Comparative characteristics of binders resistance for building composites to mold fungi

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Abstract. The article presents comparative characteristics of fungal resistance of geopolymer and cement stone. According to the data obtained, the artificial aging of samples of cement stone and a geopolymer based on fly ash promotes their capturing by some microscopic fungi. In the case of a geopolymer stone based on perlite, expressed fungicidal properties were noted.

1 Introduction

Recently, more popular in the construction industry have become new materials, which can compete with classical products, among which a worthy place is occupied by geopolymers – alkali-activated aluminosilicate binder based on renewable technogenic raw materials. Their use in the future can partially or completely replace cement in the production of a number of building materials, thereby reducing the technogenic pressure on the ecosphere of the planet.

At present, scientists of the Belgorod State Technological University named after V.G. Shukhov have *developed the compositions and successfully tested the technology of obtaining* geopolymers based on perlite and low-calcium fly-ash (FA) of thermal power plants (TPP) [1–4].

In the design of materials, particular importance is given to their ability to resist external influences during operation while maintaining the required characteristics. Among the most unfavorable impacts of the 21st century is the biological, associated with the processes of vital activity of microorganisms [5–7]. In this regard, the purpose of this work was to compare the stability of cement and geopolymer stone under the influence of mold fungi, the main biodestructor of building materials.

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2 Materials and methods

In the present work as binders we have used – Cement (PC) of grade CEM I 42.5N produced by CJSC Belgorod Cement (Belgorod, Russia) and geopolymers on the basis of natural and technogenic raw materials. The perlite of the Mukhor-Talinskoye deposit (perlite (GB_P)) as well as fly ash from the Troitskaya state district power plant (RF) (fly ash (GB_{FA})) were used as a raw material for binder production, sodium hydroxide NaOH (sodium hydroxide Pro Analyse) was used as an activator.

The compositions on the basis of binders under consideration were prepared manually. All samples were made in metal forms with size 1×1×3 cm. Samples based on cement were made from a normal density paste. After molding, the samples were hardened in a bathtub with a hydraulic shutter in the mold for 1 day, then they were unmolded and continued hardening for 27 days. Samples based on the geopolymeric binder were made from paste with a cone spread 130–150 mm, which after molding were hardening for 1 day hard in molds under natural conditions (temperature 22 ± 3 °C, relative humidity 45–50%), then were subjected to heat treatment in drying chamber according to the following conditions: rise of temperature (4 hours) – isothermal treatment at 70 °C (16 hours) – temperature reduction (4 hours).

2.1 Aging of the studying samples using the Soxhlet apparatus

To exclude the influence of increased alkalinity of materials, which provides for their temporary biostability at the initial stages of operation, the samples were artificially aged with the Soxhlet extractor (Figure 1).

This instrument allows to simulate continuous processes occurring in natural conditions for the study of rocks, as well as in real operation conditions for the analysis of building materials, namely, in an aerial (7), permanently humid environment (8) and watered (9), thereby to simulate the aging conditions of the material by washing away the basic components of hydration. The use of the unit allows us to design the most reliable model of surface leaching processes in conditions closest to natural ones.

Distilled water in a quantity of 500 ml was poured into the receiver flask of the filtrate. In the Soxhlet extractor, all water simulating atmospheric precipitation is completely drained through the samples and accumulated in the cylinder. After reaching a certain level in the cylinder, infiltration water containing substances washed from the samples was drained through the side siphon tube into the lower receiver flask. The pH of the distilled water before the start of the experiment was 5.6. Simulation of atmospheric processes was carried out for 14 days after which the samples were withdrawn and dried to constant weight under normal conditions for 2 days. To study the fungicidal properties, samples from the watered medium were used (Figure 1, 9).

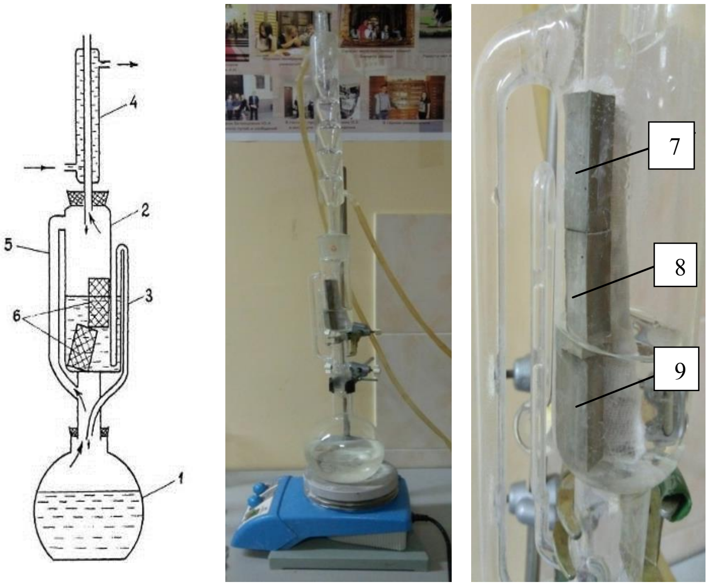

Fig. 1. Appearance of the Soxhlet extractor and the arrangement of the samples in the cylinder: 1 – flat-bottomed glass flask; 2 – extractor; 3 – siphon tube; 4 – refrigerator; 5 – reverse heat-insulated pipe; 6 – test samples; 7 – aerial environment; 8 – permanently humid environment; 9 – watered environment

2.2. Biotesting of samples (Study of the fungi-resistance properties of the test samples)

To study the fungi-resistant properties, samples from the watered medium were used (Figure 1, 9).

The effect of microorganisms on the test binders was assessed by the ability of growth and reproduction of mold fungi on them. The test was carried out in accordance with State Standart 9.048–89 (Method 3) [8]. The essence of the method was to identify the growth character of fungi on the surface of the samples and the presence or absence of an inhibitory zone (the zone of absence of fungal growth). The following micromycetes were used as test organisms: *Aspergillus niger van Tieghem; Aspergillus terreus Thorn; Penicillium cyclopium Westllng; Penicillium purpureum; Chaetomium globosum Kunze; Paecilomyces varioti Bainier*. Pure test cultures were obtained from the Russian Academy of Sciences laboratory of fungal biochemistry at the Botanical Institute named after V.L. Komarov.

Capek Dox's medium was used as a solid nutrient medium. The resulting medium was poured into sterilized Petri dishes, 15 ml each. After solidification of the medium, before placing each sample in the center of the dish, the spores of the test cultures were placed on the surface of the samples with a pipette. Petri dishes were stored under optimal growth conditions of fungi: at a temperature of 30 °C and a relative humidity of 95%. The degree of fouling of the samples by the fungi was assessed after 28 days of exposure according to the ball system for assessing the nature of fungal development. (Table 1).

Table 1. The degree of fouling of the samples by the fungi in balls

Mark	Characteristic
0	Under the microscope germination of spores and conidia were not detected
1	Under the microscope germinated spores and a slightly developed mycelium can be seen
2	Under the microscope developed mycelium is seen, possible sporulation
3	With the naked eye, the mycelium and (or) sporulation are barely visible, but clearly visible under a microscope
4	With the naked eye the development of fungi covering less than 25% of the surface of the sample is clearly seen
5	With the naked eye the development of fungi covering more than 25% of the surface of the sample is clearly seen

The material is considered to be fungi-resistant if it is estimated to be 0-2 points, and has fungicidal properties if a zone of absence of fungal growth is observed around the sample on the nutrient medium or on the surface and edges of the samples, a growth of fungi estimated 0 and 1 point is observed.

3 Results and discussions

According to the obtained data, artificial aging of samples promotes their capturing by some microscopic fungi (Figure 2, Figure 4, Table 2), which can not be said about the geopolymer on perlite (Figure 3).

Table 2. The intensity of development of microscopic fungi on the surface of binders

Test culture of mold fungi	Mark		
	PC	GB_P	GB_{FA}
Aspergillus niger	4	0	3
Aspergillus terreus	3	0	3
Penicillium cyclopium	2	0	4
Penicillium purpureu	3	0	3
Paecilomyces variotii	2	0	4
Chaetomium globosum	2	0	3

On the surface of the cement stone development of the fungus *Aspergillus niger* is the most noticeable (the intensity of development is 4 points) (Figure 2, a). It should be noted that there is no clear growth of the fungi *Chaetomium globosum, Paecilomyces variotii and Penicillium cyclopium* on the surface of the cement stone (Figure 2, c–e). The intensity of development of *Penicillium purpureum and Aspergillus terreus* was 3 points (mycelium and sporulation are barely visible to the naked eye, but clearly visible under a microscope).

On the one hand, the porous structure of the cement stone promotes the involvement of microorganisms in corrosion processes, on the other - the alkalinity of the medium prevents its capturing by fungi. Probably, in variants where there was a lack of growth, there was residual alkalinity, which prevented the development of fungi. However, as the results showed, prolonged washing of cement samples made them more vulnerable to the effects of fungi of the genus *Aspergillus* and *Penicillium*.

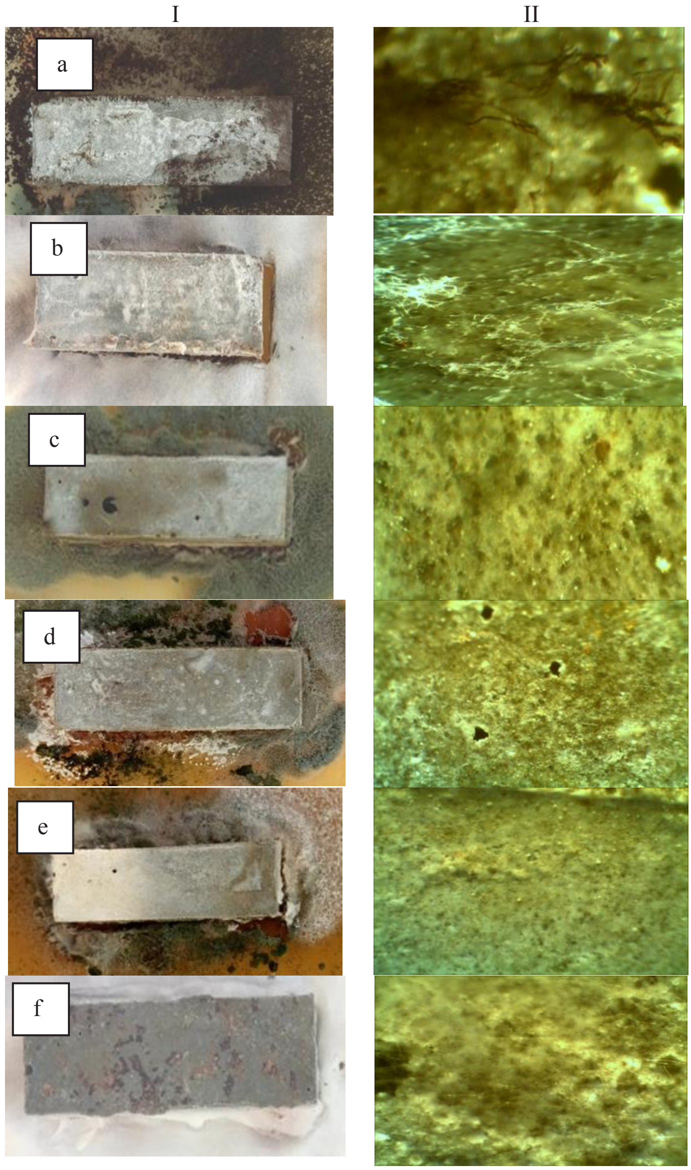

Fig. 2. Growth of fungi on the surface of cement stone: I – general view; II – survey by a microbiological microscope (× 60 times); *a – Aspergillus niger; b – Aspergillus terreus; c – Chaetomium globosum; d – Paecilomyces varioti; e – Penicillium cyclopium; f – Penicillium purpureum*

Notably for these fungi they are representative by the accumulation of various organic acids in the process of metabolism (acetic, citric, lactic, gluconic, formic, etc.). These organic acids neutralize the medium and, interacting with the cement stone silicates, form soluble complex compounds that are washed out during their operation, contributing to the degradation of the structure as a whole.

At present, the processes occurring in geopolymeric binders during their operation have not been fully studied, and therefore it is impossible to reliably predict the durability of these materials under various conditions.

According to the obtained data, the intensity of development of fungi on the surface of the perlite-based geopolymer corresponded to 0 points – «Under the microscope germination of spores and conidia were not detected» (Figure 3).

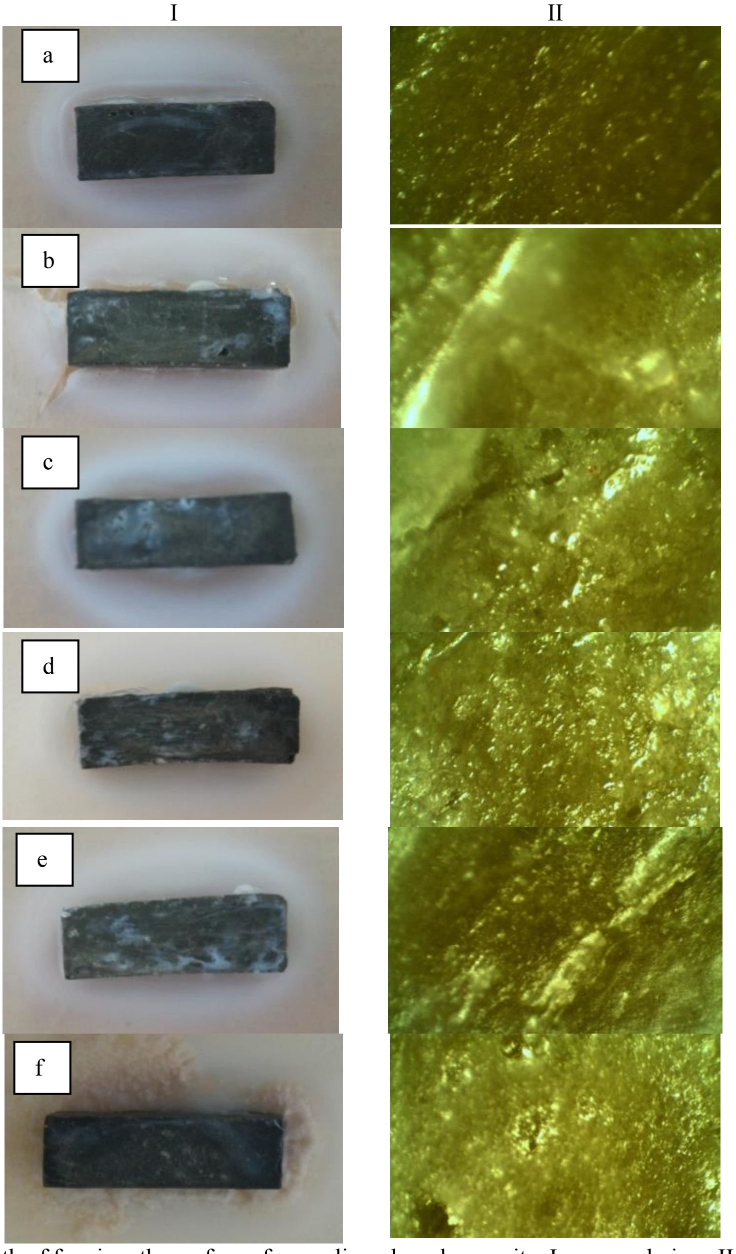

Fig. 3. Growth of fungi on the surface of geopolimer based on perite: I – general view; II – survey by a microbiological microscope (× 60 times); *a – Aspergillus niger; b – Aspergillus terreus; c – Chaetomium globosum; d – Paecilomyces varioti; e – Penicillium cyclopium; f – Penicillium purpureum*

For some variants of the geopolymer, this situation remained even after a long washing of the samples, for others – didn't. This is due to the release of free alkali to the surface of the sample, which was confirmed by the preliminary studies of the team: in the case of using perlite as the main raw material component, the degree of alkali association is somewhat lower compared to analogous indicators when using technogenic raw materials.

Geopolymer binder based on fly ash from the Troitskaya state district power plant (RF) is more vulnerable to the action of microscopic fungi (Figure 4): the intensity of Paecilomyces development (Figure 4, d) and Penicillium cyclopium (Figure 4, e) up to 4 points – development of fungi covering less than 25% of the surface of the sample is clearly seen. For the remaining test objects, the fouling is 3 points (mycelium and sporulation are clearly visible under the microscope).

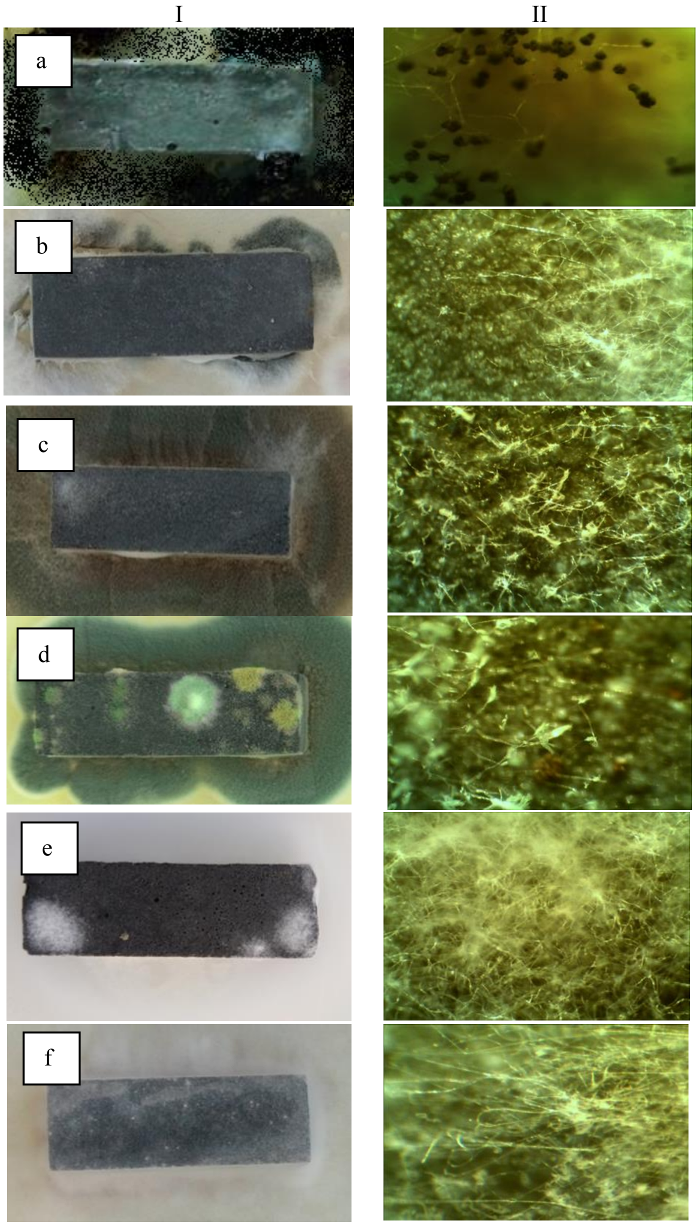

Fig. 4. Growth of fungi on the surface of geopolimer based on fly ash: I – general view; II – survey by a microbiological microscope (× 60 times); *a – Aspergillus niger; b – Aspergillus terreus; c – Chaetomium globosum; d – Paecilomyces varioti; e – Penicillium cyclopium; f – Penicillium purpureum*

4 Conclusion

Thus, the obtained results indicate a different degree of fungal resistance of the currently studied geopolymer binders, which is determined primarily by the composition of the composite, the presence in it of compounds that are a source of biogens for microorganisms. The solution to the problem may be the use of biocidal preparations at the stage of composite materials design.

The combined effect of the biocidal component and the matrix of the composite will lead to the formation of a protective film that will not only prolong the fungal resistance and/or fungicidity, but also increase the strength of the products, which will slow down the process of premature loss of technical and operational characteristics, reduce the intensity of biocorrosive processes, expand the scope of materials application.

Taking into account the increase in the number of new building materials on the domestic and foreign markets, and also taking into account the data of the specialists in mycology regarding the increase in the number of diseases caused by microscopic fungi, we consider that it is necessary to include testing of construction materials and structures put into operation for fungal resistance in the mandatory list.

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