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

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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 aggregate 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: $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$. This impact can be regarded as one producing corrosive medium in livestock buildings [4, 5].

Ammonia ($\text{NH}_3$) and hydrogen sulfide ($\text{H}_2\text{S}$) 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 ($\text{CH}_3\text{CHOHCOOH}$) 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 ($\text{NH}_3\text{OH}$) is formed during interaction of ammonia ($\text{NH}_3$) with water and a basic medium arises [9].

Calcium carbonate ($\text{CaCO}_3$) 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 ($\text{CO}_2$) necessary for radiocarbon dating of samples by the content of carbon isotope 14C using accelerated mass spectrometry (AMS). To date, kinetics of $\text{CaCO}_3$ decomposition under the action of high temperature in accordance with reaction (1) has been studied in sufficient detail.

$$\text{CaCO}_3(s) \rightarrow \text{CaO}(s) + \text{CO}_2(g),$$  

(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 $\text{CaCO}_3$. At the same time, detailed information is needed for applied studies, in particular quantitative evolution of carbon dioxide in accordance with reaction (1) for radio-carbon 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 (MgCl₂ and AlCl₃) 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 fulfilment 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 (Fe₂O₃) 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 ZrO₂, Fe₂O₃, TiO₂ and Al₂O₃ 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 (CH₃COOOH) 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 (Fe₂O₃) produced by Sumykhi-
improm 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; K₂HPO₄: 1 g; MgSO₄·7H₂O: 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: 2.0 g; K₂HPO₄: 1 g; MgSO₄·7H₂O: 0.5 g; K₂HPO₄: 1 g; MgSO₄·7H₂O: 5 g per 1,000 ml at pH=7.6). During the 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, Nitrospira species was prepared in
distilled water ((NH₄)₂SO₄: 2.0 g; K₂HPO₄: 1 g; MgSO₄·7H₂O: 0.5 g; NaCl: 2.0 g; FeSO₄·7H₂O: 0.4 g;
CaCO₃: 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 (nitrates) takes place. This is the process of nitrification, phase 1: NH₄⁺+1.5O₂→NO₃⁻+H₂O+2H⁺;
  – the medium for nitrate bacteria of Nitrobacter,
    Nitriposina species, was prepared in distilled water (NaNO₃:
1 g; CaCO₃: 1 g; NaCl: 0.5 g; K₂HPO₄: 0.5 g; MgSO₄·7H₂O: 0.5 g; FeSO₄·7H₂O: 0.4 g per 1,000 ml at pH=7.8). During
the life activity of these bacteria, conversion of nitrates 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 de-
termined applying the conventional procedure [27].

Concrete specimens in a form of 70×70×70 mm cubes
were prepared in laboratory of the Department of Archi-
tecture and Engineering Studies of Sumy National Agrar-
ian University. An appropriate admixture was introduced
based on yellow iron oxide pigment (Fe₂O₃) produced by
Sumykhiimprom 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 pene-
tration into concrete and temperature-programmed mass
spectrometry (TPMS)

Actual penetration of chloride ions into concrete speci-
mens 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 (AgNO₃) forming a white precipitate of silver chlor-
ide (AgCl). Absence or a limited presence of free chloride
was indicated by a brown precipitate of silver oxide (AgO)
formed by reaction of the AgNO₃ 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 hy-
drogen; 16 for oxygen; 18 for water; 28 for carbon monoxide
(CO) and 44 for carbon dioxide (CO₂) 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. Aerues 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. Mu-
seum 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.

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).

![Fig. 2. pH values in various nutrient media with and without microorganisms during 180 days](image)

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).

![Table 1](image)

**Table 1**

| No. | Quantity of the admixture, % of cement weight | Medium imitating livestock building medium | Medium for ammonifying bacteria (protein) | Medium for nitrose bacteria (1st phase nitrification) | Medium for nitrate bacteria (the 2nd stage nitrification) | Medium for ammonifying bacteria (urea) |
|-----|--------------------------------------------|------------------------------------------|----------------------------------------|---------------------------------------------------|---------------------------------------------------|--------------------------------------|
| 1   | 0                                          | Control                                  | With micro-organisms Control           | Control With micro-organisms Control              | Control With micro-organisms Control              | Control With micro-organisms Control |
| 2   | 0.5                                        | 2.5                                      | 5.0                                    | 3.0                                               | 5.0                                               | 4.5                                  |
| 3   | 1                                          | 4.0                                      | 5.0                                    | 4.5                                               | 5.0                                               | 4.5                                  |
| 4   | 2                                          | 4.2                                      | 5.3                                    | 4.5                                               | 5.0                                               | 4.5                                  |

![Table 2](image)

**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<sub>sm</sub>, n=6)

| Admixture quantity, w.t.% of cement | 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) |
|-------------------------------------|------------------------------------------|----------------------------------------|---------------------------------------------------|---------------------------------------------------|
| Control                            | With micro-organisms                      | Without micro-organisms                 | With micro-organisms                                | Without micro-organisms                           |
| 0.5                                | 367                                      | 375                                    | 360                                               | 375                                               |
| 1                                  | 390                                      | 395                                    | 389                                               | 390                                               |
| 2                                  | 400                                      | 410                                    | 395                                               | 405                                               |

Eastern-European Journal of Enterprise Technologies ISSN 1729-3774 5/6 (101) 2019
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.

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 shows curves of dependence of carbon monoxide (CO) and carbon dioxide (CO₂) evolution from specimens of carbon-containing substances on temperature. A detailed examination of the curves of dependence of CO and CO₂ 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 CaCO₃). 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

| Admixture quantity, wt. % | Exposition | 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).

Table 4

| No. | Concrete admixture | 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)

It was found in the study that microscopic fungi grow well on concrete. Renicilllis, 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).

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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).
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 (H₂O₂) and ions of ferric and ferrous iron (Fe(III), Fe(II)). This reaction leads to the formation of highly reactive ions: OH⁻, O₂⁻, and oxygen molecules (O₂) 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 stability of concrete compared to the control samples.

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 sulphate (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 sulphate (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 quality 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., Basarker, 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.jsbe.2016.06.003

2. Petrov, A., Pavluchenkov, M., Nanka, A., Paly, 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. Okoje, 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., Mezinskiis, 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/constr.2013-0008

6. Johansson, S. (2011). Biological growth on rendered façades. 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/ijet.2016.88.99

8. Sorbu, M. (2008). The environmental impact of the animal husbandry buildings (B). ProEnvironment, 2, 52–54.

9. Ettenuer, J. D. (2010). Culture dependent and-independent identification of microorganisms on monuments. University of Vienna.

10. Danilchenko, S. N., Chivanov, V. D., Ryalishev, 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., Veenrae, C. (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 microbiologically 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, methods, 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., Barghehi, 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/10.15587/1729-4061.2019.155469

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., 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.aqrrep.2016.09.002

23. 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/internationalconcreteabstractsporal.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. Palyi, A., Palyi, 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