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Creating Bioresistant Technogenic Waste Basted Coatings for Construction Materials

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Abstract

The biodeterioration process of concrete, having a sol-gel coating, under the impact of a wide range of live microorganisms - green algae, thionic and nitrifying bacteria and filamentous fungi - has been researched. As a biocide additive the biocidal composite material based on modified galvanic sludge in amount of 1-5% of sol mass was used. It was determined that the coating including galvanic sludge demonstrates biocidal activity. Newly formed crystals of quartz, Portlandite, calcite, larnite, ettringite, gismondite, scawtite etc. were found on the surface of samples having no protective coating and exposed to microorganisms.
Application of the suggested method of building materials protection is going to increase their durability, make it possible to recycle waste and to improve the environmental condition.

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Keywords: Biodeterioration; biocidal coatings; galvanic sludge; bioresistance of building materials.

1. Introduction

The problem of building materials durability is becoming more and more challenging due to quick material ageing and strength loss of buildings and constructions because of adverse effect of various chemical agents and microorganisms, which get to the environment with the anthropogenic pollution.

The cement stone is the most chemically active of these materials and due to this it is more prone to deterioration as a result of the aggressive environment chemical action [1-4]. In urban environment conditions the surface of

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building structures is attacked with a number of various organisms, and deterioration of materials, including concrete, develops rapidly in conditions, favorable for agents, which have predominantly aggressive type of action (chemolithotrophic bacteria and micromycetes) [5-9]. These agents can leach out the mineral matrix with the subsequent strength loss of the binding building material [2, 5, 6].

The problems of ageing and resistance to wearing-out processes, including corrosive resistance, have been paid more and more attention lately [2-8]. The resistance of building materials can be increased by introducing biocidal additives or by providing materials with special properties, which allow improving their bioresistance in the environment.

The application of special protective coatings, possessing the special properties, is one of the most promising methods of preserving building products against the environmental factors by making constructions with the given set of certain properties. Identifying the necessary characteristics of materials and managing the properties of additives in form of inorganic compounds, nanoparticles, films, colloid systems with the purpose of obtaining composite materials with new predetermined properties is the priority task of modern science.

The popularity of classical variant of sol-gel method is conditioned in the first place with the fact, that the obtained materials have high chemical uniformity and high resistance [10-12]. The application of sol-gel method allows creating the fundamentally new materials with predetermined properties, expanding the functional capabilities of products' use. One of such examples is the application of coatings to protect concretes against the aggressive action of environmental conditions and microorganisms, which cause materials biodeterioration.

The purpose of this work was the creation of bioresistant concrete products, by using galvanic sludge component as a biocidal additive for the sol-gel coatings.

It must be taken into account, that without the preparatory extraction of valuable, or quantitatively prevalent, or target components the high-efficient usage of waste is economically and environmentally impractical. The compounds of necessary metals were extracted out of waste by means of leaching, using acid solutions, which contributed to the concentration of zinc, nickel, copper, chrome, lead ions [13-16] in the obtained modified waste, which made it possible to use it further as a biocidal composite additive for the coatings of the produced building materials.

2. Materials, conditions and methods of research

In the experiment to determine bioresistance of composites, containing the biocide obtained from waste, the concrete samples were used, covered with sol-gel containing modified sludge in the amount of 1 and 5 %.

As sol precursors the Tetraethoxysilane, ethanol, nitric acid and distilled water were used. The biocidal component was added to the mixture as a part of one of the components. The preparation of silica sol was based on the two-stage method of Tetraethoxysilane hydrolysis in acid medium [10-12].

As test objects the microfungus *Aspergillus niger sp.,* bacteria (*Escherichia coli, Thiobacillus sp., Nitrosomonas sp., Nitrobacter sp.*), green and blue-green unicellular algae were used.

The algae were cultured in the Tamiya liquid growing medium, the thionic bacteria – in the Beyerinck medium, the nitrifying bacteria – in the Vinogradsky medium, the filamentous fungi – in the Czapek-Dox medium, the amount of heterotrophic microorganisms in the plain broth [17,18].

The biocidal activity of sol-gel mixture, containing modified waste, was evaluated by spreading the microorganisms' suspension on object plates, covered with gel preliminarily. The test specimen was a variant of coating without the biocidal additive.

The number of microorganisms' cells was determined with Axio Scope A1 (Carl Zeiss Jena) microscope by count-up method; the fungicidity area at working with microfungi was calculated after measuring the area around the sample under research, where the culture was not growing [2].

3. Results and their discussion

The criterion of the of sol-gel mixture biocidal activity was the percentage of dead microorganism cells on its surface , which was calculated as a ratio of living cells to dead cells after examining the material, dyed with vital stain, under the microscope. The findings of the experiment are shown in tab. 1.

Table 1. Bacteria and algae death rate on the surface of coating, containing the biocidal component.

Type of coating	Green algae (%)	Bacteria (%)	Biocenosis, including algae and bacteria (%)
Sol-gel coating with biocidal galvanic sludge component	40-50	0-10	10-20
Coating without additive	0-10	0-10	0-5

As follows from experimental data, presented in tab. 1, the coating containing biocide component of sludge waste, possesses the biocidal activity. The most sensitive to biocide were green algae, the death rate of them amounted to 50%. In the biocenosis comprised of algae and bacteria this rate was reduced to 20%. Probably, this occurs, as has been shown before [7,8], because of consolidation of microorganisms' conglomerates due to bacteria forming a similigley substance, which appears to protect the living systems against the biocide action.

On an object plate without coating the microorganisms were not dying. It has been discovered, that the pure sol-gel coating (without additive) has a minimal biocidal effect on microorganisms of itself (the death rate of cells 0-10%), which is within the limits of statistical discrepancy.

The growth of microfungus on solid medium near the shaped gel mass, containing the additive, was not observed (the fungicidity area amounted to over 50%).

At making products with coatings, the sol-gel was placed on the surface of concrete cubes by the dipping method. The samples of building materials were then placed into mediums, simulating the submerged cultivation conditions (in case with bacteria and algae [6,8]) or onto the solid medium, having spread preliminarily the culture suspension onto the sample's surface (in case with microfungi [2]), after which they were kept in conditions, optimal for microorganisms growth for a month. After the experiment the state of samples under research was evaluated visually (integrity, new formations, the degree of surface encrustation with microorganisms), and by alteration of mass content and strength.

The results of the samples' visual inspection after the experiment are presented of Fig. 1- 5.

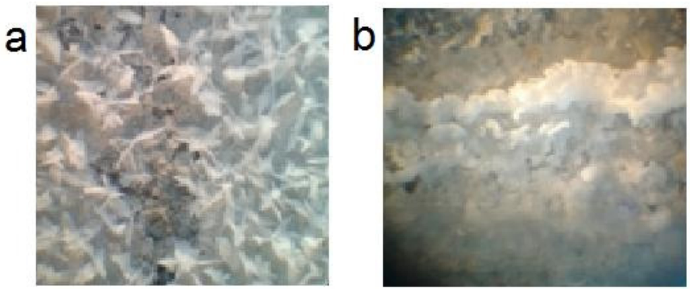

Fig. 1. Test medium with thionic bacteria (a) surface with coating; (b) without coating.

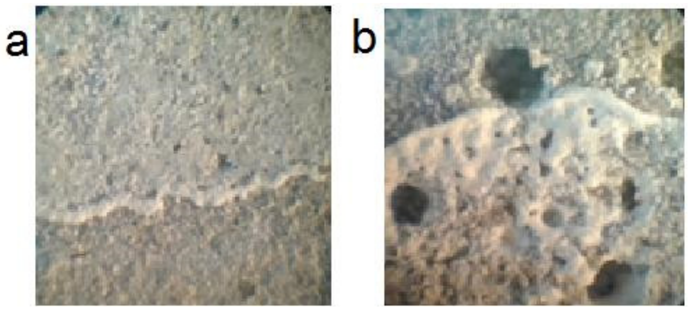

Fig. 2. Test medium with nitrifying bacteria (a) surface with coating; (b) without coating.

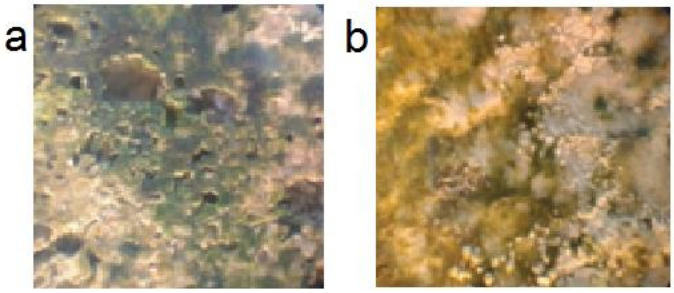

Fig. 3. Test medium with algae (a) surface with coating; (b) without coating.

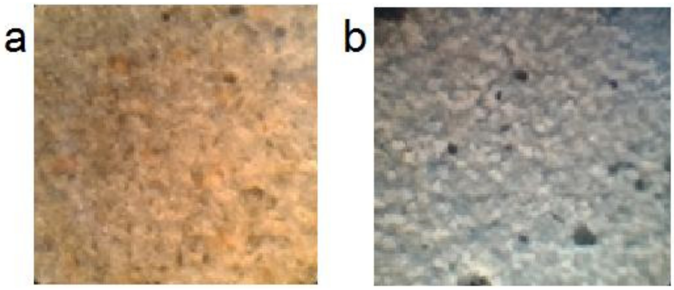

Fig. 4. Tap water (a) surface with coating; (b) without coating.

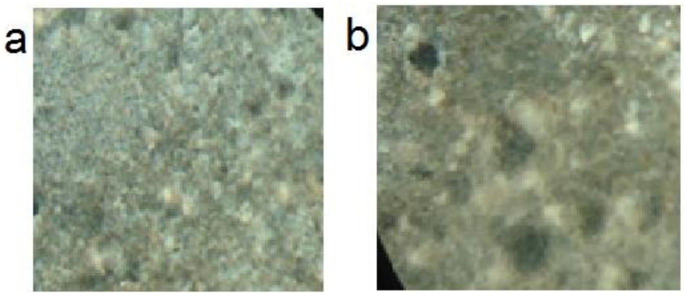

Fig. 5. Test medium with micromycetes (a) surface with coating; (b) without coating.

The encrustation rate of concrete samples with the coating, placed into the medium with algae, was no more than 25%, while for the test samples it amounted to 70-75%.

The growth of fungi, covering less than 25% of the test samples' surface, was seen distinctly with the unaided eye. The presence of gel matrix obviously increased the resistance of the cubes to fungi: the germinated spores and underdeveloped mycelium were observed at the microscopic examination of the surface.

It was discovered, that the surface of samples without coating in all cases had undergone more changes, than the samples with coatings. These changes were presented by various newly-formed crystalline structures. In the case of samples, placed into the medium with algae, where the transformation of $Ca(OH)_2$ to $CaCO_3$ was observed, the carbonates may have accumulated on the surface.

Apart from the above-mentioned crystals in the variants with bacteria and algae the presence of such minerals as quartz, Portlandite, calcite, larnite, ettringite, gismondite, scawtite etc. was identified on the damaged surfaces. The certain increase of the weight of samples without coatings (in some cases by 10%) was also due to crystal formation. In the variants with biocidal coatings there were virtually no such effects.

The damage of the samples' integrity was also indicated by the alteration of the pH value: when keeping the samples without coating in the tap water the alkalinization of medium to pH= 10,5÷11,0 was observed, which is conditioned by the more intensive washing-out of Ca^{2+} due to the absence of coating.

In the test medium with thionic bacteria, and, in a lesser extent, with nitrifying bacteria, the leaching of Ca^{2+} ions into the solution at the absence of coating was accompanied with encrustation of samples with calcium sulfate crystals ($CaSO_4 \cdot 2H_2O$– calcium sulfate dihydrate) and the certain reduce of of pH (5,9-8,0). The increase of pH to 8,9÷9,3 in the medium of algae culturing, where corrosion is less intensive, comports with a certain amount of new crystalline formations.

The strength tests of the samples have indicated that even without any special treatment or dipping into test mediums the samples, covered with sol-gel coating, containing modified waste, are characterized, at an average, with strength by 15% higher, than the samples without coatings. More than that, the samples, covered with sol-gel coating, after keeping them in test mediums during two months, are mostly characterized with higher strength (increase by 30-100%), than the samples, placed into the same test mediums, but without any coatings.

After comparing the strength characteristics of samples without sol-gel coating, we can conclude, that the highest strength loss is observed for samples under the action of thionic and nitrifying bacteria (to25%).

4.Conclusion

The findings of the carried-out integrated research of the sol-gel coatings, containing biocide, obtained from galvanic sludge, demonstrate the possibility of creating bioresistant products by using such coatings, which would provide resistance to the action of various microorganisms, while preserving or even improving the strength characteristics of the products.

It must be pointed out that the coating makes it impossible for microorganisms to grow inside the concrete; in the environmental conditions it will reduce considerably the amount of microgerms in a volume unit and create the adverse conditions for the growth of a number of live microorganisms, due to low humidity level and adhesion.

Therefore, the building materials, having the sol-gel coating with biocidal composite material on the base of modified galvanic sludge are less prone to biodeterioration in the urban environment or in industries. So, the engineering measures of preventing the biodeterioration of building structures will require less economic costs, and will contribute to the preservation of urban buildings and production facilities, and to the improvement of population's health [19, 20].

5. Inferences

The coating based on modified galvanic sludge possesses the biocidal activity. The most sensitive to it are green algae, the death rate of which amounted to 50%. In the biocenosis comprised of algae and bacteria this rate reduced to 20%.

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