UDC 614.48:631.223
DOI: 10.15587/1729-4061.2019.179177

IMPROVEMENT OF FUNCTIONAL PERFORMANCE OF CONCRETE IN LIVESTOCK BUILDINGS THROUGH THE USE OF COMPLEX ADMIXTURES

O. Shkromada
Doctor of Veterinary Sciences, Associate Professor*
E-mail: oshkromada@gmail.com
And. Paliy
Doctor of Agricultural Sciences, Associate Professor**
O. Nechyporenko
PhD, Associate Professor*
O. Naumenko
PhD, Professor**
V. Nechyporenko
PhD, Associate Professor
Department of Marketing and Logistics
Sumy National Agrarian University
Herasyma Kondratieva str., 160, Sumy, Ukraine, 40021
O. Burlaka
PhD
Department of Construction and Civil Engeneering***
A. Reshetnichenko
Doctor of Agricultural Sciences, Associate Professor
Department of Veterinary Hygiene, Sanitation and Expertise
Odessa State Agrarian University
Panteleimonivska str., 13, Odessa, Ukraine, 65012
O. Tsereniuk
Doctor of Agricultural Sciences, Associate Professor
Department of Small Animal Husbandry and Horsbreeding
Institute of Animal Science of the National Academy of Agrarian Sciences of Ukraine
Tvarynnykiv str., 1-A, Kharkiv, Ukraine, 61026*
O. Shvets
PhD, Senior Lecturer*
A. Paliy
Doctor of Veterinary Sciences, Senior Researcher
Laboratory of Veterinary Sanitation and Parasitology
National Scientific Center «Institute of Experimental and Clinical Veterinary Medicine»
Pushkinska str., 83, Kharkiv, Ukraine, 61023
*Department of Therapy, Pharmacology, Clinical Diagnostics and Chemistry
Sumy National Agrarian University
Herasyma Kondratieva str., 160, Sumy, Ukraine, 40021
Department of Technical Systems and Animal Husbandry Technologies*
***Kharkiv Petro Vasylenko National Technical University of Agriculture
Alchevskykh str., 44, Kharkiv, Ukraine, 61002

При дослідженні бетонів у тваринницьких приміщеннях були виявлені ознаки корозії і руйнування бетонних підлог і стін. Експериментальними дослідженнями встановлені основні критичні моменти, які безпосередньо впливали на порушення цілісності бетону. У тваринницьких приміщеннях були виявлені надмірна волога; використання кислотних або лужних агресивних дезінфікуючих засобів, та наявність природних випорожнень тварин (сеча і фекалії).

Для вирішення цієї проблеми були запропоновані добавки – жовтий залізоокисний пігмент та рідке скло, які покращують міцністні характеристики бетону, термостійкість та зменшують проникаючу здатність.

В результаті проведених досліджень доведено, що введення у бетон добавки від 0,5 % до 2 % глибина проникнення хлоридів знижується у 2,8 рази, порівняно до контролю. Це відбувається за рахунок зменшення поглинання бетоном води при введенні в нього добавок оксиду заліза, купруму сульфату, надоцтової кислоти та силікату натрію, які викликали зменшення пор у зразках.

Запропоновано як новацію для визначення термостійкості бетону використання методу температурно-програмованої десорбційної мас-спектрометрії (ТПД-МС), основаного на залежності виходу оксиду вуглецю CO і діоксиду вуглецю CO_2 з зразків карбонатвміских речовин від температури нагрівання зразка.

При проведенні мікробіологічних досліджень визначені мікрогриби роду Penicillium та Fusariumта, бактерії Escherichia coli та Pseudomonas aeruginosa, які є причиною корозії бетону у тваринницьких приміщеннях. Ряд проведених експериментів доводить, що запропоновані добавки до бетонів (на основі жовтого залізоокисного пігменту (1,5–2,0 мас. %), надоцтової кислоти (0,2–0,3 мас. %), рідкого скла (2–3 мас. %) та купрум сульфату (0,5–1,0 мас. %)) мають протимікробні властивості та перспективи їх застосування у тваринництві

Ключові слова: тваринницькі приміщення, агресивне середовище, біологічна корозія бетонів, бактерицидні добавки, міцність бетону

Received date 02.08.2019
Accepted date 23.09.2019
Published date 31.10.2019

1. Introduction

In the study of cement stone, there are two levels: macroscopic and microscopic. The macroscopic level is made up of large air bubbles, cavities and pits formed, for example, by poor compaction of concrete mixture. These defects can be greatly reduced by using plasticizers. The whole spectrum of binders including the strongest fractions form the microscopic level. It also includes some new formations such as calcium hydroxide in an amount of about 15 % of the total mass of the solid phase of cement stone, gypsum and basic salts. Besides, a number of products that cause corrosion of concrete and crystallize in its pores, as well as precipitate on its surface as salts are characterized by particles of such sizes.

Ammonifying and sulfate-reducing bacteria actively proliferate in livestock buildings. Resistance of microorganisms to adverse environmental factors requires careful disinfection of buildings in which pathogens of infectious diseases of animals were identified. Chemical disinfectants are used in solid, liquid or gaseous forms. The most commonly used disinfectants include chlorine lime, alkalis, acids, chlorine-containing preparations and oxidizers, phenols and salts of heavy metals.

Numerous measures are taken to increase corrosion resistance of concrete structures. Service life extends through reduction of humidity in buildings and reconstruction of ventilation systems. Also, to repair old livestock buildings, such measures as partial repair and elimination of cracks and holes that aggravate danger of surface contamination with microorganisms can be taken. Plastering with bactericidal admixtures in mortar is used in major repair of buildings. This is intended to impart such surface form to the building structures that would prevent concentration of organogenic media on this surface. Also, outlet gutters are arranged and corrosive media are neutralized.

Currently, there is a wide range of choice of concrete admixtures and high-strength concretes are offered, however, most of them are of high cost and are down on demand in the agricultural industry. Bactericidal admixtures for concrete must retain their properties for a long time, that is they must not be prone to inactivation by other substances and products of cement hydration. At the same time, admixtures should not have a corrosive effect on concrete reinforcing bars nor impair physical and mechanical properties of concrete.

2. Literature review and problem statement

Structure of cement stone represents a solid phase and a pore space filled with liquid and gas. Concrete properties depend on physical and chemical characteristics of its solid phase and pore space.

Continuity is important for the solid phase and pH of liquids, moisture content and constant temperature are important for the pore space. A comprehensive approach to capillary-porous structure in concrete makes it possible to take into account formation of its solid phase and pore space on which physico-mechanical and deformation properties of concrete depend [1, 2].

Interior surfaces of building structures (both for residential and livestock buildings) are usually of concrete or cement mortar plaster. It was established that concrete has bactericidal properties at the first stage of operation due to the alkaline medium of the cement stone pore fluids [3]. This is explained by presence of moisture and dissolved calcium hydroxide in the pores formed during hydration of clinker materials. However, a year later, the outer layer of concrete structures completely loses its bactericidal properties. This is explained by neutralization of alkaline medium of the cement stone pore fluid caused by carbonation of calcium hydroxide with carbon dioxide of air: $Ca(OH)_2+CO_2=CaCO_3+H_2O$. This impact can be regarded as one producing corrosive medium in livestock buildings [4, 5].

Ammonia (NH_3) and hydrogen sulfide (H_2S) are components of animal excrements. Ammonia has a negative impact on building structures: floors, fencing, walls and sewage. Sulphurated hydrogen has a pronounced corrosion effect on concrete and steel reinforcement bars as well. Over time, iron sulfides (FeS) are formed, especially in places where concrete layer is too thin [6].

Moisture content grows in livestock buildings and a constant use of disinfectants brings about change of concrete pH. In addition, lactic acid ($CH_3CHOHCOOH$) is released from sour milk and silo. For example, fermentation of feeding staff in silo is associated with formation of organic acids (lactic, butyric, acetic acids in concentrations of 0.5–1.0 %) which is accompanied by temperature growth. In an anaerobic fermentation situation, temperature reaches 30–50 °C. Corrosive action of lactic acid on concrete is characterized by $pH<5$ [7, 8].

Relative humidity is very high in almost all livestock buildings often reaching 85 %. Condensate of water vapor on the surface of building structures penetrates the pore spaces and eventually leads to dehydration and cracking. Ammonium hydroxide (NH_4OH) is formed during interaction of ammonia (NH_3) with water and a basic medium arises [9].

Calcium carbonate ($CaCO_3$) is one of the most common substances found in the Earth's crust. It forms limestone and chalk rocks there and in building materials. Chemical and structural parameters of carbonates are immensely diverse which complicates their analysis. For example, it is difficult to isolate certain chemical ingredients, in particular, when producing carbon dioxide gas (CO_2) necessary for radiocarbon dating of samples by the content of carbon isotope 14C using accelerated mass spectrometry (AMS). To date, kinetics of $CaCO_3$ decomposition under the action of high temperature in accordance with reaction (1) has been studied in sufficient detail.

$$CaCO_3(s)\rightarrow CaO(s)+CO_2(g)\uparrow, \qquad (1)$$

where s is the solid phase state of the substance, g is the gas phase state of the substance. In particular, influence of various experimental factors on the reaction course (1) was studied, namely, rate of heating, particle size, composition of the gas medium, presence of impurities in carbonates of organic and inorganic nature, course of reaction under isothermal and non-isothermal conditions [10]. Note that the studies have been limited in most cases to the study of kinetics of decomposition of chemically pure synthetic $CaCO_3$. At the same time, detailed information is needed for applied studies, in particular quantitative evolution of carbon dioxide in accordance with reaction (1) for radiocarbon dating by the AMS method. This is the information on qualitative and quantitative reaction parameters associated with real samples having complex chemical and morphological structures. Based on the above, objective of [10] consisted in establishing limits of the temperature range and time of heating of concrete samples of complex composition for quantitative evolution of carbon dioxide from the samples to be subsequently used in radiocarbon dating by the AMS method.

Phenomenon of corrosion is common in concretes with low cement content or low cement grade. This often takes place at agricultural enterprises and is caused by cutting construction costs. Chlorine compounds lead to calcium levitation from concrete. Magnesium chloride and aluminum chloride ($MgCl_2$ and $AlCl_3$) react with calcium lime which increases risk of concrete corrosion. Calcium chloride destroys concrete if it is not well fixed and compacted [11, 12].

Studies [13] have found that destruction of concrete and loss of its strength over a large surface area took place in exposure of test specimens to environment of microorganisms. In addition to bacteria effect, concrete is very vulnerable to the effects of microscopic fungi. Appropriate admixtures should be introduced to provide concrete with long-lasting bactericidal activity.

No effective admixture has been developed so far to improve concrete service and antimicrobial properties and make it resistant to alkalis and acids used in livestock facilities. Another important aspect consists in environmental safety of building materials obtained: they should not emit substances toxic to animals and humans [14].

An option to overcome this problem may consist in introduction into the concrete used for flooring in the livestock buildings such admixtures that would protect it against biological damage and animals against pathogenic microflora [15, 16].

When thickness of the carbonized concrete layer and the protective layer becomes the same, corrosion of reinforcement bars starts. Steel corrosion products that have a larger volume than metal cause concrete cracking along the reinforcement bars and facilitate gas penetration. Destruction of structures caused by gas corrosion can occur both as a result of failure of reinforcement bars and concrete destruction [17, 18].

Analysis of importance of the factors determining fulfillment of the given conditions makes it possible to state that the most important contribution to ensuring reliability and durability of concrete is made by cement component. This is also confirmed by the data of cement importance in adaptive evolution of concrete. The modern notion of cement stone structure makes it possible to classify it with regard to such important characteristics as level and dispersion of the solid phase, size of pores, energy and forms of water binding. Particular place in concrete industry, in terms of providing specified properties, is taken by the study of the solid phase formed during hydration and curing of cement. It is formation of cement stone and its genesis that will determine, first and foremost, reliability and durability of the material under influence of variable factors [19, 20].

This problem is solved by introducing a composition of yellow iron oxide (Fe_2O_3) pigment, liquid glass, cuprous sulfate and acetic acid into concrete for floors of livestock buildings as basic components.

Admixtures are those ingredients that are added to the concrete mixture immediately before or during stirring. Iron oxides attributed to the coloring mixture improve certain mechanical properties [21]. Scientists prove that the use of nano ZrO_2, Fe_3O_4, TiO_2 and Al_2O_3 at a constant content enhance mechanical properties of fresh and cured concrete, for example, compressive strength [22].

Composition of the experimentally developed biocidal admixture to concrete was selected due to physicochemical characteristics of its components. Liquid glass is known as the substance commonly used in construction to coat building structures. Its addition to concrete improves insulating and strength properties of the latter [23].

Acetic acid (CH_3COOOH) is formed by interaction of concentrated hydrogen peroxide with glacial acetic acid. Under the action of peracetic acid, the cell membrane and enzyme system of bacteria are destroyed and they die at high concentrations. The range of action of acetic acid is quite wide. Peracetic acid concentration in a range of 0.005–0.2 % is sufficiently effective for action duration from 30 s to 30 min to ensure complete destruction of fungi and their spores. Peracetic acid has a corrosive effect, so low acid concentrations were used in the studies and cuprous sulfate was added [24, 25].

Copper tailings have a slight negative effect on sedimentation when time and porosity of mixtures are determined. However, mixtures containing copper tailings have improved mechanical strength and abrasion resistance, as well as reduced chloride penetration. In general, there is a potential in the use of copper tailings as a zero eco-friendly admixture to concrete, especially at a 5 % addition level [26].

Current trends in disinfectology served as a theoretical basis for designing the biocidal admixture. In particular, this is a combination of different active substances in one preparation to enhance beneficial (biocidal activity) and inhibition of undesirable properties (corrosive activity) as regards synergistic dependences.

Therefore, use of the proposed admixture based on yellow iron oxide pigment, liquid glass, peracetic acid and cuprous sulfate is advisable to increase strength and improve corrosion and biocidal resistance of concrete for flooring.

3. The aim and objectives of the study

The study objective was to develop an admixture to enhance corrosion resistance, increase strength and extend service life of concrete in livestock buildings.

To achieve this objective, the following tasks were solved:

– to determine physical and mechanical properties of concrete (pH, heat resistance, permeability) exposed to organic media;

– to study chloride penetration into concrete applying temperature-programmed mass spectrometry (TPMS) technique;

– to determine antimicrobial properties of the building materials obtained.

4. The materials and methods used in making concrete with bactericidal admixtures

4. 1. The procedure of studying the bacterial effect on corrosion resistance of concrete exposed to organic media

The studies were conducted at Sumy Oblast Veterinary Laboratory (Sumy, Ukraine). The test specimens were prepared in Laboratory of Architecture and Engineering Studies of Sumy National Agrarian University during 2019. The studies were performed using M 400 Portland cement produced in Kryvyi Rih (Ukraine) and river sand and gravel excavated in Sumy.

Improvement of service performance of floors and their protection against biological damage (effect of corrosive environment and biological corrosion) occurred due to the use of yellow iron oxide pigment (Fe_2O_3) produced by Sumykhimprom PJSC (Ukraine), liquid glass, cuprous sulphate and peracetic acid as main mixture components.

The proposed composition of the biocidal admixture to concrete, wt. %, was as follows:

– yellow iron oxide pigment (DSTU GOST 30333:2009): 1.5–2.0;
– liquid glass: 2–3;
– cuprous sulfate: 0.5–1.0;
– peracetic acid: 0.2–0.3;
– water: up to 100 wt. %.

In order to study the effect of bacteria on corrosion resistance of concrete in organic media, five nutrient media were prepared:

– the medium for ammoniating bacteria of *Bacillus, Pseudomonas* and *Achromobacter* species was prepared in distilled water (peptone: 5 g; K_2HPO_4: 1 g; $MgSO_4{\cdot}7H_2O$: 0.5 g; NaCl: traces per 1,000 ml at pH=7.5). The end product of life activity of these microorganisms is carbon dioxide, water, ammonia and salts of sulfuric and phosphoric acids;

– the medium for ammoniating bacteria of *Bacillus, Micrococcus* and *Sporosarcina* species was prepared in distilled water ($CO(NH_2)_2$: 5 g; potassium citrate ($K_2C_6H_5O_7{\cdot}H_2O$): 5 g; K_2HPO_4: 1 g; $MgSO_4{\cdot}7H_2O$: 5 g per 1,000 ml at pH=8.0). In the course of life activity of these bacteria, decomposition of urea with urease enzyme with formation of ammonium carbonate and then final products: ammonia, carbon dioxide and water;

– the medium for nitrous bacteria of *Nitrosomonas, Nitrosolobus, Nitrosococcus, Nitrosopira* species was prepared in distilled water ($(NH_4)_2SO_4$: 2.0 g; K_2HPO_4: 1 g; $MgSO_4{\cdot}7H_2O$: 0.5 g; NaCl: 2.0 g; $FeSO_4{\cdot}7H_2O$: 0.4 g; $CaCO_3$: 5 g per 1,000 ml at pH=7.6). During the life activity of these bacteria, oxidation of ammonium salts to salts of nitrous acid (nitrites) takes place. This is the process of nitrification, phase 1: $NH_4^+ + 1{,}5O_2 \rightarrow NO_2^- + H_2O + 2H^+$.

– the medium for nitrate bacteria of *Nitrobacter, Nitrispina* species, was prepared in distilled water ($NaNO_2$: 1 g; $NaCO_3$: 1 g; NaCl: 0.5 g; K_2HPO_4: 0.5 g; $MgSO_4{\cdot}7H_2O$: 0.5 g; $FeSO_4{\cdot}7H_2O$: 0.4 g per 1,000 ml at pH=7.8). During the life activity of these bacteria, conversion of nitrites to nitrates, that is salts of nitrous acid are oxidized to salts of nitric acid. This is the process of nitrification, phase 2;

– specimens were exposed to a medium imitating that of livestock buildings (distilled sterile water at pH=7.0 was served as a control sample).

Physical and mechanical properties of concrete were determined applying the conventional procedure [27].

Concrete specimens in a form of 70×70×70 mm cubes were prepared in laboratory of the Department of Architecture and Engineering Studies of Sumy National Agrarian University. An appropriate admixture was introduced based on yellow iron oxide pigment (Fe_2O_3) produced by Sumykhimprom PJSC (Ukraine), liquid glass, cuprous sulfate and peracetic acid according to the weight of cement and the control sample which did not contain admixtures.

4. 2. The method used in determining chloride penetration into concrete and temperature-programmed mass spectrometry (TPMS)

Actual penetration of chloride ions into concrete specimens was assessed by immersion of concrete cubes with all their sides except one exposed to a 3 % NaCl solution for 28 days. After that, the samples were split and sprayed with a 0.1 % solution of silver nitrate to determine depth of chloride penetration [28]. These depths were determined as points in the samples where free chlorides exceeded 0.15 wt. % of cement. They reacted with the 0.1 % solution of silver nitrate ($AgNO_3$) forming a white precipitate of silver chloride (AgCl). Absence or a limited presence of free chloride was indicated by a brown precipitate of silver oxide (AgO) formed by reaction of the $AgNO_3$ solution and hydroxides in the concrete specimens.

A temperature-programmed mass spectrometry (TPMS) unit consisting of a high-temperature oven and an MX-7304A gas mass spectrometer (SELMI OJSC, Sumy, Ukraine) was used in the studies (Fig. 1).

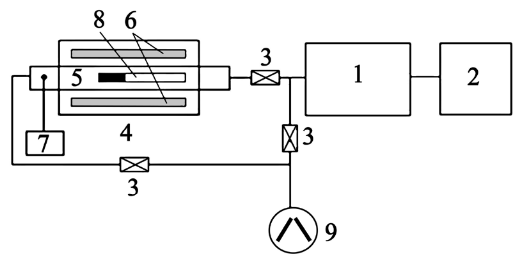

Fig. 1. The temperature-programmed mass spectrometry (TPMS) unit: 1 – mass spectrometer; 2 – PC; 3 – vacuum taps; 4 – 1,200 °C oven; 5 – vacuumized quartz tube; 6 – heating elements; 7 – thermocouple; 8 – quartz tube with a specimen; 9 – turbomolecular pump

2–3 mg samples were taken for the experiment.

The technical details of the experiment are presented in detail in [29].

Peaks of ions with molecular weights (*m/z*) of 2 for hydrogen; 16 for oxygen; 18 for water; 28 for carbon monoxide (CO) and 44 for carbon dioxide (CO_2) were subjected to unique identification in the obtained mass spectra.

4. 3. Methods used in assessment of the antimicrobial action of building materials

After a 28-day curing, the samples were placed in Petri cups on MPA with test microbes. 20 ml of sterile MPA was poured into the cups and after complete cooling, 1 ml of a 2 billion exposure of one-day *E. Coli* or *S. Aureus* broth culture was applied and evenly spread over entire surface of the cup. After 40–60 min, excess cultures were aspirated and samples of building materials were introduced. Cups were placed in a thermostat for 18–24 hours at a temperature of +37.6 °C. Museum strains of *Escherichia Coli* and *Pseudomonas Aeruginosa* were used [30].

5. Results obtained in the study of concretes with bactericidal admixtures

5. 1. Results of studying the physical and mechanical properties of concrete exposed to organic media

Specimens for corrosion resistance studies were made in which the biocidal admixture content was 0; 0.5; 1; 2 % of cement weight. After 28 days of normal curing, the samples were placed in flasks with nutrient media and sterilized in an autoclave at 121 °C and pressure of 0.1 MPa. Half of the nutrient media were infected with bacteria corresponding to each nutrient medium. The rest of the media were left for control.

The medium pH was measured once a month. Initial pH values ranged from 4.5 to 5.0. The study results are given in Table 1.

The pH level in media with nitrating (2nd phase nitrification) and ammoniating (urea ammonifiers) bacteria decreased by 10–15 % compared to the initial level. In media with microorganisms, pH should be reduced by 50–60 % compared to the initial pH of 4.5–5.0. This change in pH is due to the life activity of bacteria that create an acidic medium and, as a consequence, corrode concrete. The study results are presented graphically in Fig. 2.

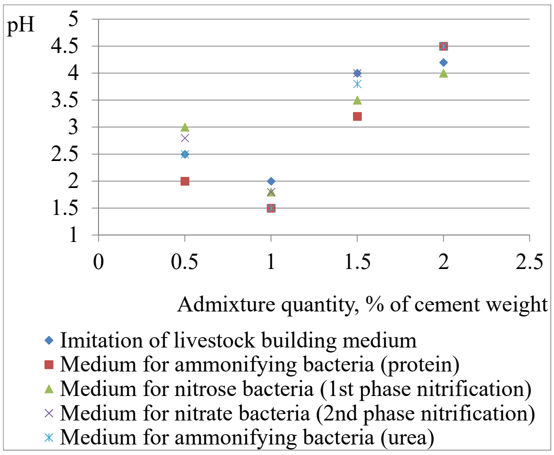

Fig. 2. pH values in various nutrient media with and without microorganisms during 180 days

Thus, it can be concluded that a concrete admixture of 1 and 2 % concentration does not change pH in corrosive bacteria media.

At the next study stage, strength properties of concrete specimens exposed for 6 months to media with and without microorganisms were assessed (Table 2).

For example, compressive strength of control specimens having no admixtures exposed to various media was lower than that of the test specimens having a complex admixture.

Strength of the test specimens grew with an increase in concentration of the admixture relative to the cement weight despite the corrosive effect of various media. This is especially pronounced in the media with ammoniating bacteria (protein ammonifiers). No influence of microorganisms in the media with nitrating and ammoniating urea was observed which is confirmed by the pH values (Table 1).

As noted earlier, this effect is caused by the adsorption reaction when surface of the iron oxides is covered with OH ions. These types of ions are called surface functional groups. Due to this effect, peculiar adsorption of various anions occurs. This reaction limits electrostatic interactions between ions. Surface adsorption acts through Fe-OH groups. These groups obtain negative or positive charge by dissociation or association of protons depending on pH of the ions surrounding them. On the other hand, the occurrence of different degrees of iron oxidation and creation of different phases must increase compressive strength of concrete.

Introduction of biocidal admixtures in amounts of 0, 0.5 and 1 % of cement weight has shown the same increase in the specimen strength. Most of all, this was evident from the results of studies in a medium imitating the livestock medium and in a medium with nitrous bacteria. Introduction of a biocidal admixture in an amount of 2 % of cement weight improved strength properties of concrete specimens compared to the standard specimen. Studies of biocidal properties have shown that the most pronounced bactericidal properties were in samples with a biocidal admixture in an amount of 2 %.

Concrete admixture can significantly increase strength and corrosion resistance, improve biocidal resistance of building materials for flooring the livestock buildings (Fig. 3, 4).

Table 1

Medium pH values in different nutrient media with and without microorganisms during 180 days

No.	Quantity of the admixture, % of cement weight	Medium imitating livestock building medium		Medium for ammonifying bacteria (protein)		Medium for nitrose bacteria (the 1st stage nitrification)		Medium for nitrate bacteria (the 2nd stage nitrification)		Medium for ammonifying bacteria (urea)	
		With microorganisms	Control	With microorganisms	Control	With microorganisms	Control	With microorganisms	Control	With microorganisms	Control
1	0	2.5	5.0	2.0	5.0	3.0	5.0	2.8	4.5	2.5	4.5
2	0.5	2.0	5.0	1.5	5.0	1.8	5.0	1.8	4.5	1.5	4.5
3	1	4.0	5.0	3.2	4.5	3.5	5.0	4.0	5.0	3.8	4.5
4	2	4.2	5.5	4.5	5.0	4.0	4.5	4.5	5.0	4.5	5.0

Table 2

Compressive strength of concrete specimens after exposure for 6 months to various nutrient media (imitating medium, protein, 1st phase nitrification) with and without microorganisms ($M \pm m$, n=6)

Admixture quantity, wt.% of cement	Variation of strength of the specimens exposed to various media, (kg/cm^2)					
	Medium imitating livestock building medium		Medium for ammonifying bacteria (protein)		Medium for nitrose bacteria (the 1st stage nitrification	
	With microorganisms	Without microorganisms	With microorganisms	Without microorganisms	With microorganisms	Without microorganisms
Control	367	370	360	375	367	370
0.5	375	380	375	382	375	380
1	390	395	389	390	397	400
2	400	410	395	405	400	420

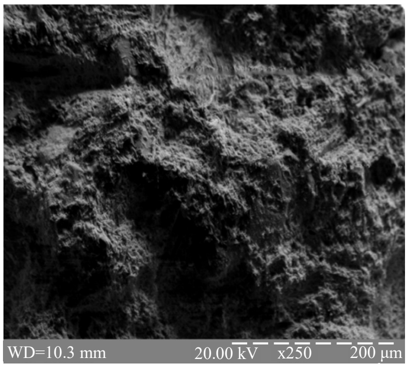

Fig. 3. Consolidation of concrete structure due to the admixture

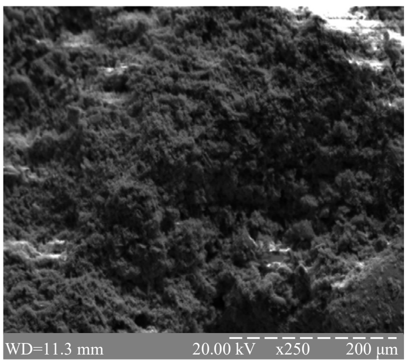

Fig. 4. A looser concrete structure in a control specimen without admixtures

For example, when 0.5 % of the admixture is introduced to concrete, strength of the specimens exposed to the medium with bacteria has reduced by only 4–5 % compared to the control specimens. Concentration of 1–2% of the admixture maintained the strength of concrete specimens exposed to corrosive medium by 98–99 %.

5. 2. Results obtained in the study of chloride penetration into concrete and temperature-programmed mass spectrometry (TPMS)

Depths of chloride penetration into the specimens immersed in a 5 % NaCl solution for 28 days were assessed (Fig. 5). These results have shown that chloride penetration was higher in control samples of concrete compared to the experimental ones.

Penetration depth was 19.5 % in the concrete specimens without admixtures.

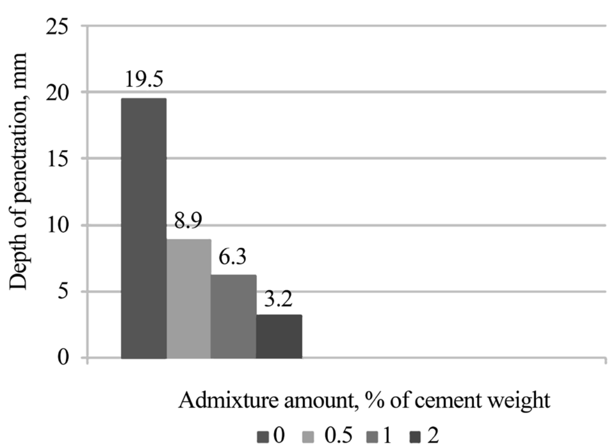

Fig. 5. Depth of chloride penetration into concrete specimens

When admixtures were introduced to the concrete in amounts of 0.5 % to 2 %, depth of chloride penetration has decreased from 8.9 mm to 3.2 mm, respectively. Reduced depths of chloride penetration are due to a decrease in absorption of concrete water by introduction of admixtures of iron oxide, cuprous sulfate, peracetic acid and sodium silicate which caused decrease in specimen porosity. Therefore, due to the admixtures, the formed structure had intermittent pores and significantly reduced penetration of chlorides in the specimens.

The use of the TPMS method for predicting the direction and intensity of influence of some biocidal admixtures on physical and chemical properties of concrete has confirmed effectiveness of the developed admixture (Fig. 6).

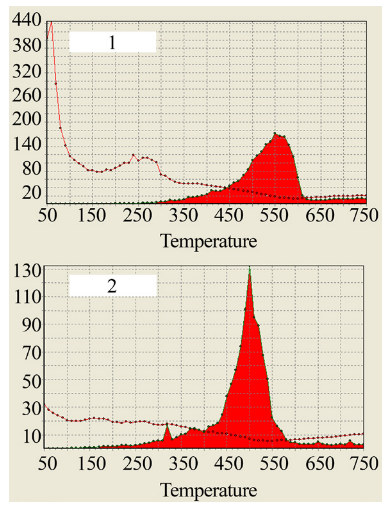

Fig. 6. Thermograms of CO_2 ions built for the specimens of concrete modified with an admixture based on yellow iron oxide pigment and the control sample. Ordinate axis: signal intensity, a.u.; abscissa axis: temperature; cement (control) (1); cement+yellow iron oxide pigment 1 % Fe (OH)O, $FeHO_2$ (2)

Fig. 6 shows curves of dependence of carbon monoxide (CO) and carbon dioxide (CO_2) evolution from specimens of carbon-containing substances on temperature. A detailed examination of the curves of dependence of CO and CO_2 evolution from the samples on temperature (Fig. 6) shows a clearly pronounced tendency to the shift of maximum evolution of gaseous substances in the direction of the heating temperature growth depending on presence of admixtures in the specimens. In particular, a concrete enriched with iron oxide gives a clearly delineated intense peak at 500–650 °C. At the same time, the reference sample of concrete begins to evolve carbon dioxide as soon as temperatures reach 400 °C which causes a looser concrete structure.

Thus, it was found in the experimental studies that the temperature range of heating for quantitative evolution of calcium carbonates from all studied specimens of concrete was 400–500 °C. At the same time, shape of the thermograms of carbon dioxide evolution intensity differs significantly in width and intensity depending on the temperature for each of the concrete specimens compared to the control sample (chemically pure synthetic $CaCO_3$). It can be assumed that different behavior of concrete samples when heated relates to the presence of different chemical admixtures.

The method of temperature-programmed desorption mass spectrometry (TPMS) has shown that addition of yellow iron oxide pigment to concrete increases its thermal resistance which is a positive property for building materials used in the construction of livestock buildings.

5. 3. Results obtained in the study of antimicrobial properties of the obtained building materials

The studies have shown that concrete admixtures in a concrete improve its corrosion and biocidal resistance and strength. In order to provide these characteristics, an aqueous solution of environmentally friendly admixture with bactericidal properties based on yellow iron oxide pigment (1.5–2.0 wt. %), liquid glass (2–3 wt. %), peracetic acid (0.2–0.3 wt. %) and cuprous sulfate (0.5–1.0 wt. %) has to be introduced into concrete.

To study bactericidal properties of the obtained concrete, the concrete samples were immersed in cups with a nutrient medium and microorganisms (Table 3).

Table 3

Assessment of bactericidal properties of biocidal admixtures to concrete

Admixture quantity, wt.%	Exposure			
	2 hrs.	3 hrs.	30 days	60 days
No admixtures	+	+	+	+
0.5	–	–	–	+
1	–	–	–	–
2	–	–	–	–

It was proved that concrete with addition of admixtures in 1 and 2 % concentrations retains its bactericidal properties and as a result, is not amenable to biological corrosion (Fig. 7, 8).

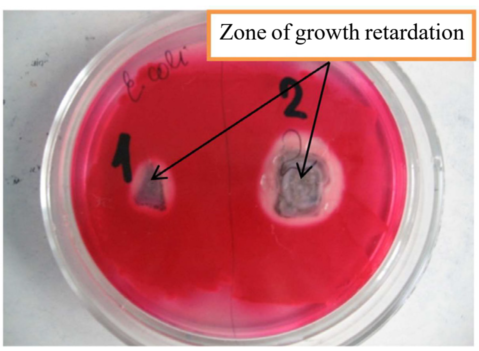

Fig. 7. The zone of *Escherichia coli* culture growth retardation around samples of concrete with an admixture

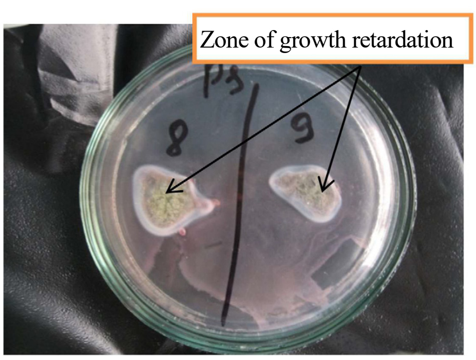

Fig. 8. The zone of *Pseudomonas aeruginosa* culture growth retardation around the samples of concrete with an admixture

It was found in the study that microscopic fungi grow well on concrete. *Renicillis, Aspergillus, Cladosporium, Fusarium* were most commonly detected [31, 32]. Therefore, studies were conducted to identify fungicidal effect of the obtained concrete with a biocidal admixture. Duration of exposure of the experimental and control specimens in the livestock buildings was six months. During this time, specimens of building materials were contaminated. The specimens were crashed and examined in the laboratory for the presence of colonies of microscopic fungi (Table 4).

Table 4

Determination of bactericidal properties of admixtures to a concrete used in livestock buildings for microscopic pathogenic fungi ($M \pm m$, n=3)

No.	Concrete admixture	Number of fungi colonies, pcs				
		Penicillium	*Aspergillus*	*Cladosporium*	*Fusarium*	Total colonies
1	Control specimen (with no admixtures)	65±0.12	29±0.53	150±0.42	44±0.28	288±0.12
2	Yellow iron oxide pigment: 2 g; Liquid glass: 3 ml; peracetic acid: 0.3 ml; cuprous sulfate: 0.2 g; tap water to 100 ml	8±0.22**	–	–	–	8±0.22***

Note. $^{*}P<0.05$; $^{**}P<0.01$; $^{***}P<0.001$ *compared to the control specimen (with no bactericide admixtures)*

The experiment has confirmed presence of antifungal action of the admixture added to concrete as the number of fungi colonies decreased by 98 % compared to the control samples (without admixtures). All isolated fungi germinating in the concrete pores can have a significant destructive effect on the concrete. Their spores are toxic to animals and humans (Fig. 9–11).

Fig. 9. Colonies of *Penicillium* and *Fusarium* fungi in Chapek medium, extracted from a concrete without admixtures

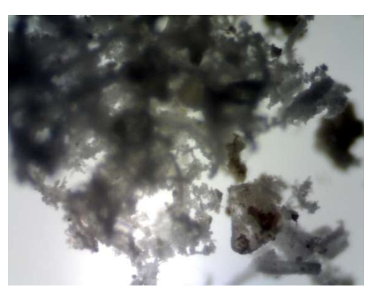

Fig. 10. Fungus mycelium under microscope (×400)

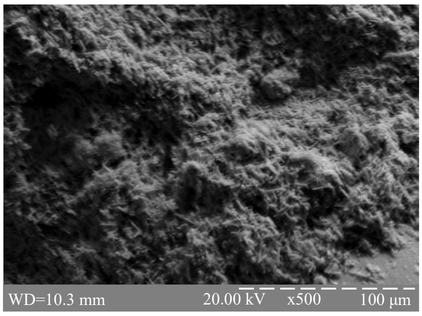

Fig. 11. Fungus mycelia in concrete (scanning electron microscopy)

Therefore, introduction of admixtures can significantly increase strength of concrete floors, improve their functional performance, reduce the amount of microflora on the surface and inside.

6. Discussion of results obtained in the study of concretes with bactericidal admixtures

Studies have shown that concrete is destroyed and signs of corrosion occur in livestock buildings. This problem can be solved by introduction of admixtures that increase corrosion resistance of concrete, extend to some extent duration of its bactericidal activity. This is due to neutralization of the concrete surface layer. Therefore, in order to provide concrete with long-lasting antimicrobial activity, it is necessary to add bactericidal admixtures. This will not only protect animals against re-infection with diseases but also increase durability of structures by eliminating biological corrosion [33]. Introduction of bactericidal admixtures reduces microbiological pressure on animals [34].

It has been experimentally proven that the use of yellow iron oxide pigment improves strength characteristics of concrete, heat resistance and reduces penetrability. Biocidal action of this component is based on Fenton's advanced oxidation processes (AOP) and the combination of hydrogen peroxide (H_2O_2) and ions of ferric and ferrous iron (Fe (III), Fe (II)). This reaction leads to the formation of highly reactive ions: OH^-, O^{2-}, and oxygen molecules (O_2) capable of destroying microorganisms by oxidation [35, 36].

In addition, it was proved by the studies that an effect of surface adsorption occurs due to the addition of iron oxide to concrete. This reaction limits electrostatic interactions between ions. The presence of different degrees of iron oxidation in concrete and creation of different phases contributes to the growth of its compression strength.

A method of studying properties of building materials with the help of TPMS technique was also used in the work. As a result of temperature-programmed mass spectrometry of concrete samples, it was found that introduction of an admixture based on iron oxide increases thermal stability of concrete compared to the control samples.

Disadvantage of this method consists in chemical differences of artificial carbonates as well as their low content in concrete compared with limestone. Therefore, comparison of different concretes and interpretation of the data obtained is a time-consuming process.

When tested for penetration of 5 % NaCl solution into concrete, possibility of its reduction was proven by adding a 2 % admixture based on yellow iron oxide pigment, peracetic acid, liquid glass and cuprous sulphate to 3.2 mm compared to the control specimen (19.5 mm). Such changes in concrete occur due to the introduction of fine crystalline powder of yellow iron oxide pigment as a filler and liquid glass, as a plasticizer reducing the pore holes. Introduction of admixtures changes concrete structure and reduces absorption of water and various chemical disinfectants used in cattle breeding. However, destruction of concrete will occur if sodium hydroxide (NaOH) and non-hydrated lime are used if the livestock buildings.

At the same time, studies [31, 37, 38] note that microorganisms live and actively reproduce on the surface of building structures destroying them and secreting toxic products and allergens. This leads to deterioration of environmental situation in buildings and structures. Thus, in agricultural buildings affected by pathogenic microorganisms, animal weight gain is reduced and death of animals is noted.

It has been established experimentally that corrosion of concrete in the livestock buildings is caused by microscopic fungi of *Penicillium, Fusarium and Cladosporium, Aspergillus* species and *Escherichia coli* and *Pseudomonas aeruginosa* bacteria. Microscopic examination with immersion of concrete samples in agar proved that the proposed concrete admixtures (based on yellow iron oxide pigment (1.5–2.0 wt. %), peracetic acid (0.2–0.3 wt. %), liquid glass (2–3 wt. %) and cuprous sulfate (0.5–1.0 wt. %) demonstrate antimicrobial properties. However, the problem consists in a limited term of antimicrobial properties. Therefore, the aim of further studies is to determine limits of bactericidal properties of concretes with complex admixtures and correct their composition taking into account previous disadvantages.

It should be noted that the use of the proposed measures can improve corrosion resistance of concrete by improving its physical, mechanical and antimicrobial properties. This is a prerequisite for the use of this concrete admixture in the construction of new livestock buildings.

7. Conclusions

1. It was found that biocidal admixture based on yellow iron oxide pigment (1.5–2.0 wt. %), peracetic acid (0.2–0.3 wt. %), liquid glass (2–3 wt. %) and cuprous sulfate (0.5–1.0 wt. %) improves concrete strength, heat resistance and reduces penetrability. A 1–2 % concentration of admixture maintains strength of concrete in a corrosive environment by 98–99 %.

2. It was established that when adding admixtures in concrete in a quantity from 0.5 % to 2 %, depth of chloride penetration decreases from 8.9 mm to 3.2 mm, respectively, and application of the TPMS method to predict direction and intensity of impact of some biocidal admixtures on physical and chemical parameters of concrete has confirmed effectiveness of the developed admixture.

3. This admixture exhibits bactericidal properties directed against microflora: the number of fungi colonies is reduced by 98 %, which gives grounds for its use in the livestock buildings.

References

1. Prusty, J. K., Patro, S. K., Basarkar, S. S. (2016). Concrete using agro-waste as fine aggregate for sustainable built environment – A review. International Journal of Sustainable Built Environment, 5 (2), 312–333. doi: https://doi.org/10.1016/j.ijsbe.2016.06.003
2. 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
3. Okojie, L. O. (2014). Cement Production and Sustainable Rural Farming Livelihood in Nigeria: Striking a Sensible Balance Through Environmental Legislation and Enforcement. European Journal of Sustainable Development, 3 (3), 251–262. doi: https://doi.org/10.14207/ejsd.2014.v3n3p251
4. Hilal, A. A. (2016). Microstructure of Concrete. High Performance Concrete Technology and Applications. doi: https://doi.org/10.5772/64574
5. Justs, J., Bajare, D., Korjakins, 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, 50–57. doi: https://doi.org/10.2478/cons-2013-0008
6. Johansson, S. (2011). Biological growth on rendered fa ades. Lund University, Division of Building Materials.
7. 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
8. Sorbu, M. (2008). The environmental impact of the animal husbandry buildings (B). ProEnvironment, 2, 52–54.
9. Ettenauer, J. D. (2010). Culture dependent and-independent identification of microorganisms on monuments. University of Vienna.
10. Danilchenko, S. N., Chivanov, V. D., Ryabishev, A. G., Novikov, S. V. et. al. (2016). The Study of Thermal Decomposition of Natural Calcium Carbonate by the Temperature-programmed Mass Spectrometry Technique. Journal of Nano- and Electronic Physics, 8 (4 (1)), 04031-1–04031-3. doi: https://doi.org/10.21272/jnep.8(4(1)).04031
11. Sanchez, F., Sobolev, K. (2010). Nanotechnology in concrete – A review. Construction and Building Materials, 24 (11), 2060–2071. doi: https://doi.org/10.1016/j.conbuildmat.2010.03.014
12. Li, X., Kappler, U., Jiang, G., Bond, P. L. (2017). The Ecology of Acidophilic Microorganisms in the Corroding Concrete Sewer Environment. Frontiers in Microbiology, 8. doi: https://doi.org/10.3389/fmicb.2017.00683
13. Vincke, E., Verstichel, S., Monteny, J., Vrerstraete, W. (1999). A new test procedure for biogenic sulfuric acid corrosion of concrete. Biodegradation, 10 (6), 421–428. doi: https://doi.org/10.1023/A:1008309320957
14. Ramamurthy, K., Kunhanandan Nambiar, E. K., Indu Siva Ranjani, G. (2009). A classification of studies on properties of foam concrete. Cement and Concrete Composites, 31 (6), 388–396. doi: https://doi.org/10.1016/j.cemconcomp.2009.04.006
15. 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
16. Grengg, C., Mittermayr, F., Ukrainczyk, N., Koraimann, G., Kienesberger, S., Dietzel, M. (2018). Advances in concrete materials for sewer systems affected by microbial induced concrete corrosion: A review. Water Research, 134, 341–352. doi: https://doi.org/10.1016/j.watres.2018.01.043
17. Ferrari, C., Santunione, G., Libbra, A., Muscio, A., Sgarbi, E., Siligardi, C., Barozzi, G. S. (2015). Review on the influence of biological deterioration on the surface properties of building materials: organisms, materials, and methods. International Journal of Design & Nature and Ecodynamics, 10 (1), 21–39. doi: https://doi.org/10.2495/dne-v10-n1-21-39
18. 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
19. Kazemian, S., Huat, B. K. B., Mohammed, A. T., Barghchi, M. (2011). The Effect of Sodium Silicate on Cement-Sodium Silicate System Grout. Modern Methods and Advances in Structural Engineering and Construction(ISEC-6). doi: https://doi.org/10.3850/978-981-08-7920-4_s2-g01-cd
20. The Effect of Using Commercial Red and Black Iron Oxides as a Concrete Admixtures on its Physiochemical and Mechanical Properties. (2015). International Journal of Science and Research (IJSR), 4 (12), 1389–1393. doi: https://doi.org/10.21275/v4i12.nov152049
21. Kosmatka, S. H., Wilson, M. L. et. al. (2011). Design and Control of Concrete Mixtures, EB001. Portland Cement Association, 444.
22. Shekari, A. H., Razzaghi, M. S. (2011). Influence of Nano Particles on Durability and Mechanical Properties of High Performance Concrete. Procedia Engineering, 14, 3036–3041. doi: https://doi.org/10.1016/j.proeng.2011.07.382
23. Loganina, V. I., Kislitsyna, S. N., Mazhitov, Y. B. (2018). Development of sol-silicate composition for decoration of building walls. Case Studies in Construction Materials, 9, e00173. doi: https://doi.org/10.1016/j.cscm.2018.e00173
24. Liu, D., Behrens, S., Pedersen, L.-F., Straus, D. L., Meinelt, T. (2016). Peracetic acid is a suitable disinfectant for recirculating fish-microalgae integrated multi-trophic aquaculture systems. Aquaculture Reports, 4, 136–142. doi: https://doi.org/10.1016/j.aqrep.2016.09.002
25. Gad, S. C. (2014). Peracetic Acid. Encyclopedia of Toxicology, 788–790. doi: https://doi.org/10.1016/b978-0-12-386454-3.01197-0

26. Onuaguluchi, O., Eren, O. (2012). Copper tailings as a potential additive in concrete: consistency, strength and toxic metal immobilization properties. Indian Journal of Engineering and Materials Sciences, 19 (2), 79–86.
27. DSTU B V.2.7-224:2009. Building materials. Concretes rules for the strength control. Minrehionbud Ukrainy. Kyiv, 27.
28. Otsuki, N., Nagataki, S., Nakashita, K. (1992). Evaluation of AgNo 3 solution spray method for measurement of chloride penetration into hardened cementitious matrix materials. Journal aci mater, 89 (6), 587–592. Available at: https://www.concrete.org/publications/internationalconcreteabstractsportal.aspx?m=details&ID=4036
29. 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.
30. Metodychni vkazivky po vyznachenniu chutlyvosti mikroorhanizmiv do antymikrobnykh preparativ metodom dyfuziyi v ahar za dopomohoiu standartnykh dyskiv z antybiotykamy (zatverdzheni naukovo-metodychnoiu radoiu DKVM Ukrainy vid 20.12.2007 r.) (2010).
31. Bertron, A. (2014). Understanding interactions between cementitious materials and microorganisms: a key to sustainable and safe concrete structures in various contexts. Materials and Structures, 47 (11), 1787–1806. doi: https://doi.org/10.1617/s11527-014-0433-1
32. Fomina, M., Podgorsky, V. S., Olishevska, S. V., Kadoshnikov, V. M., Pisanska, I. R., Hillier, S., Gadd, G. M. (2007). Fungal Deterioration of Barrier Concrete used in Nuclear Waste Disposal. Geomicrobiology Journal, 24 (7-8), 643–653. doi: https://doi.org/10.1080/01490450701672240
33. Li, X., O'Moore, L., Song, Y., Bond, P. L., Yuan, Z., Wilkie, S. et. al. (2019). The rapid chemically induced corrosion of concrete sewers at high H2S concentration. Water Research, 162, 95–104. doi: https://doi.org/10.1016/j.watres.2019.06.062
34. Shkromada, O., Skliar, O., Paliy, A., Ulko, L., Gerun, I., Naumenko, O. et. al. (2019). Development of measures to improve milk quality and safety during production. Eastern-European Journal of Enterprise Technologies, 3 (11 (99)), 30–39. doi: https://doi.org/10.15587/1729-4061.2019.168762
35. Goldstein, S., Meyerstein, D., Czapski, G. (1993). The Fenton reagents. Free Radical Biology and Medicine, 15 (4), 435–445. doi: https://doi.org/10.1016/0891-5849(93)90043-t
36. Zhou, W., Zhao, H., Gao, J., Meng, X., Wu, S., Qin, Y. (2016). Influence of a reagents addition strategy on the Fenton oxidation of rhodamine B: control of the competitive reaction of ·OH. RSC Advances, 6 (110), 108791–108800. doi: https://doi.org/10.1039/c6ra20242j
37. George, R. P., Ramya, S., Ramachandran, D., Kamachi Mudali, U. (2013). Studies on Biodegradation of normal concrete surfaces by fungus Fusarium sp. Cement and Concrete Research, 47, 8–13. doi: https://doi.org/10.1016/j.cemconres.2013.01.010
38. Paliy, A., Paliy, A., Nanka, A., Chalaya, O., Chalyi, O. (2019). Establishment of the efficiency of animal breeding premises disinfection by modern disinfectants. EUREKA: Life Sciences, 4, 3–8. doi: https://doi.org/10.21303/2504-5695.2019.00959