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Smolnikova V. V., Ledovskaya N.V.

THE CURRENT CHARACTERISTICS OF SOIL BIOREMEDIATION TECHNOLOGIES UNDER CONDITIONS OF HYDROCARBON POLLUTION NORTH CAUCASIAN FEDERAL UNIVERSITY

Soil fertility rehabilitation after petroleum hydrocarbon influence on the ecosystem lasts much longer then under the other anthropomorphic conditions. As natural self-purification processes are durable and under a medial or high pollution level are considered to be ineffective, it requires an implementation of hydrocarbon pollution elimination technologies being effective in a short term. With this purpose mechanical, chemical, physical-chemical and biological methods are used.

Mechanical methods include a territory covering with inert or unpolluted materials (concrete dust), transferring of the polluted soil to the disposal area, oil or oil-products process water run-off from the polluted soil surface, using of soil washing drum-type plants. These methods either are not recommended to be used on the agricultural land, or connected with transferring of the polluted soil bulk, or very expensive.

Chemical methods are represented by burning-off and reagent neutralization. Oil burning-off in the specially constructed furnaces requires preliminary soil preparation to remove heavy metals, and also leads to toxic gas pollution of the environment. Oil burning-off on the soil surface is considered to be a dangerous form of oil pollution elimination. Use of this method leads to the environment pollution with secondary pollutants having toxic and cancerogenic effect, soil fauna demise, burning of plants, seeds and organic substances being a part of soil composition. It is considered allowable to use burning-off under the sufficient oil spill able to cause the pollution of drinking water consumption sources or surface groundwater, which is situated far from the inhabited locality.

Reagent soil cleaning of oil and oil-products makes it possible to conduct chemical hydrocarbon encapsulation. The method provides high-efficient oil pollution deactivation (94-99%); the derived powder is environmentally appropriate, suitable for long-term storage and used as an inert admixture in road building, landfill operations. The main disadvantage of this method is the expensive realization.

Physical-chemical soil washing methods include use of water, surfactant solutions, detergents, electrosmosis, sorbents, ultrasonic and composting.

Soil washing in the field environment makes it possible to realize the surface oil elimination only, without washing of deep soil layers. Use of specific washing plants is connected with necessary transferring of the polluted soil bulk and has a high cost. As a result of this method, the cultivated soil structure is destroyed, and the waste water requiring additional purification arises. The soil washing method provides low-efficient purification and requires obligatory biological recultivation.

The electrosmos is based on use of direct-current flow field for its moving to the electrodes of soil moisture containing dissolved polluted substances. Electrochemical oil cleaning technology belongs to expensive methods and is most efficient for clayed soil. Electrosmos makes it possible to achieve high-efficient cleaning in a short time, however it requires the complex equipment and has a high realization cost.

Use of sorbents leads to potting soil deterioration and sometimes is able to cause a phytotoxic effect. It has been recently suggested to use single-component sorbents derived from natural raw material as petroleum sorbents, however natural sorbents are selective to different petroleum components and do not provide the necessary degree of purification. The sorbent spent material must be disposed.

It has been suggested to use ultrasonic under purification of oil-contaminated soil to intensify the process at the mobile equipment. Ultrasonic vibrations make it possible to catalyze soil deoiling, intensify oxidation and polymerization processes and vaporize liquid hydrocarbons.

The main biological disadvantage of mechanical, chemical and physical-chemical oil elimination methods is the capacity to reduce or totally annihilate soil ecosystem biotic potential. In this case biological methods make it possible not only to decrease the initial hydrocarbon concentration, but also to activate metabolic potential of soil ecosystem biological components (bioremediation).

Composting soil rehabilitation involves mechanical gathering of soil and storage on a recultivation ground for biological composting. The advantage of this method is a low cost. The main disadvantage is a long endurance. Besides, it is necessary to take into account, that earth excavation causes structural morphological distortion of the cultivated land and can disturb the current of both surface and subsoil water.

Agronomical soil rehabilitation. The polluted soil is treated with petroleum sorbents, and after this agronomical measures including reclaiming and fertilizing are used. These measures make it possible to normalize soil solution acidity and stabilize agronomical soil features. The main disadvantages of this method are long endurance and unsteadiness of the results.

Rotary tillage and fertilizer dressing under a medial or high level of hydrocarbon environmental pollution turn out to be insufficient to improve air regime and intensify self-purification processes. In this case this long-term process of succession endures from 5 to 7 years.

Complex soil cleanup technology. To eliminate hydrocarbon pollution, biologies, containing a complex of special oil-degrading bacteria are used. To intensify vital activity of hydrocarbon oxidizing microbial flora, there are taken agronomical measures including reclaiming, recurrent tillage and fertilizing. This technology makes it possible to achieve total degradation of petroleum products into environmentally sound substances, it does not requires use of expensive reagents and petroleum sorbents and promotes biological rehabilitation of reclamated substrates. The main disadvantages of this technology are the long-term soil fertility rehabilitation and the seasonality, as using of biologies is efficient at a temperature above 5 degrees C.

Stimulation of soil native microbial flora. This technology involves application of different biogenic substances in oil-contaminated soil. The process of rehabilitation measures activates the natural microbial flora having a capacity to destruct organic matter. At the same time the amount of motile nitrogen, phosphorus and kalium forms increases. There are main disadvantages of this technology: 1) low effectiveness at the sufficiently polluted soil lots; 2) it is impossible to achieve total decompounding of petroleum hydrocarbons by means of natural bioremediation; 3) it is necessary to conduct long-term monitoring of cultivated area; 4) the dependence on weather conditions.

Biologies purification at the testing area. Purification technology involves the moving of oil-contaminated environment to the special testing area. Of polluted soil the rows are made and treated with bacteria preparations containing strains of hydrocarbon oxidizing microorganisms. At the present time a lot of bacteria preparations are developed: “Devoroil”, “Bioprin (Oleovorin)”, “Putidoil”, “Soilex”, “Destroil”, etc. The composition of most bacteria preparations containing hydrocarbon oxidizing strains includes the following microorganisms: Rhodococcusmaris., Rh. sp., Rh. erythropolis, Pseudomonasstutzeri, Ps. sp, Artrobactersp., Azotobactersp., Candidasp., C. maltosa, Acinetobactercalcoaceticus, Bacillussubtilis, Micrococcussp., etc. Most of them are isolated from oil-contaminated environment for the following directional selection. Bacteria preparations make it possible to eliminate both new and old pollutions rapidly and effectively, however it has a high cost, depends significantly on the climatic and environmental conditions, the initial pollution level, the acidity of the environment, the biogenous micro-elements and the pollution intensity.

Use of an injector bioreactor involves two successive stages. At the initial stage of purification in a bioreactor microbiological degradation of petroleum hydrocarbons arises. At the second stage soil humification proceeds. Use of a bioreactor provides high-speed hydrocarbon recovery (from 15 to 60 g/kg per day). The disadvantages are considered to be the necessity to remove oil-contaminated substrates and an extensional working area of a bioreactor (minimum 6 m3/t of polluted soil).

Phytomelioration is based on use of plants, which are resistant to petroleum hydrocarbons, to activate rhizosphere microbial flora and stimulate microbiological self-purification at the polluted area. Oil-contaminated soil is sowed with sorghum, field pea, medic, melilot, barley, oat and etc. Swampy areas and high humidity lots are sowed with mace reed, meadow grass, ribbon grass, sedge, etc. Phytomelioration is usually considered as the final stage of oil-contaminated soil rehabilitation, it is notable for a low cost and simplicity of use. Among the main disadvantages of the method are the necessity to recover plant remains as potentially dangerous biowaste and a long-term period of rehabilitation measures. The general phytomelioration endurance depends on the soil and climatic conditions, the character and the level of pollution. Most intensively it proceeds in steppe, forest-steppe and subtropical areas, in this conditions a short-term vegetational season makes this method hardly suitable for northern regions.

Thus, a choice of a soil purification method should be made according to the features of the purification itself (like oil, endurance, area of pollution, landscape), as well as definite soil and climatic region conditions. Using of soil biota potential forms a basis of current biological methods. The main disadvantage of considered methods is the necessity to provide optimal ecological conditions for a vital activity of microbial flora by means of physical impact on substrates (frequent reclaiming, tillage, etc.).

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Tokachi YE, Rubanov JK, Vasilenko MI, Goncharov EN

DEVELOPMENT OF BIOSTABLE BUILDING COMPOSITE MATERIALS WITH HIGH PROTECTION FROM MICROBIOLOGICAL DEGRADANTS

Belgorod State Technological University named after Shoukhov V. G.

Introduction. Meeting the challenges in improving the biological protection of living and public buildings requires examination of buildings, expert analysis, establishment of specialized laboratories for studying biodeterioration processes and bio-resistance of materials, ensuring proper protection and safety of buildings and structures. Microbiological corrosion is an important factor in residential and public buildings in areas with high humidity influencing the reliability and durability of building structures. There is an environmental aspect of the problem in addition to the technical aspect. Microscopic fungi fouling of constructions, generation of bacteria in porous building materials worsen sanitary conditions of the premises.

One of the most effective and long-acting way to protect all building materials and structures from contamination by microorganisms is the use of biocidal products.

The solution is to use biocide additives in building materials. The compounds of copper, chromium, zinc, silver, and organotin biocide are used as inorganic antimicrobial systems. Among the polymer compounds, the polymeric compounds on the basis of guanidine and chloromethyl derivatives of aromatic hydrocarbons with pyridine are widely used.

The issue of biodeterioration of materials in various mediums

At present, the problem of improving the durability of products and structures of buildings and constructions is of growing concern. This results from the fact that the constant chemicalization of the national economy and increasing the deployment of biotechnological processes in the production, an increasing number of aggressive media affects the building materials and products among which are microorganisms and their metabolic products. It turns out that more than 50% of total damages recorded in the world are connected with activity of microorganisms. Biodeterioration destroys almost all materials, including cement mortars and concretes, composite materials with other binders, wood, etc., exploited under conditions which are favorable for the growth of microorganisms: at meat and dairy plants, at vegetable stores, livestock buildings, etc. Traces of mold can often be found on the inner walls of churches and monasteries, wine cellars, various premises of the food industry and on various architectural monuments. Bacteria and filamentous fungi are constantly presented everywhere in the environment of human habitation using organic and inorganic compounds as nutrient substrate. In recent years, there has been the growth in the number and diversity of microorganisms causing biodeterioration of materials and structures. Aggressiveness of known species has increased. Scientists have discovered more than 250 species of microorganisms that live inside spaceships. The damage to facilities caused by biodeterioration is estimated at tens of billions of dollars.

Statistics show that, the filamentous fungi have the most deleterious effect on the building and industrial materials among various types of microorganisms [1, 2]. Their high destructive activity is due to the ability to adapt to the materials of different chemical nature, which is associated primarily with the presence of well-developed, powerful and mobile enzymatic complex. Metabolic features of fungi causing damages lie in the fact that they have the systems of highly oxidative, glycolytic and other enzymes performing a variety of chemical transformations of complex substrates. Cleavage of such substrates may occur by oxidation, hydroxylation, rupturing of ring and double bonds in the cyclic compounds, transformation of molecules and compounds, biochemical synthesis and other methods.

The big problem is the biological damage from microorganisms, seaweed, shellfish, which grow on the hulls of ships and offshore structures. Biofouling of vessels negatively affects the hydrodynamics of the body due to the higher power and fuel consumption. Methods of inhibiting organic and inorganic growth on such surfaces are different, but most of the methods are based on the use of the protective coating.

The process of biological contamination includes initial accumulation of adsorbed organic substances, growth of bacteria creating a biofilm, which leads to the growth of micro- and macroorganisms.

Bacteria and other microorganisms release extracellular polymeric substances, thereby changing the local chemical processes. It stimulates further growth of macroorganisms. The biofilms of microorganisms and polymeric materials create a matrix gel (Fig. 1), providing enzymatic interaction, exchange of nutrients, protection against environmental factors and even better resistance to biocides. The biofilms also stop the flow of water and ions to the substrate surface, acting as a diffusion barrier, and the reduction of localized oxygen of cathode reactions in the electrolyte may accelerate the corrosion of the metal substrate.

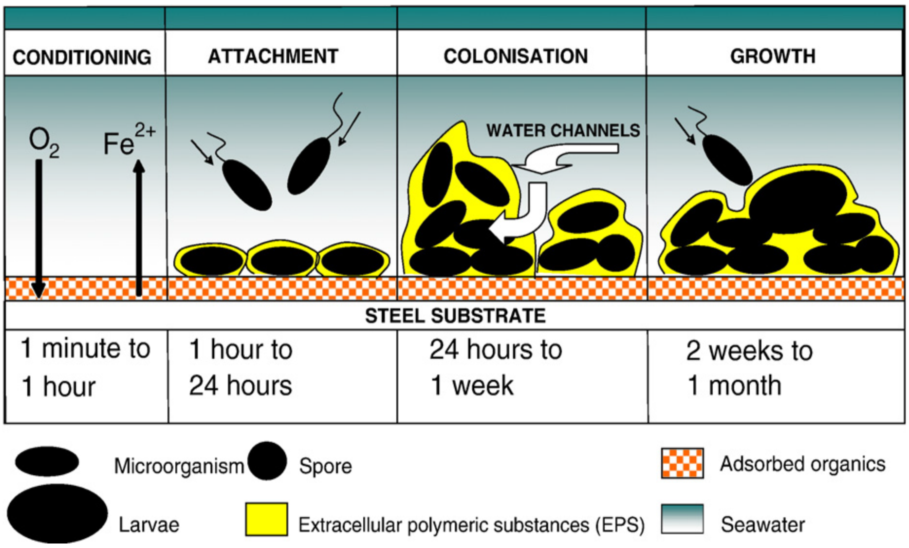

Fig. 1. The stages of fouling [3]

Thus, in addition to protection against fouling, modern coatings must give adequate protection against corrosion, have a long service life and low cost, be chemically stable and well compatible with protected material and safe for the environment [4].

Investigation of the mechanisms of microbial deteriorations by fungi, bacteria, algae of building materials taking into account the their operating conditions

Main bio destructors of building materials

The biodeterioration of inorganic building materials is mostly connected with bond failure of the components of these materials because of impact of mineral or organic acids of microbial origin. Concrete structures are destroyed due to the chemical reactions between cement stone and products of microorganisms.

The biodeterioration of metals and metal structures is usually called bio-corrosion or microbial corrosion. Since among live organisms (agents of bio-corrosion), bacteria and microscopic fungi are the basic types, therefore the terms "bacterial" and "fungi" corrosion are used in the literature. Currently, the terms bio-corrosion and microbial corrosion include non-metallic materials, such as concrete, when the intensity of destruction of the building material is high enough [5].

The biodeterioration include all undesirable changes in the properties of materials caused by intravital activity of the organisms. The biodeterioration occurs because of various types of impact of live organisms on building materials (Fig. 2).

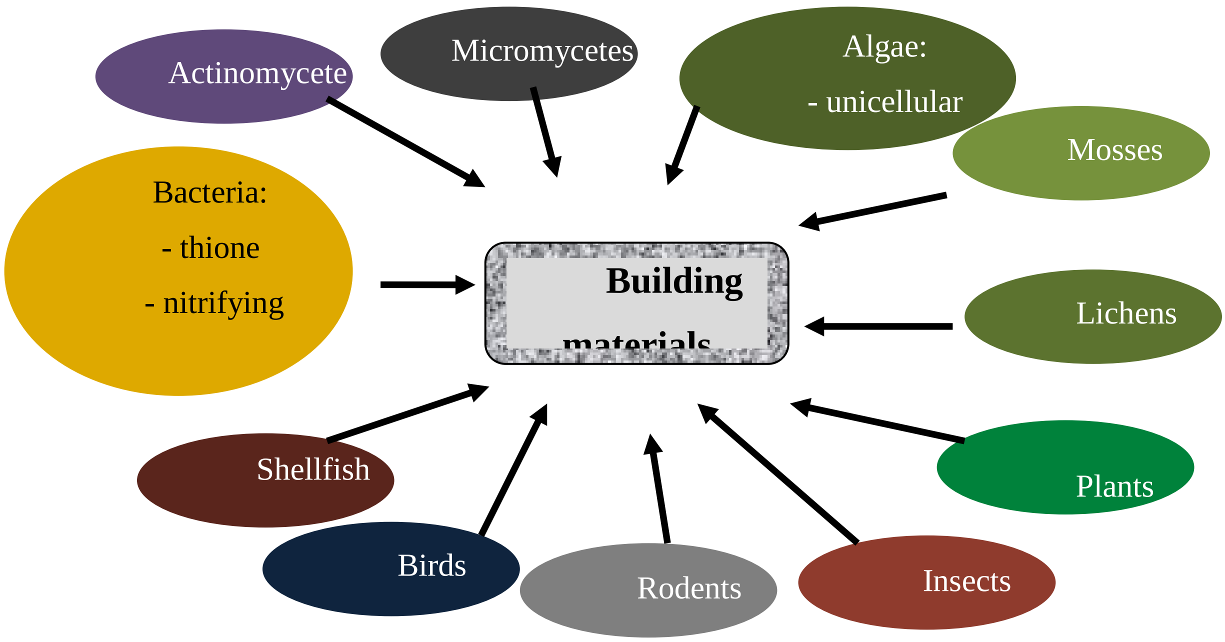

Fig. 2. Living organisms involved in the processes of biodeterioration of building materials [6]

The main bio destructors of building materials are bacteria, fungi, algae, lichens, mosses, plants, insects and other. The colonization and growth of these live organisms on concrete surfaces lead to external biodeterioration (Fig. 3) and a significant deterioration of the physic-technical properties of the material until fracture.

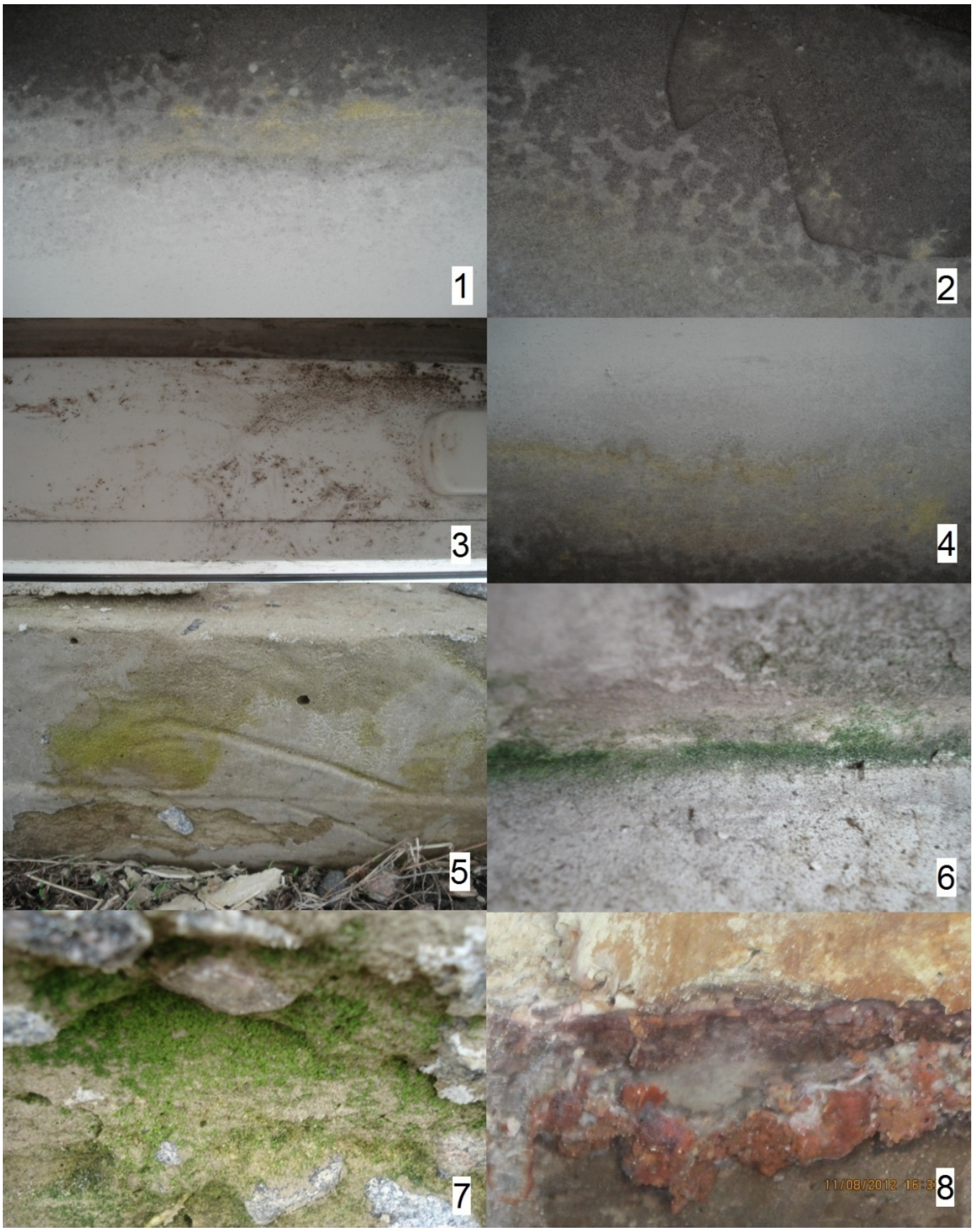

Fig. 3. The biodeterioration of building materials
1, 2, 3, 4 – filamentous fungi; 5, 6 – algae;
7 – mosses; 8 – iron and thiobacteria

There are three main types of action of microorganisms. The first is the creation of corrosive media as a result of the accumulation of waste products such as acids, alkalis, sulfides and other aggressive substances, which can make any indifferent environment more corrosion-dangerous (assimilation pathway). The second is connected with situation when corroding substrate is directly involved in one or more reactions on the surface (dissimilation). The third is connected with the presence on the surface of building structure and direct physical impact on building materials (mechanical).

The microbial corrosion of metals. External displays of metal corrosion do not differ significantly from the usual corrosion accompanied by rust, for example, in the case of atmospheric corrosion. Therefore, even corrosion experts are not always able to recognize biological corrosion, and they have to turn to microbiologists to determine its biological nature.

The impact of microorganisms on metals can be different. First, metal corrosion may be caused by aggressive exometabolites of microorganisms – mineral and organic acids and bases, enzymes, etc. They create a corrosive medium, in which the corrosion proceeds in the presence of water according to the usual laws of electrochemistry. Colonies of microorganisms can create erosion scabs and film of mycelium or mucuson on the surface of the metal, under which may occur a pitting corrosion as a result of the electric potential difference at various parts of the surface of metal and assimilation of metal ions by the microorganisms.

The most dangerous type of microbiological corrosion is an aerobic corrosion inflicting huge damage to the oil and gas industry, water recycling systems, offshore structures, etc. [7].

This type of corrosion is observed in cases where there is a large amount of free or dissolved oxygen in the water. The activators of aerobic corrosion are thionic, nitrifying bacteria and iron bacteria. Because of the activities of thiobacteria and nitrifying bacteria, corrosive media can occur due to the accumulation of sulfuric and nitric acids (products of their metabolism). Corrosion under anaerobic conditions can be caused by sulfate-reducing bacteria developing within the range pH 6,8–8 with sulfate in medium. The hydrogen sulfide (result of their metabolism) is able to bind divalent iron and desoxydate the ferric hydroxide with thick sediment of iron sulfide [8].

The biodeterioration of concrete. Concrete structures at plants of chemical, food, medical industry, as well as sewage collectors and facilities for wastewater are particularly intense subject to damage. The specifics of these industries are the presence of good breeding ground for microorganisms. The degradation process of cementitious materials is accelerated because of microbiological corrosion, especially in very humid environments with high temperature and reduced air supply. During operation under atmospheric conditions, the biological stability of concrete structures worsens because of the growth of technogenic contaminants in the environment in the form of dust, aerosols and gas impurities, which lead to accelerated corrosion processes [9].

Bio resistance of cement composites is limited by their nature, because the capillary-porous materials tend to active interreaction with microorganisms and their metabolic products. Frequently, concrete with good physical and mechanical properties is not resistant in organogenic mediums.

The metabolic byproducts of microorganisms such as acids, sulfides, ammonia and other are aggressive and cause destruction of concrete and reinforcement in concrete structures.

Inorganic and organic acids and hydrogen sulfide are formed with thionic, nitrifying, hydrocarbon, sulfate-reducing bacteria, fungi, yeasts and other microorganisms. The most active in terms of corrosion are lithotrophic bacteria oxidizing inorganic compounds: sulfur, sulfides, polythionate, ammonia to form sulfuric acid and nitric acid [10].

Destruction by micromycetes of composite materials based on natural and synthetic polymers

Fungicidal destruction of materials proceeds in steps. The technology of formation of bio chemically resistant coatings is developed taking into account the stepwise mechanism of growth of bacteria and fungi on material. First, species of fungi, which are least demanding to moisture are growing, and then fungi more demanding to moisture are growing. The first type gives extra moisture in lifetime. During the sequential process of colonization, the biochemical features of fungi play an important role. Products of growing of a certain types of fungi inhibit life of other types reserving the space. When the object to be protected by chemicals, first, fungi capable of destroying harmful substances are developing, then fungi, which use the elements of disrupted chemicals as food are growing. In the study of the formation of microbial associations on materials, it is necessary to consider the physiological features of each component. Component activity of separate associations determines the intensity of destruction by association as a whole.

Harm from fungi is not related only and perhaps not so much to the mycelium fouling of materials, and primarily to the destructive action of fungi metabolites. Therefore, the efficiency of the destructive action should be measured not by the assessment of fouling, but by the intensity of excretion of metabolites contributing to the destruction of materials and by the resulting corrosion. This demonstrates the need for the development of new test methods for fungal resistance based on measuring the activity of metabolites.

A great deal of attention is now being paid to obtaining polymer compositions based on natural (chitin, chitosan, starch, cellulose) and synthetic polymers. When such hybrid polymer compositions are created, particular attention should be given to the compatibility of components and the development of technological methods of synthesis (co)polymers based on natural polymers and broad spectrum of vinyl monomers.

The advantage of such materials is their adjustable resistance to microorganisms, which allows obtaining bio resistant compositions and easily biodegradable compositions.

Polymethyl and polyacrylonitrile have the greatest resistance to micromycetes. Chitosan, polyvinyl chloride, polyvinyl alcohol, starch, sawdust, and methylcellulose are easily recyclable polymers [11].

The polymer materials based on acrylate (organic glass, paints) are widely used in industry and construction. However, under conditions of high humidity and temperature, the polymeric material based on acrylates can be deteriorated by microbiological damages, mainly by fungi. The composition of the film-forming polymer and the physical properties of film coating obtained from it (swelling properties, hardness, porosity, hydrophobicity, etc.) are crucial for the microbiological resistance of paint coatings.

Currently there is practically no absolutely bio stable polymer materials based on acrylates. Depending on their chemical composition and structure, we can only mention compositions more or less resistant to biodeterioration.

The development of diagnostic systems and process control of biodeterioration of materials

Against the background of floods, fires, landslides, radiation, vibration fields and other natural and anthropogenic impacts, the biological degradation of materials and structures, unnoticeable and permanent destruction of buildings by microorganisms receive insufficient attention of builders and operators. It does not attract attention because of its invisibility. The danger and intensity of biological contaminations of environment and destruction of buildings and structures are steadily increasing, venturing by human activities. These include the neglect of environmental norms during the construction of buildings, ignorant and careless operation (countless damage to the roof, leaks, flooding basements, sanitary ware failure, and other factors) [12].

In real combined environmental conditions, the deterioration occurs from exposure to sunlight, water, low temperature, temperature changes, humidity changes and from the complex effects, connected with the growth of living organisms on construction materials. Prolonged exposure of these factors leads to a loss of mass, reduction of physical and mechanical properties, frost resistance and operating characteristics [13]. There is an environmental aspect of the problem in addition to the technical aspect. Microscopic fungi fouling of constructions, breeding of bacteria in porous building materials worsen the hygienic conditions in the premises, and afterwards have a negative effect on people's health.

There are various contaminants in the air of urban areas (solid - in the form of dusts, gases - formaldehyde, phenols, nitrogen dioxide, in the form of liquid and aerosols - heavy metals, drops of inorganic acids and others), which settle on the outer surface of building. The contaminants, including contamination of biological nature, attack the materials, construction of buildings and structures in the process of construction and operation during precipitation in conditions of additional impact of variable temperature worsening aesthetic look of building, contributing to the premature destruction of materials and increasing the risk of disease. Such impact is manifested visually in the form of white plaque of efflorescence, mosaic of colonies of fungi of different colors, destruction (flaking) of paint and plaster layers, color change, the most noticeable on the surface of porous building materials used to improve the thermal insulation of buildings and normal heat exchange of building.

Groundwater also contribute to the hydration of materials and structures taking into account high horizons, penetrating into them provided bad or broken insulation of foundations and rising further in the walls of buildings. Groundwater consist of soil salt, mainly chlorides and sulfates of sodium, calcium and magnesium, and complex organic substances serving as a breeding ground for soil microbes, which also come up at least to the first floors of building. Soil microbes often form colonies inside walls and on the surface in the area of the first floor. Moreover, the atmospheric moisture can get into the building elements when the drainage devices are broken or even when there are no bends at the lower parts of downpipes.

Comparative examination for external damage of the surfaces of buildings of different zones of large city has shown, that 80% of buildings located along roads and near industrial areas have local areas of biodeterioration, 40% of homes in residential areas, whereas this indicator did not exceed 20% in the recreational area [14].

The Set of Rules "Protection of building structures from corrosion" adopted in 2013 [15] shows a classification of damaged structures made of concrete, brick and natural stone (Table 1), which enables to perform complex diagnosis of the materials and structures on the extent of their biological destruction.

Table 1

Determination of the extent of biological damage of constructions and structures, caused by the action of bio destructors

The extent of biological damage	Characteristics of construction	Characteristics of damage
I	Constructions made of brick and concrete, the surface of which is covered with finishing material	Plaster mold on the surface of finishing material: plastering, painting layer, wallpaper or other covering
	Constructions made of unprotected brick, concrete, reinforced concrete	Surface plaster mold without visible damage
	Constructions made of natural stone	Surface plaster mold without visible damage
II	Constructions made of brick and concrete, the surface of which is covered with finishing materials	Local damage of finishing coats, blistering and flaking of paint, putty and plaster layers
	Constructions made of unprotected brick, concrete, reinforced concrete	Surface damage to 2 cm depth (for concrete - without uncover of reinforcement)
	Constructions made of natural stone	The surface is covered with dense crust of biological origin, the stone surface has a slight visible damage up to 0.5 cm
III	Constructions made of brick and concrete, the surface of which is covered with finishing materials	Flaking, peeling of plaster, putty, loss of the paint or other finishing coats, peeling of tile trim
	Constructions made of unprotected brick, concrete, reinforced concrete	Scaling, crumbling of brick, masonry mortar; scaling and crumbling of concrete and reinforced concrete, exfoliation of corrosion layer of

		concrete reinforcement
IV	Biodeterioration of II and III extent is typical for 50-60% of constructions of building or structure	

Such works should include:

- on-site examination of the objects (both interior and external surfaces of buildings and structures) to establish the existence and nature of biodeterioration;
- sampling from the surface of the damaged building materials and indoor air testing for microbiological contamination, which is the result of a wide range of health problems;
- study of environmental factors affecting the bio degradation processes in order to find their causes.

The fact of appearance of various bio destructors on the external surfaces of buildings and interiors requires further study of microbial features with estimation of the extent of biological contamination of materials and potential health risk to human.

Bio diagnostics of a wide selection of promising building composites regarding the biological stability, the creation of systems to control their antimicrobial properties are extremely important.

Thus, the issues concerning the improvement of biological protection of residential and public buildings requires organizing the inspection of buildings, expert analysis, establishment of specialized laboratories for the study of bio degradation processes and bio-resistance of materials. It also requires the development of program to prevent biodeterioration of cities and systems of control of corrosive and biochemical processes in the construction, ensuring adequate protection and safety of buildings and structures.

Development of a complex of measures, which can significantly improve the quality of the human environment under conditions of working and living in civil and industrial buildings and structures

Improving the quality of the human environment is directly connected with the need to maintain appropriate hygienic conditions, not only indoors, but also in the territories of housing units. The biocidity as a characteristic of building materials, on the one hand, allows ensuring sterility mode, for example, in the premises of medical purposes and at factories of food, pharmaceutical and other industries. On the other hand, it allows preventing biodeterioration processes of buildings and structures by organisms, which are often unsafe for human.

Currently there is no universal protection against microbial corrosion. The most reliable way to control it would be to remove microorganisms causing or intensifying the corrosion process. However, it is nearly impossible to solve this problem. The method aiming to create materials that are resistant to microbial attack is more realistic.

One of the most effective and long-acting methods of protection of building materials and structures from attack by microorganisms is the use of biocidal products. However, not fully understood mechanisms of interaction with construction materials, high adaptability of microorganisms to a changing environment make the issue of protection of building materials and structures rather complex and challenging.

The use of special chemical compounds, which are toxic to microorganisms, is one of the most promising method of protection of both materials and environment from biological contamination.

Toxicants are divided into the following groups by the nature of their action:

- biocides which destroy microbial pathogens of biodeterioaration;
- biostatics inhibiting the growth of microorganisms;
- repellents causing deterrent effect of the agents of biodeterioaration.

Since microflora affecting materials and products is very diverse and often includes organisms belonging to different groups, it is mostly appropriate to apply a broad-spectrum biocides and mixtures of various compounds.

According to the chemical composition, the biocides are classified as follows [16]:

a) inorganic compounds (including heavy metals - silver, copper, nickel, zinc, cadmium, chromium and other);

b) hydrocarbons (the most common - diphenyl), halogenated hydrocarbons and nitro compounds;

c) alcohols, phenols and their derivatives (2-hydroxy-diphenyl, n-nitrophenol, hexachlorophene, etc.);

d) aldehydes (formaldehyde), ketones, organic acids and their derivatives;

e) amines, amine salts and quaternary ammonium compounds (metatsid, catamine AB and other);

f) organoelemental compounds (organic mercury compounds, organotin, organoarsenic and other compounds);

g) heterocyclic compounds (furacilin, copper 8-oxyquinolate and other).

Given the presence of heavy metals in various industrial wastes, heavy metal can be regarded as the source of components, which could be a base of biocidal composites. Such direction requires the development of technologies of selective release of target components, their modifications and methods of inclusion in composition of construction composite materials. However, the economic efficiency of such processes with the option of recycling large tonnage wastes of 3-4 hazard classes makes such studies meaningful.

Thus, recycling of wastes of gas purification from metallurgical enterprises using hydrometallurgical methods is implemented at some plants in Italy and the USA. Dust of gas purification is leached in a solution of ammonium chloride. The reaction of the leaching of heavy metals is (1):

$$MeO+2NH_4Cl \rightarrow Me(NH_3)_2Cl_2+H_2O \quad (1)$$

After leaching, the solution is electrolyzed with titanium electrodes (2):

$$Me(NH_3)_2Cl_2+2/3NH_3 \rightarrow Me+2NH_4Cl+1/3N_2 \quad (2)$$

The extraction of heavy metals from steelmaking wastes may be carried out by leaching with a solution of acetic acid [17] to form the corresponding soluble metal complexes and further sulfide deposition by hydrogen sulfide (3, 4).

$$MeO+2CH_3COOH \rightarrow (CH_3COO)_2Me+H_2O \quad (3)$$

$$(CH_3COO)_2Me+H_2S \rightarrow MeS+2CH_3COOH \quad (4)$$

The authors carried out the study aimed at obtaining biocidal compositions for building materials, buildings and structures from wastes of galvanic manufacture, containing compounds of copper, chromium, zinc, nickel.

Method of processing of sludge of galvanic manufacture includes grinding, leaching, separation of the solution from the sediment and extraction of heavy non-ferrous metals from the solution obtained. Sludge grinding is carried out using mechanochemical activation by wet grinding in the form of sludge suspension with pH ≤ 3 in the ratio s: l = 1:(0,4-1) at 60-90 ^{0}C.

After grinding the activated slurry was leached by acidic wastewater of own galvanic production at 70 ^{0}C and pH=3. After leaching the sediment was washed with pure water.

The solution after separation from the sediment by filtration was placed in electro flotation cell. The flotation process was performed at current densities 50 mA/cm^2 within 20 minutes at elevated pH = 8-10. The anionic SAW – potassium alkylbenzolsulfonate (sulphonol) in the amount of 5 mg / l and potassium xanthate in the amount of 3 mg per 100 mg of metal ions in solution were used as the foaming agent and collector in the flotation extraction of metals.

Foam concentrate was dried and calcinated at 600^{0}C to obtain a metal powder [18].

Biocidal properties of the powders obtained were determined by the ways in which they affect a variety of living organisms, which most commonly cause biodeterioration of building materials.

Studies have shown that introduction of additives, obtained after processing of galvanic sludge, contributed to the reduction of the extent of fouling of the samples on average about three times in the case with green and blue-green algae. Therefore, it could be concluded that component, obtained from galvanic sludge using new technologies, is effective as a biocidal additive of concentration 1-2%, which prevents the growth of algae.

Among the biocidal substances, the photocatalysts are very interesting, because they are able to provide long-term biosecurity without additional energy. They often preclude the use of dangerous disinfectants and do not emit toxic substances. For this reason, new developments connected with photocatalytic biocidal coating of the materials used for the construction of crowded buildings and structures are necessary and relevant. Furthermore, such materials should be used to improve sterility at medical institutions and factories, which produce food.

To date, there are a number of reviews on the use of photocatalytic chemistry in solving the problems of disinfection of materials and premises in general [19].

Sterility of the premises of medical purpose and enterprises of food, pharmaceutical and other industries is a complex issue and requires a focused selection of disinfectants. Ultraviolet radiation, chemicals such as chlorine-containing and phenol-containing agents, guanidine derivatives, and others are traditionally used to disinfect the premises [20, 21]. However, the above antimicrobial agents have a number of disadvantages: ultraviolet radiation is characterized by low penetration ability; chlorine-containing and phenol-containing agents are very toxic, unstable, and interreact with materials processed. It is also important that long-term use of chemicals can lead to artificial selection of resistant forms of microorganisms. The need to overcome these disadvantages requires the development of more efficient disinfection technology. One of perspective directions in this field is to create photocatalytically active coatings (primarily TiO_2-based). There is a reagentless destruction of microorganisms on the surface of these coatings. The basis of biocidal activity of such photocatalysts is the deactivating effect of various forms of active oxygen (•OH radical and $•O_2$, radical, and hydrogen peroxide radical), which are formed in the presence of semiconductor photocatalysts with both the photoelectrons from the conduction band and photo hole from the valence band.

The targets of disinfection are pathogenic microorganisms, including viruses, bacteria, fungi, protozoa and algae. Each option of impact poses a problem of structures and protection mechanisms that must be overcome. The disinfection technology is based on the induction of chemical or photochemical damages or physical removal. The photocatalytic disinfection using irradiated titanium dioxide is effective to kill a wide range of microorganisms and cell structures. The process can be used in the air and water media and can be used in vivo. The photocatalytic method includes several methods of influencing microorganisms. They can work together – titanium dioxide adsorption on the surface of cell wall with further penetration inside and formation (on the cell wall and inside the cell) of reactive oxygen intermediates in both cases (with oxidative aggression towards the components of cells) and devastating effect of other direct and indirect photochemical processes [22]. The result of vital activity of invisible germs is the damage of the buildings and other engineering structures. There are cases when biodeterioration of structures was the main or one of the main reasons, which led to collapse of buildings, engineering structures. The resistance of building materials could be improved by introduction of biocidal additives or coating the materials with special protective films. The use of special protective materials with special properties is one of the most perspective methods of protection of the materials from environmental factors by creating products with specific properties.

The popularity of the classic sol-gel method is associated primarily with the fact that the resulting products have the unique properties: high chemical homogeneity allowing to increase the resistance of building materials to external impacts and the ability to control the particle size and pore structure of materials. The sol-gel method allows obtaining fundamentally new materials with required properties, which can be used under other conditions and perform certain functions. One example is the use of sol-gel coatings to protect building materials from aggressive environmental conditions and microorganisms considering bio deterioration [23]. Additional elements included in the sol may be, for example, nanoparticles of silicon oxide, which eventually transform into hydrous calcium silicate. They fill the pores contributing to their significant reduction [24].

Conclusions

Thus, a range of measures to improve the quality of living environment includes the following items:

- creation of composite construction and finishing materials with photocatalytic coatings;

- development of technology of separation of biocide component (containing heavy metal compounds) from solid waste of industries;

- development of technology of inclusion of obtained biocides in the composition of composite materials;

- biological control of the quality (checking biocidity) at all stages of the technology.

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N. Grigorova, M. Kuzmina

THE MAGNESIUM AND COPPER CONTENT IN BLOOD LYMPHOCYTES AND GRANULOCYTES OF ANIMALS WHILE ZINC, MAGNESIUM AND COPPER SULFATES INTRODUCTION

Zaporizhzhya National University

Introduction. The magnesium and copper are important elements of the human and animals organisms [2]. They determine different processes state that exert to cells activity including lymphocytes and granulocytes [2, 3, 6]. It was found the role of metals in regulation of leukocytes enzymatic system activity [2-4, 6]. The magnesium ions strengthen lipoprotein membrane by linking of negative charge carboxylic group [2, 3]. The copper also support the cytolemma stability. It includes with zinc in superoxide dismutase active center. This enzyme performs primary detoxification of the oxygen active forms in organism [7]. Property of phagocytes chemoattraction stimulating effect is representative for the copper in addition to antioxidant activity. The phagocyte consume activity directly depends on amount of the copper-bearing protein in it [2, 6]. The magnesium effects on granulocytes ability to accumulate and secrete the histamine [3, 4]. When it is insufficient the quantity of polymorphonuclear and eosinophilic cells in blood drops, B- and T-cells activity decreases [2, 3]. The copper also has a pronounced immunomodulatory effect, which was neatly detected while research of the primary and secondary immune responses [1, 2, 6]

Considering the role of metals in the lymphocytes and granulocytes functioning, it was interesting to research the influence of the salts of these metals and also of the zinc, that is the functional synergist of the magnesium and the antagonist of the copper, on the intracellular magnesium and copper amount.

The aim of the work was to define the magnesium and copper content in blood lymphocytes and granulocytes of animals while zinc, magnesium and copper sulfates introduction.

Materials and methods of testing. It was used the peripheral blood smear preparations of 47 mouses and 49 rats, 30 of which were control (intact). The zinc and magnesium sulfates solutions were injected intraperitonealy in a dose of 10 mg/kg, and the copper sulfates solution – in the same mode in a dose of 5 mg/kg. In 12 hours after injection the metal sulfates solutions the animals were taken blood counts from tail for cytochemical analysises.

The smears were fluorochromized by spirit solution of lumomagneson (LM) to determine the magnesium in the blood lymphocytes, and by water solution of lumocupferon (LC) - to determine the copper. Then oil immersion was applied to blood smears and they were viewed in the luminescent microscope (light filters V-1, Y-18). The lymphocytes cytoplasm rose-coloration intensity when setting LM-reaction and this cells cytoplasm yellow-green coloration intensity when setting LC-reaction was measured by microfluorimeter. The intensity of fluorescence was evaluated into reference unit (ref. un.).

For the magnesium content detection in granular leucocytes the blood smears were fixed in the ascending vapors of formalin, then were stained in the mixture comprising solution of magneson, sodium acetate, ammonium hydroxide and distilled water. In case of the copper cytochemical detection fixed in the same mode smears were stained with dithiooxamide solution (DTO) composed of a mixture of saturate spirit solution of ruberythric acid, water solutions of sodium acetate and ammonium hydroxide. The preparations were viewed in the optical microscope. The magnesium was detected in granular leucocytes cytoplasm by red coloration of the granules, and the copper - by dark-green color of them.

The intensity of cytochemical reactions in the blood granulocytes were evaluated according to the three-grade system into reference unit. Obtained results were statistically processed by Student's t-criterion with the use of the Statistica, 6.0 program. It was calculated Pearson's correlation coefficient (r) to assess the degree of binding between studied characteristic changes.

Results and their discussion. Obtained results show that after zinc and magnesium sulfates injections the magnesium content in blood lymphocytes was increased by 34 i 40% ($p<0,05$) in mouses, by 32 i 38% ($p<0,05$) – in rats. In case of the copper sulfate prescription was observed the decrease of metal amount in cells by 26% ($p<0,05$) in mouses, by 25% ($p<0,05$) – in rats.

The copper amount in blood lymphocytes of the mouses and rats was increased by 49% ($p<0,001$) and 44% ($p<0,01$) under the influence of this metal salts, and was dropped after zinc salt injections by 25% ($p<0,01$) and 23% ($p<0,05$), magnesium salt – by 37 i 33% ($p<0,001$) respectively (table 1).

The negative correlation of the magnesium and copper content changes in the blood lymphocytes of the experimental animals was prescribed.

Table 1

The magnesium and copper contents (M±m) in the blood lymphocytes of the mouses and rats and their interaction (r) while the zinc, magnesium and copper salts injection

Group of animals	The mouses		The rats		r_1	r_2
	LM method, ref. un.	LC method, ref. un.	LM method, ref. un.	LC method, ref. un.		
Control	125±10,8 (n=14)	67±4,2 (n=14)	133±12,5 (n=16)	75±5,8 (n=16)	- 0,46*	- 0,44*
Animals with zinc sulfate introduction	167±14,2 * (n=10)	50±3,3** (n=10)	175±15,8* (n=10)	58±4,2* (n=14)	- 0,36*	- 0,35*
Animals with magnesium sulfate introduction	175±15,0 * (n=12)	42±2,5*** (n=12)	183±16,7* (n=12)	50±3,3*** (n=12)	- 0,35*	- 0,34*
Animals with copper sulfate introduction	92±5,8* (n=11)	100±7,5*** (n=11)	100±8,3* (n=11)	108±9,2** (n=11)	-0,92***	-0,91***

Note. There and in table 2. *$p<0,05$; **$p<0,01$; ***$p<0,001$ comparing to control; r_1 – correlation coefficient of magnesium and copper content changes in the blood cells of the mouses; r_2 – correlation coefficient of magnesium and copper content changes in the blood cells of the rats.

The similar changes were observed in the blood granulocytes of animals while the zinc, magnesium and copper salts introductions (table 2).

Table 2

The magnesium and copper contents (M±m) in the blood granulocytes of the mouses and rats and their interaction (r) while the zinc, magnesium and copper salts injection

Group of animals	The mouses		The rats		r_1	r_2
	Magneson method, ref. un.	DTO method, ref. un.	Magneson method, ref. un.	DTO method, ref. un.		
Control	0,7±0,05 (n=14)	0,5±0,03 (n=14)	0,8±0,06 (n=16)	0,5±0,02 (n=16)	- 0,71**	- 0,64*
Animals with zinc sulfate introduction	0,9±0,06* (n=10)	0,3±0,01*** (n=10)	1,0±0,07* (n=10)	0,3±0,04*** (n=10)	- 0,48*	- 0,39*
Animals with magnesium sulfate introduction	1,0±0,08** (n=12)	0,4±0,01* (n=12)	1,1±0,09* (n=12)	0,4±0,02* (n=12)	- 0,47*	- 0,38*
Animals with copper sulfate introduction	0,5±0,02*** (n=11)	0,7±0,05** (n=11)	0,5±0,05*** (n=11)	0,7±0,06** (n=11)	-0,72**	-0,76***

The zinc sulfate injection was caused the increase of magnesium amount in cells by 29% ($p<0,05$) in the mouses, by 25% ($p<0,05$) – in the rats. In so the copper content in both kinds of animals was decreased by 40% ($p<0,001$). After magnesium sulfate injection experimental parameter changes made respectively 43% ($p<0,01$) and 20% ($p<0,05$) in mouses, 38 i 20% ($p<0,05$) – in rats.

Under the copper sulfate in the granular leukocytes was found the decrease of magnesium content and increase of the copper amount by 29% ($p<0,001$) and 40% ($p<0,01$) in mouses, and by 37% ($p<0,001$) and 40% ($p<0,01$) in rats accordingly. In all cases the negative correlation coefficient of the metal content changes in the blood granulocytes of the experimental animals was prescribed.

So under the magnesium and zinc sulfates influence the magnesium accumulation was arisen in the blood lymphocytes and granulocytes of mouses and rats against the copper deficiency. The increase of copper content and deficit of magnesium in researched cells was observed in case of the copper sulfate prescription.

Antagonistic character of metals content changes in the in blood lymphocytes and granular leukocytes was confirmed by negative correlation link.

Conclusions

1. In the blood lymphocytes and granulocytes of the mouses and rats that were injected with the zinc and magnesium sulfates, was observed the magnesium accumulation against the copper deficiency.

2. The copper sulfate obtained by animals causes the copper amount augmentation and the magnesium content decrease.

3. The correlation analysis showed an antagonistic character of the magnesium and copper content changes interaction in blood cells of the experimental animals.

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