that the acidic environment formed by microflora destroys primarily the surface layers of carbonate structures with their loosening and loss of ability to withstand the effects of elevated temperatures. It is these structures that are the source of CO_2, which is the first conditional peak (420–530 °C) of the wide diffuse peak of total CO_2 from thermally degraded carbonates.

The results of thermoprogrammed mass spectrometry showed that when the sample was heated to a temperature of 100 °C, H_2O was released with an intensity of up to 0.09 a.u. Carbonates were released when the sample was heated to a temperature of 600 °C, the peaks of CO_2 release corresponded to 0.045 a.u. (22.5 %), and CO – 0.015 a.u. (25 %) are smaller compared to the control sample. However, the intensity of carbonate release is much higher compared to the sample affected by microscopic fungi (Fig. 3, *a*), there is also no peak of burnout of organic substances due to the use of disinfectant. Thus, the intensity of release was 50 % greater than CO_2 and CO compared to the most affected raw concrete sample at the highest peak. Note that the peak corresponding

to carbon dioxide CO_2, although it remains two-component, but its shape is more closely close to control due to the fact that the absence of microrganisms that cause chemical destruction of concrete due to the acidic environment is almost imperceptible due to the action of disinfectants.

Our study shows that the use of a two-component disinfectant at a concentration of 3 % destroys microorganisms, which makes it possible to inhibit the process of biological corrosion of concrete and strengthens the structure of concrete.

5. 2. The results of studying the composition of microflora in the pigsty and determining the effective concentration of disinfectant

In order to study the composition of the circulating microflora in the pigsty, samples were obtained from working surfaces and air. The effective concentration of disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride was determined in relation to the isolated field isolates (Table 1).

Table 1

The results of studying the composition of the circulating microflora in the pigsty

The number of test samples, pcs.	Microorganisms	%, of the total number of samples
20	*Aspergillus fumigatus*	54
20	*E. coli*	42
27	*Penicillium oxalicum*	29
35	*S.aureus*	27
32	*S. enteritidis*	32
22	*S. epidermidis*	25
31	*S. choleraesuis*	23
25	*C. perfringens*	16
25	*E. fecalis*	10

It was found that microflora circulates on the surface of objects and in the air, a significant part of it is made up of bacteria: *S.aureus, E. coli*, and microscopic fungi: *Aspergillus fumigatus* and *Penicillium oxalicum*. Microorganisms whose proportion was less than five percent were not taken into consideration. Of all the microorganisms isolated, microscopic fungi of the genus *Aspergillus* and *Penicillium* are of the greatest importance since they are autotrophs.

The growth of micromycetes of the genus *Aspergillus* and *Penicillium* is promoted by high humidity and poor ventilation in the room. The source of microsporidia in the pigsty can be animals and feed affected by mold fungi. Microscopic fungi are those microorganisms that are the first to begin the assimilation of concrete and create conditions for the existence of other microorganisms. However, other microorganisms given in Table 1, are not aggressive to building materials and do not have the ability to assimilate concrete.

To determine the effective concentration of the experimental disinfectant, a study was conducted to determine the sensitivity of the isolated field strains of microorganisms in the pigsty. Identified as the most aggressive for construction materials are the microorganisms *Aspergillus fumigatus* and *Penicillium oxalicum*. In addition, *E. coli* and *S. aureus* were used as a control of the sensitivity of bacteria to the disinfectant. The presence or absence of these microorganisms is an indicator of the quality of disinfection (Table 2).

Table 2

Sensitivity of microorganisms to the experimental liquid complex disinfectant (M±m), n=7

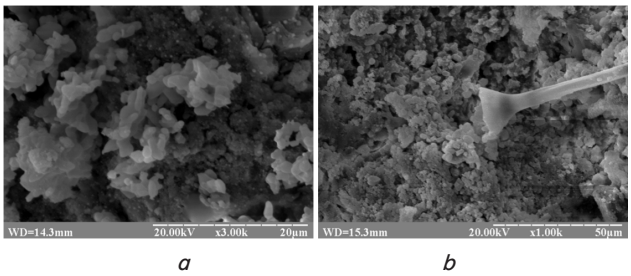
Culture	Disinfectant	Zone of growth retardation, mm
Aspergillus fumigatus	1 %	26.52±0.10
	2 %	53.30±0.18
	3 %	96.41±0.22*
Penicillium oxalicum	1 %	27.62±0.15
	2 %	79.43±0.25
	3 %	88.04±0.48*
E. coli	1 %	46.36±0.16
	2 %	73.72±0.25
	3 %	145.51±0.82*
S. aureus	1 %	31.09±0.14
	2 %	69.55±0.27
	3 %	125.28±0.12*

*Note: * – $p \leq 0,05$ compared to the lowest concentration*

As a result of the research, it was established that the experimental disinfectant showed bactericidal properties in relation to the specified microorganisms. The growth retardation zone is considered sufficient if it is at least 25 mm. Therefore, the concentration of the disinfectant at 1 % is considered the minimum permissible according to the procedure used. The largest zone of growth retardation of microorganisms was probably manifested by an experimental disinfectant at a concentration of 3 % with *Aspergillus fumigatus* by 36.3 %, *Penicillium oxalicum* – by 31.8 %, *E. coli* – by 31.3 %, *S. aureus* – by 40.2 %, compared with 1 % ($p \leq 0.05$). Our results make it possible to conduct the following study on the effectiveness of the disinfection of microorganisms in construction materials.

5. 3. Results of studying the antimicrobial activity of disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride

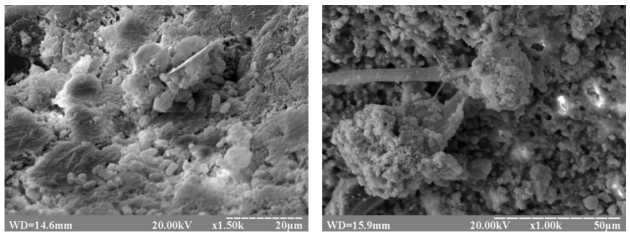
To determine the effectiveness of the destruction of microorganisms inside the concrete, samples were treated with a disinfectant at a concentration of: 1 %, 2 %, and 3 %. The result of the study was determined using electron microscopy. The disinfectant showed activity at a concentration of 1 % against *Penicillium oxalicum* (Fig. 5, *a*) and *Aspergillus fumigatus* (Fig. 5, *b*) causing the colony to be destroyed into separate small groups.



a *b*

Fig. 5. Raster electron microscopic image of concrete samples after treatment with 1 % disinfectant solution, colony destruction: *a* – *Penicillium oxalicum*; *b* – *Aspergillus fumigatus*

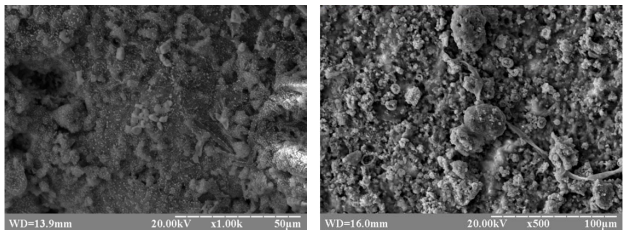
Microorganisms suffer more significant damage from the disinfectant upon contact with a 2 % solution. There is a destruction of colonies of *Penicillium oxalicum* into separate structures and damage to the shell (Fig. 6, *a*). Conidia of micromycete *Aspergillus fumigatus* also lose their shell and the contents of the cytoplasm are released, but the hyphae retain their integrity (Fig. 6, *b*).



a *b*

Fig. 6. Raster electron microscopic image of concrete samples after treatment with 2 % disinfectant solution, destruction of the colony and shell of micromycetes: *a* — Penicillium oxalicum; *b* — Aspergillus fumigatus

The maximum bactericidal effect is registered when using a disinfectant at a concentration of 3 %. There is a complete destruction of the integrity of microorganisms and biofilm. To protect their colonies from environmental influences, microorganisms form a biofilm that is able to withstand a concentrated solution of disinfectants. However, the experimental disinfectant destroys the biofilm around *Penicillium oxalicum* (Fig. 7, *a*) and *Aspergillus fumigatus* (Fig. 7, *b*)



a *b*

Fig. 7. Raster electron microscopic image of concrete samples after treatment with 3 % disinfectant solution, destruction of microorganism biofilm: *a* — Penicillium oxalicum; *b* — Aspergillus fumigatus

Our studies have established that in the premises of pigsty concrete is exposed to microbiological effects and, as a result, chemical corrosion. Isolated microscopic fungi cause a change in the structure of concrete. The use of the proposed disinfectant at a concentration of 1 % to 3 % destroys microscopic fungi, which makes it possible to suspend the process of further destruction of concrete.

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

Our studies have established that the bulk of the circulating microflora in the pigsty (Table 1) are *E. coli, S .aureus*, *Aspergillus fumigatus,* and *Penicillium oxalicum*. In [25], microscopic fungi and bacteria were also the cause of biological corrosion of concrete.

The minimum determined permissible concentration of disinfectant is 1 % (Table 2). However, the largest zone of growth retardation of microorganisms was shown by a disinfectant at a concentration of 3 % with *Aspergillus fumigatus* by 36.3 %, *Penicillium oxalicum* – by 31.8 %, *E. coli* – by 31.3 %, *S. aureus* – by 40.2 %, compared to 1 % ($p \leq 0.05$). The authors of [26] also confirmed in their experiments that disinfectants have different effects on microorganisms, depending on the concentration.

A comparative analysis of the relative content of compounds (H_2O; CO_2; CO) in concrete prototypes (Fig. 3–5, *a*) was carried out. The established and explained mechanism for the formation of chemical compounds in concrete was compared to control samples. The disadvantage of the TPD MS method is that it shows the qualitative composition of the research material, rather than quantitative. Therefore, in the experiment, the method of comparative analysis is always applied to the control sample.

Since calcium carbonate is one of the constituent components of concrete, a decrease in its amount in the material inevitably leads to the destruction of its structure. Our studies have proven the presence in the samples of microscopic fungi *Aspergillus fumigatus* and *Penicillium oxalicum,* which were the main cause of microbiological corrosion in the pigsty (Fig. 1, *a*, *b*). Thus, in work [27], it was established that microscopic fungi can be one of the causes of concrete destruction.

Using the method of thermoprogrammed mass spectrometry, it was established that in the control sample of concrete that retained its integrity and was not subjected to corrosion when heated to a temperature of 600 °C, calcites were intensively released, namely: CO_2 (m/z=44) with an intensity of 0.2, and CO (m/z=28) with an intensity of 0.06 (Fig. 2, *a*). Electron microscopy shows the preservation of a homogeneous structure of concrete (Fig. 2, *b*).

The study of a concrete sample by TPD MS obtained from a pigsty that has signs of corrosion and is affected by microscopic fungi showed a low intensity of carbonate release, the peaks are not clear (Fig. 3, *a*). The first peak of CO_2 release appears due to the burnout of microorganisms, the second – as a result of the destruction of $CaCO_3$ in concrete. A similar situation is with the release of CO with a low intensity of two peaks.

There is a certain pattern in our studies; the more concrete is affected by microorganisms and has a destroyed loose structure [28], the faster it undergoes destruction when heated at lower temperatures with a low intensity of carbonate release. The authors of [29] in their laboratory studies also found that there was a decrease in calcium content by about 41 % after the growth of fungi on concrete.

This is explained by the fact that acidic exotoxins of microscopic fungi prevent the formation of gypsum. The formation of citrate (citric) acid (Fig. 3, *b*) is especially characteristic of micromycetes *Aspergillus* [20] and *Penicillium* [30].

As a result of the interaction of concrete carbonates with citric acid, insoluble solid calcium citrate crystals are formed (1):

$$3Ca(OH)_2 + \underset{\text{citric acid}}{2C_3H_4(OH)(COOH)_3} = \underset{\text{calcium citrate}}{= Ca_3\left[C_3H_4(OH)(COO)_3\right]_2} + 6H_2O. \quad (1)$$

A sample of concrete obtained from the pigsty that showed signs of corrosion and damage by microscopic fungi was treated with a disinfectant at a concentration of 3 % (Fig. 4, *a, b*). As a result, the intensity of CO_2 and CO release was 50 % higher compared to the most affected untreated concrete sample at the highest peak. The obtained result became possible thanks to the use of a two-component disinfectant based on glutaraldehyde [31] and didecyl dimethyl ammonium chloride in a concentration of 3 %, which made it possible to inhibit the process of biological corrosion of concrete and strengthen the concrete structure. Strengthening of concrete occurs through the use of a component of the disinfectant – glutaraldehyde, which has the ability to fix organic and inorganic substances [32]. In addition, glutaraldehyde in the composition of other biocides was tested to protect building structures from damage by microscopic fungi [33].

In the study, the working concentration of the disinfectant in the laboratory with cultures of microorganisms was preliminarily calculated and then tested during the treatment of concrete contaminated with micromycetes. As a result of our experiment, it was found that didecyl dimethyl ammonium chloride interacted with the cytoplasmic membrane of micromycetes (Fig. 6), destroyed their colonies (Fig. 7), and destroyed their protective biofilm (Fig. 8) [34].

The experiment can be an example of microbiological corrosion of concrete, which is caused by microscopic fungi *Aspergillus fumigatus* and *Penicillium oxalicum*.

The limitation of this paper is that all studies to determine the effective concentration of the disinfectant were carried out in the laboratory. However, it should be borne in mind that the minimum permissible concentration of 1 % of the product may not work under industrial conditions due to the presence of additional circumstances: high humidity, organic contamination of concrete, etc., which significantly reduces the effectiveness of the proposed disinfectant.

The disadvantages of this study are that the peculiarities of the influence of the composition of concrete on the effectiveness of the proposed disinfectant to limit the microbiological corrosion of concrete have not been considered.

The area of further research is to find a way to reduce corrosion for concrete sewer systems at livestock facilities.

7. Conclusions

1. The presence of microbiological corrosion of concrete in the pigsty room, which is caused by micromycetes *Aspergillus fumigatus* and *Penicillium oxalicum*, has been experimentally proven. The result of the growth of microscopic fungi in concrete is interrelated chemical corrosion, which destroys the micro- and macrostructure of concrete and contributes to the formation of calcium citrate crystals.

2. The composition of the microflora of the pigsty has been determined, and the minimum concentration of disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride was established.

3. It is proved that the use of a disinfectant based on glutaraldehyde and didecyl dimethyl ammonium chloride at a concentration of 1 % destroys colonies of micromycetes, in 2 % – the shell of microorganisms, and in 3 % – biofilm. Treatment of concrete with a disinfectant at a concentration of 3 % destroys microorganisms, inhibits the process of biological corrosion of concrete, and strengthens its structure.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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