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BIO-RESISTANT CEMENT COMPOSITES WITH ACTIVE MINERAL ADDITIVE

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Abstract: Bio-damage is a serious problem affecting all stages of the life cycle of building materials, from the production and storage of raw materials to the transportation and operation of finished products. Bacteria and fungi, being the main agents of biodegradation, can significantly reduce the performance characteristics of materials, which leads to economic losses and a decrease in the quality of building structures. As part of this study, a comprehensive assessment of the biostability of cement composites was carried out. Special attention was paid to the study of the species composition of micromycetes colonizing the surface of composites, as well as the determination of fouling indices. The mechanisms of the effect of microorganisms on the physico-mechanical properties of composites, including their effect on mass content and strength characteristics, were studied in detail. The data obtained are important for the development of new strategies for protecting building materials from biodegradation, which will increase their durability and reliability under operating conditions.

Keywords: bio-resistance, physical and mechanical properties, biocidal cements, composites, active mineral additives, strength, biocorrosion

БИОСТОЙКИЕ ЦЕМЕНТНЫЕ КОМПОЗИТЫ С АКТИВНОЙ МИНЕРАЛЬНОЙ ДОБАВКОЙ

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Аннотация: Биоповреждения представляют собой серьезную проблему, затрагивающую все этапы жизненного цикла строительных материалов, начиная от производства и хранения сырья и заканчивая транспортировкой и эксплуатацией готовых изделий. Бактерии и грибы, являясь основными агентами биодеструкции, способны существенно снижать эксплуатационные характеристики материалов, что приводит к экономическим потерям и снижению качества строительных конструкций. В рамках данного исследования была проведена комплексная оценка биостойкости цементных композитов. Особое внимание уделялось изучению видового состава микромицетов, колонизирующих поверхность композитов, а также определению показателей обрастаемости. Были детально исследованы механизмы воздействия микроорганизмов на физико-механические свойства композитов, включая их влияние на массосодержание и прочностные характеристики. Полученные данные имеют важное значение для разработки новых стратегий защиты строительных материалов от биодеградации, что позволит повысить их долговечность и надежность в условиях эксплуатации.

Ключевые слова: биостойкость, физико-механические свойства, биоцидные цементы, композиты, активные минеральные добавки, прочность, биокоррозия

INTRODUCTION

The problem of bio-damage covers a wide range of scientific and practical tasks related to the protection of raw materials, materials and goods from damage by bacteria and fungi, both in conditions of long-term storage, as well as during production, transportation and operation. Currently, one of the main tasks in building

materials science is to increase the durability of building materials and products. In this case, the problem of biological corrosion is given a primary role, since the negative effects of bacteria, mycelial fungi and actinomycetes in buildings and structures pose a serious danger to human health [1-3]. With insufficient resistance of materials to microbiological corrosion, the operational reliability of products and structures decreases, their appearance and the environmental situation in buildings and structures deteriorate. To date, a large number of facts of destruction of industrial buildings and structures under the influence of microorganisms have been established. For example, the destruction of reinforced concrete structures at Kievsky, Kirovogradsky, Kamenets-Podolsky and other meat processing plants, the canopy of the Sennaya Ploshchad metro station in St. Petersburg, the outer concrete walls of the Svir-HPP power and gateway stations, and other building structures fully proves the destructive ability of microorganisms [3-5]. Every year, huge amounts of money are spent all over the world on repairing damaged structures, treating patients, and preventing diseases.

Increasing the biosafety of building materials can be achieved through various measures, including the use of biocidal cements. Giving Portland cement, sulfate-resistant, hydrophobic, plasticized and other cements fungicidal and bactericidal properties, as well as the creation of special biocidal cements is the most important direction of modern construction [1, 3-5]. Recently, in world practice, preference has been given to various types of mixed cements [6-9]. The development of technology for the production and optimization of compositions of biocidal Portland cements with an active mineral additive for the manufacture of building composites with biocidal properties that have increased resistance in biological and chemical aggressive environments, resistance to various climatic factors, as well as improved physico-mechanical properties is one of the urgent tasks being solved in this work.

The purpose of the research was to evaluate the bio-stability of cement composites based on Portland cement with an active mineral additive, identify the dominant species of microorganisms on their surface, and study the effect of mycelial fungi on changes in the strength and mass content of materials.

METHODS

The studies were carried out on samples of cement stone obtained from a solution of normal density. The following materials were used as binders in the manufacture of composites: portland cement M–500–D0-H Russia Standard GOST 10178-85 (CJSC Eurocement Group, Komsomolsky settlement, Russia) as a mineral additive, metallurgical plant slags of three types – blast furnace, granular and converter with a specific surface area of 2900-3000 cm^2/g, Russia Standard GOST 3476-74 (Novolipetsk Metallurgical Kombinat, Lipetsk, Russia). The samples were made in the form of beams with dimensions of 1×1×3 cm, which hardened for 28 days in humid conditions before testing.

Cement stone samples were tested for fungus resistance and fungicidal properties in accordance with Russia Standard GOST 9049-91. The following micromycete species were used as test organisms: *Aspergillus oryzae (Ahiburg) Cohn, Aspergillus nigerien Tieghem, Aspergillus terreus Thom, Chaetomium globosum Kunze, Paecilomyces varioti Bainier, Penicillium funiculosum Thom, Penicillium chrysogenum Thom, Penicillium cyclopium Westling, Trichoderma viride Pcis, e*x Fr.

The fouling of cement composites by mold fungi was determined by two methods. Method 1 (without additional sources of carbon and mineral nutrition) and method 3 (on solid nutrient medium of Chapek–Doks) with the establishment of fungal resistance and fungicidal activity, respectively. The coefficient of biological resistance was determined as the ratio of compressive and flexural strength of the samples soaked in the medium used for testing

for 6 months according to method 3. To determine the change in mass content, the samples removed from the medium were wiped with a cotton swab soaked in alcohol. Then the control samples and the samples kept in the medium were dried for 5 hours in a drying cabinet at a temperature of 50 °C, after which they were weighed. The number of tested samples ensured an experimental accuracy of at least 95%.

The identification of micromycetes was carried out based on their morphological and cultural characteristics.

RESULTS AND DISCUSSION

Table 1 shows the studied formulations and test results. In the studied formulations, the content of slag fillers varied up to 60%. From the conducted fouling studies of cement stone (Table 1), the growth of fungi was established: by the method of 1-0 points, by the method of 3 – 1-3 points. In addition, the resistance of the cement composite to mycelial fungi was revealed, with a concentration of active mineral additives of 20-40%, these composites are fungicidal. Identification of micromycetes on the surface of cement stone after one month of testing according to Method 3 (see Table. 1) established the dominance of *Aspergillus terreus (1), Penicillium cyclopium (2) and Penicillium chrysogenum (3)* on almost all cement composites.

As research practice shows, it is the above-mentioned microorganisms that are the most dangerous and aggressive against reinforced concrete structures and are more common in the food and processing industry. Conditionally pathogenic strains capable of causing various human diseases are found among the destructive fungi isolated from the surface of composites. Thus, the fungus *Aspergillus terreus* (1) causes mycoses of the pulmonary and cardiovascular systems, cerebral mycoses, and also affects the musculoskeletal system. *Penicillium chrysogenum (3)* is capable of causing mycoses of the spleen, kidneys, heart, skin; ear inflammation, tongue and eye lesions. No less harmful are other micromycetes identified on the surface of cement composites.

Table 1 Fouling of cement stone and species composition microorganisms on its surface

№ Sample	Granular Slag (G), %	Blast Furnace Slag (D), %	Converter Slag (C), %	Portland Cement, %	Growth assessment		Property: Fungicide (F) / Mushroom-resistant (MR)	The species composition of the dominant microorganisms (method 3)
					Method 1	Method 3		
1	5	-	-	95	0	2	MR	*2,3*
2	20	-	-	80	0	1	F	*2*
3	40	-	-	60	0	1	F	*2*
4	60	-	-	40	0	3	MR	*1, 2*
5	-	5	-	95	0	2	MR	*1,2, 3*
6	-	20	-	80	0	1	F	*1*
7	-	40	-	60	0	1	F	*1, 2*
8	-	60	-	40	0	2	MR	*1, 2, 3*
9	-	-	5	95	0	3	MR	*1, 2, 3*
10	-	-	20	80	0	1	F	*2,3*
11	-	-	40	60	0	1	F	*1, 2, 3*
12	-	-	60	40	0	3	MR	*1, 2*
13	-	-	-	100	0	2	MR	*1, 2, 3, Penicillium funiculosum*

According to a number of authors, the destructive effect of micromycetes on cement composites is due to the aggressive effects of fungal metabolites – organic acids, hydrolytic and redox enzymes - on individual components of materials [7, 8]. The results of changes in the mass content and strength characteristics of composites after exposure to standard mycelial fungi are shown below (Fig. 1, 4, 7).

From the results obtained (Fig. 2, 3, 5, 6, 8 and 9) It can be seen that after six months of exposure in a standard environment of mycelial fungi, the strength of cement stone samples from a dough of normal density changed depending on the slag content.

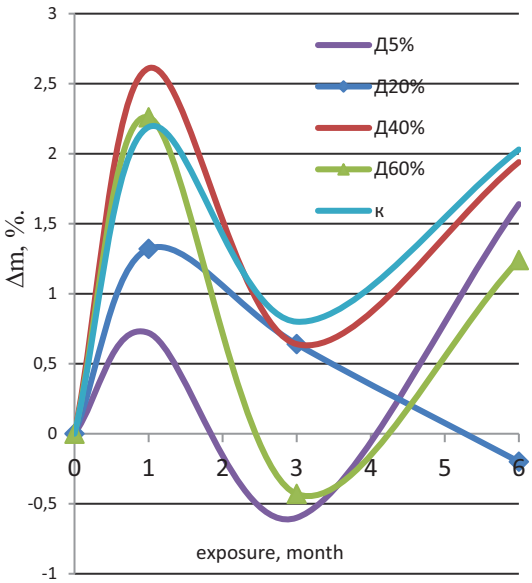


Figure 1. Dependence of the change in the mass of cement composites modified with blast furnace slag in the medium of micellar fungi

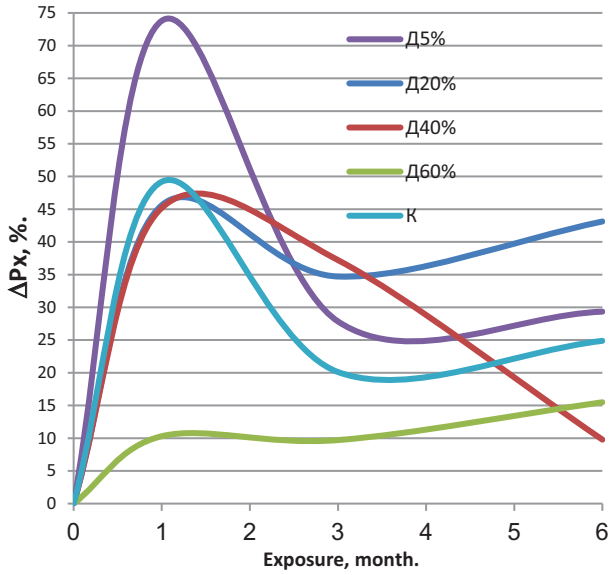


Figure 2. Dependence of the change in compressive strength (P_x,%)of cement composites modified with blast furnace slag in the in the medium of mycelial fungi

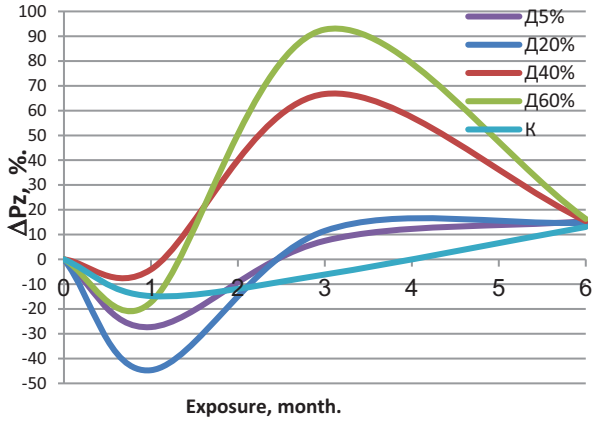


Figure 3. Dependence of bending strength changes (Pz, %) of cement composites modified with blast furnace slag in the in the medium of mycelial fungi

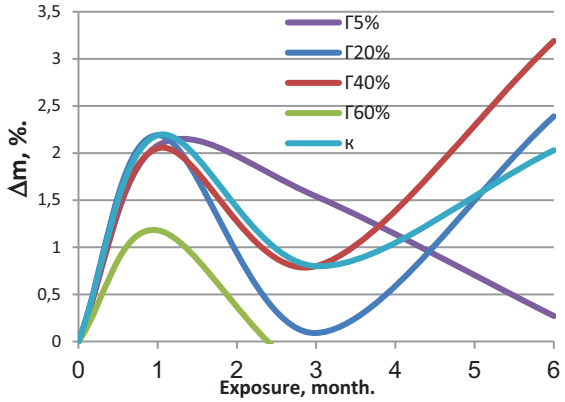


Figure 4. Dependence of the change in the mass of cement composites modified with Granular slag in the medium of mycelial fungi

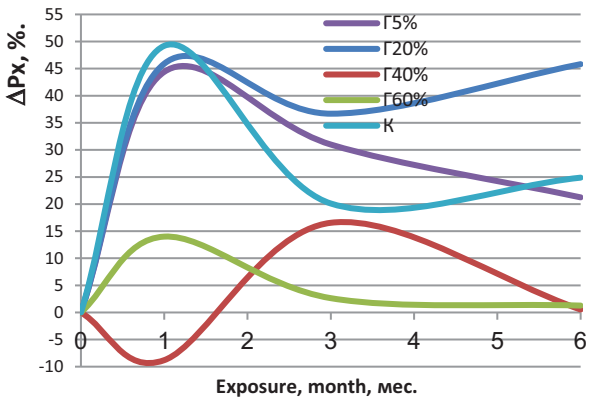


Figure 5. Dependence of the change in compressive strength (ΔP_x,%)of cement composites modified with Granular slag in the in the medium of mycelial fungi

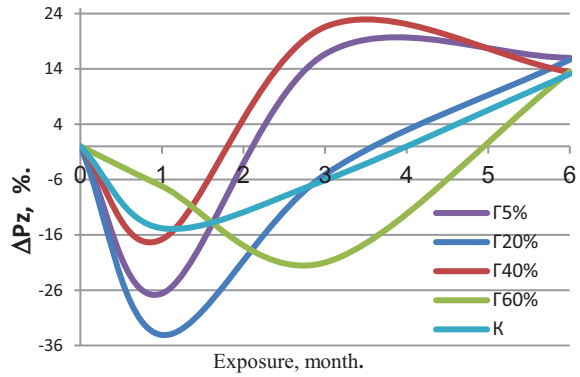


Figure 6. Dependence of bending strength changes (ΔPz, %) of cement composites modified with Granular slag in the in the medium of mycelial fungi

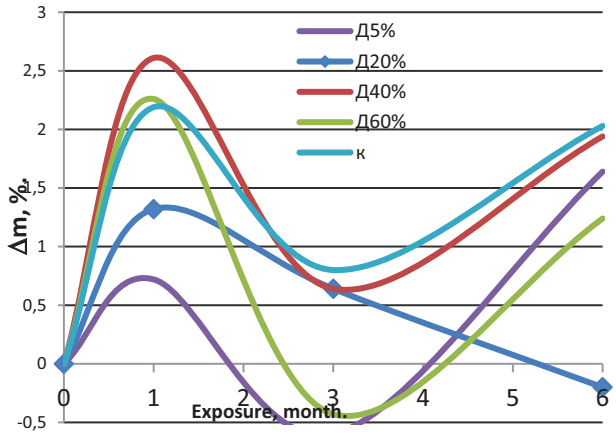


Figure 7. Dependence of the change in the mass of cement composites modified with Converter Slag in the medium of mycelial fungi

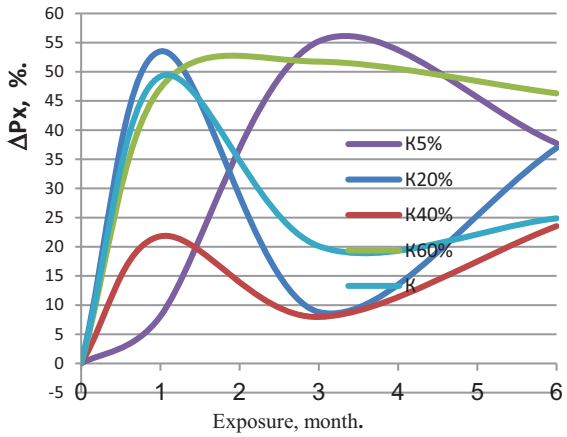


Figure 8. Dependence of the change in compressive strength (P_x,%)of cement composites modified with Converter Slag in the in the medium of mycelial fungi

It can be seen from the presented graphs that the change in the mass content of cement composite samples during exposure is not the same, which is expressed by the different content of mineral additives.

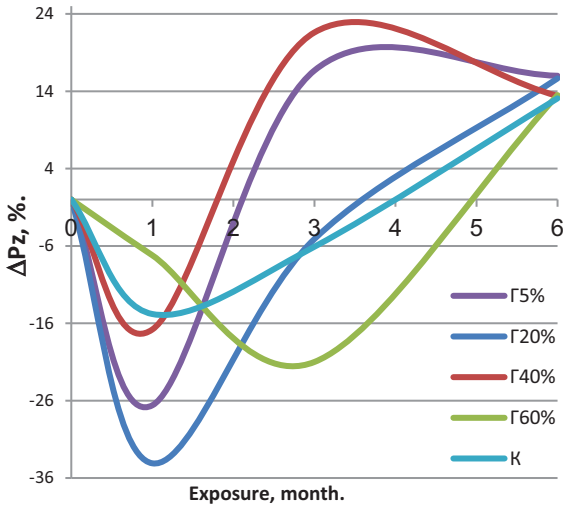


Figure 9. Dependence of bending strength changes (Pz, %) of cement composites modified with Converter Slag in the in the medium of mycelial fungi

This is probably expressed by the highest water absorption value of the mineral additive. Analyzing the changes in the mass content and strength characteristics of cement composites modified with active mineral additives, the following can be distinguished: after 30 days of holding samples in a standard environment of mycelial fungi, an increase in mass is observed, this is due to the fact that when samples are immersed in a biological medium, microorganisms sorption occurs in the pores of cement composite samples. At the same time, the presence of microorganisms also affects the strength characteristics, they increase. Further exposure of the samples leads to a decrease in strength characteristics. After three months, there is a decrease in strength and mass content, as the degradation of materials begins in the external diffusion-kinetic region, i.e. destruction occurs in the surface layer of the sample. Then, after six months, there is a second stage of

increasing the mass content and strength. The increase in characteristics begins due to the repeated adhesion of microorganisms to the pores of the already new surface of the samples.
Summing up these studies, it should be noted that one of the main factors affecting the biostability of cement composites, according to the conducted research, is the chemical and mineralogical composition of cements. It determines the nature of the structure formation of composites, the pore space, as well as the species composition of microorganisms on their surface at the first stages of operation, which in turn determines the aggressiveness of the operating environment. As a result of the interaction of the biologically active medium with the composite, the chemical composition of the surface and then the inner zones of the material changes, which leads to a change in the species composition of microorganisms and, as a result, the operating environment.

CONCLUSION

The compositions of cement composites have been developed, characterized by increased resistance to the effects of microbiological aggressive media. Based on the research, the following cement compositions are recommended for the manufacture of composites: with an optimal content of active mineral additives: (20% and 40%) having fungal and fungicidal properties.
The identification of microorganisms inhabiting cement composites was carried out, after a month of testing in a standard environment of mycelial fungi, three dominant species of micromycetes of the genus *Penicillium* (*Penicillium cyclopium, Penicillium chrysogenum, Penicillium funiculosum*) were identified. In addition to the above-mentioned micromycetes of the genus *Penicillium*, one species of the genus *Aspergillus (Aspergillus terreus*) has been identified. The change in mass content and strength characteristics under the conditions of the standard environment of mycelial fungi (Russia Standard GOST 9.049-91, Method 3) was studied.

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