Development of a fungicidal glaze for ceramic tiles resistant to biological corrosion

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Abstract – The aim of the work is the development of biological corrosion-resistant glass-ceramic glaze for ceramic tiles. The choice and optimal content of fungicidal agents are substantiated. The synergistic effect of gardistonite, volostonite and zinc oxide in the structure of glazes on their prolonged fungicidal effect has been established.

Keywords – fungicidal glaze, inhibitory agents, wollastonite, zinc oxide, biological corrosion.

Introduction

To date, the growth of technogenic impact leads to the transformation of natural ecosystems, which contributes to the activation of environmental pollution and changes in the mechanism of action of organisms in the ecosystem. In the aspect of this problem, a special place is occupied by the intensification of the action of destructor organisms that damage materials through biological corrosion. One of the main factors determining the rate of wear of buildings and architectural construction details is the biodamage of materials. This serious problem can adversely affect the safety and efficiency of the operation of facilities. Along with this, microscopic fungi can cause serious diseases and infections, in particular aspergillosis, the incidence of which has been increasing in recent years, causing new challenges for the scientific community. In particular, *Aspergillus niger* can lead to significant complications in people with respiratory problems or weakened immune systems. Inhalation of spores can lead to infection of the lungs and bronchi, which in some cases can be fatal. It is mass immunosuppressive therapy administered to patients suffering from SARS-CoV-2 that has created favorable conditions for the selection of pathogenic fungi and their reproduction [1]. Therefore, today the urgent problem of protecting human life, the environment from the influence of pathogenic microorganisms and objects of vital activity from biocorrosion is the creation of environmentally friendly fungicidal materials with controlled surface properties.

The choice of effective materials for the simultaneous protection of protection against biocorrosion and environmental pollution by pathogenic microorganisms should be carried out taking into account the ecology of destructor organisms, the physicochemical properties of materials, and issues of environmental management and environmental safety.

The causes of biocorrosion involving microorganisms are three main processes of biodegradation: mechanical, assimilation (materials are a source of nutrition and energy for microorganisms), dissimilation (interaction of materials with aggressive metabolites of microorganisms, such as acids and enzymes). A feature of the use of silicate materials containing mineral components is their ability to act as a nutrient matrix for microorganisms that produce oxidative enzymes – peroxidase, catalase, glucose oxidase and polyphenol oxidase.

Biocorrosion of silicate materials of different composition and structure has its own characteristics. So ceramic building silicate materials with a developed porous structure are most susceptible to biocorrosion. It is known [2] that porosity and surface roughness play an important role in biosusceptibility to colonization. Glass materials having zero porosity are subject to insignificant biodegradation of the material surface due to high structural strength and chemical resistance.

Protection against biocorrosion consists mainly of preventing and slowing down the development of bacteria and microorganisms, as well as the destruction of dangerous bioagents. arious methods are used for this: γ-radiation, the use of special substances – biocides (for example, compounds of arsenic, mercury, antimony, etc., most of them are poisonous and dangerous for humans), as well as the creation of an optimal microclimate (temperature, humidity, air exchange) preventing the development of bioagents. In some cases, gaseous antiseptics are used to kill bacteria: methyl bromide, ozone, propylene oxide, formaldehyde, ethylene oxide, and others, which are expensive and have a negative impact on the environment. The need for constant periodic processing does not allow the effective use of these methods in the event of various kinds of pandemics, natural disasters, etc.

An effective method of simultaneous protection against biocorrosion of human objects and the negative impact of pathogenic fungi is the creation of fungicide glass materials using inexpensive and environmentally friendly biocides in their compositions. Given the significant demand for competitive building materials, the development of new types of glass coatings for ceramics with special properties is of great importance.

The authors [3] developed antibacterial glass-ceramic glazes containing zinc oxide, which are characterized by a prolonged action against E. Coli bacteria due to the synergistic action of the zinc-containing crystalline phase and the filler. However, a different mechanism of reproduction and growth of bacteria and filamentous fungi determines the need to search for effective inhibitory agents with respect to the typical biocorrosive agent *Aspergillus niger*. A significant fungicidal effect of glass-ceramic coatings for metals containing crystals of zinc titanates and/or calcium phosphates in relation to *Aspergillus niger* is known [4]. It should be noted that the use of expensive compounds based on titanium, zinc and phosphorus oxides is economically justified in the development of fungicidal glass-ceramic coatings for special-purpose materials, in particular, medical applications. Considering the cost of agents, when developing fungicidal glass coatings for ceramic materials for architectural and construction purposes, inexpensive and available non-toxic components should be used. In particular, those that are widely used in the production of ceramic tiles with other purposes.

Experimental part

As a basis for obtaining a fungicidal glass coating for ceramic tiles, zinc-containing glaze (produced by PJSC «Kharkiv Tile Plant») was chosen, which is used for interior wall cladding of sanitary and hygienic premises in common areas. It was synthesized based on the SiO_2–CaO–ZnO system with the following content of the main components (wt. %): SiO_2 30–35; Al_2O_3 3–6; Na_2O 3–4; K_2O 2–3; CaO 11–12; ZnO 10–12; ZrO_2 8–9; $TiO_2 < 0,1$ [3].

To ensure fungicidal action, zinc oxide (5 wt. %) and wollastonite were added to glass-ceramic coatings containing hardistonite in an amount of 1–5 wt. % per 100 wt. % glaze slip. The choice of fungicidal fillers was based on the results of studies [5] of the fungi resistance of Mg, Ca, Zn oxide powders, which were placed in distilled water for 28 days and showed maximum fungi resistance (0-1 point). The antibacterial activity of volostonite as a bactericidal component is based on a change in the pH of the medium at the site of its contact with microorganisms. It can be assumed that this decrease in pH will be sufficient for an effective fungicidal action. The interaction of wollastonite and *Aspergillus niger* consists in the formation of an organo-inorganic complex with the formation of calcium oxalate under acidic conditions ($1 \leq pH \leq 5,5$) [6].

The fungicidal effect (toxicity) of the experimental materials was evaluated by the change in the dehydrogenase activity (DHA) of the biotest cultures.

Study of the fungicidal properties of experimental glazes with a content of 1 to 5 wt. % wolastonite showed a delay in the growth and development of microscopic fungi *Aspergillus niger* within 7 and 14 days. The maximum effect on the decrease in the level of DHA is already noted upon contact with a sample containing 4 wt. % hairstonitis. During the first 7 days, the DHA value for this sample decreases by 2 times compared to the beginning of cultivation and does not change over the next 7 days. While the level of DHA of microscopic fungi in the control variant increased by 6 times during this period. As a result of interaction with the *Aspergillus niger* bioassay suspension for 7 days, no spore germination is observed under the microscope on the surface of the specified sample, fungal and bacterial conidia were not detected (0 point). Such a high resistance to biocorrosion is determined by the structure of the material, namely: zero porosity and high chemical resistance to mineral and organic acids, which is realized due to the high structural strength and the content of chemically stable and biologically active crystalline phases of gardistonite, volostonite and zinc oxide.

Conclusions

It has been determined that the provision of a prolonged fungicidal action and resistance to biocorrosion of the developed glass-ceramic coating is realized due to the synergistic action of the zinc-containing crystalline phase and fillers. The use of the developed fungicidal zinc-containing glaze with prolonged action based on domestic raw materials in the production of ceramic tiles with high performance properties will significantly increase the competitiveness of products for this purpose. In addition, it is important to solve the important tasks of stopping the spread of fungicidal load on the environment, eliminating the negative impact of pathogenic fungi on human health and maintaining the performance properties of architectural and construction products during their operation.

References

[1] Hakamifard, A, Hashemi, M, Fakhim, H, Aboutalebian, S, Hajiahmadi, S, & Mohammadi R. (2021). Fatal disseminated aspergillosis in an immunocompetent patient with COVID-19 due to Aspergillus ochraceus. *J Mycol Med*, 31(2), 101124. DOI: 10.1016/j.mycmed.2021.101124

[2] Coutinho, M. L., Miller A. Z., & Macedo M. F. (2015). Biological colonization and biodeterioration of architectural ceramic materials: An overview. *Journal of Cultural Heritage*, 16(5), 759- 777. DOI: 10.1016/j.culher.2015.01.006

[3] Savvova, O. V., Shevetovsky, V. V., & Pokroeva, Ya. O., (2022) Development of antibacterial glazing for ceramic tiles. *Voprosy Khimii i Khimicheskoi Tekhnologii*, (3). 60–66. DOI: 10.32434/0321-4095-2022-142-3-60-66

[4] Savvova, O. V., Bragina, L. L., & Babich, E. V. (2012) Study of the biocidal properties of R_2O–RO–TiO_2–P_2O_5–R_2O_3–SiO_2 glass ceramic coatings. *Glass and Ceramics*, 69(1-2), 20-25. DOI: 10.1007/s10717-012-9407-3

[5] Mendes, C. R., Dilarri, G., Forsan, C. F., Sapata, V. R., Lopes, P. R. M., Moraes, P. B., Montagnolli, R. N., … Bidoia, E. D. (2022). Antibacterial action and target mechanisms of zinc oxide nanoparticles against bacterial pathogens. *Scientific Reports*, 12, 2658. DOI: https://doi.org/10.1038/s41598-022-06657-y

[6] Hu, S., Ning, C., Zhou, Y., Chen, L., Lin, K., & Chang, G. (2011). Antibacterial activity of silicate bioceramics. *J. Wuhan Univ. Technol.-Mat. Sci. Edit.*, 26, 226-230. DOI: https://doi.org/10.1007/s11595-011-0202-8