

Проведеними дослідженнями встановлено, що керамічна лицьова цегла характеризується капілярною пористістю, що призводить до підвищення показників водопоглинання та капілярного підтягування, а також утворення висолів на її поверхні. Для захисту поверхні такої цегли та надання їй підвищених експлуатаційних властивостей використано гідрофобізуючі речовини. Експериментальними дослідженнями визначено, що при нанесенні гідрофобізаторів на основі ПМФС та АП пористість зменшується в 1,2–1,3 рази, водопоглинання – в 1,2–2,3 рази, водопоглинання при капілярному підтягуванні – 1,1–3,2 рази. Дослідженнями морозостійкості встановлено, що для керамічної цегли, покритої ПМФС морозостійкість збільшується на 15 циклів, а при обробленні поверхні цегли АП – на 20 циклів порівняно з необробленою цеглою (F50). Методом електронної мікроскопії встановлено, що після поперемінного заморожування і відтавання на поверхні цегли, обробленої ПМФС та АП спостерігається утворення мікротріщин (при цьому водопоглинання збільшилося на 42 та 28 %). Методом математичного планування експерименту визначено, що найбільш ефективною гідрофобізуючою речовиною є модифікатор з вмістом порошку нано- Al_2O_3 (нано-рідина). Визначено, що при обробленні поверхні нано-рідиною (кількість нано- Al_2O_3 – 0,8 %) водопоглинання зменшується до 1,2–1,6 %, показник водопоглинання при капілярному підтягуванні – до 0,08–0,12 $кг/м^2 \cdot год^{0,5}$. Методом дефектоскопії за допомогою трубки Карстена встановлено, що водопоглинання для цегли, поверхня якої покрита нано-рідиною знижується від 0,15 до 0,002 $мл/см^2$, що свідчить про високий рівень гідрофобізації. Методом електронної мікроскопії підтверджено, що модифікування поверхні керамічної цегли гідрофобізуючими нано-рідинами дозволяє ущільнити структуру за рахунок колювання пор і мікротріщин, що забезпечує зниження капілярного підтягування кладки. Також це призводить до підвищення атмосферостійкості та морозостійкості цегляних будівельних конструкцій.

Таким чином, є підстави стверджувати про можливість покращення фізико-технічних показників цегляної будівельної конструкції шляхом модифікування поверхні керамічної цегли нано-рідиною

Ключові слова: керамічна лицьова цегла, пористість, водопоглинання, гідрофобізуючі речовини, нано-рідина

STUDYING THE EFFECT OF NANOLIQUIDS ON THE OPERATIONAL PROPERTIES OF BRICK BUILDING STRUCTURES

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1. Introduction

The durability of the outer walls of buildings is decisive, both in economic and aesthetic aspects [1, 2]. Deformations and stresses in wall building materials that arise under the influence of cyclic atmospheric effects at a temperature and humidity change lead to a decrease in the operational properties of buildings and structures [3, 4]. It should be noted that the destructive effect on masonry is largely exerted by the high porosity of wall building materials [5, 6]. This leads to intensive pulling of moisture, causing the migration of saline solutions with the formation of salt efflorescence, which reduces the technical and decorative properties of the outer walls of brick structures [7, 8].

In civil construction, a ceramic face brick is widely used as a decorative facade facing [9, 10]. At the same time, the physical and technical parameters of the wall material play a decisive role in the regulation of operational properties of the brick structure. A wide range of hydrophobizing substances of different classes and their controlled application allows predicting the properties of external walls of brick structures. The formation of the relationship between a hydrophobizing material and the elements of material's structure, as well as the depth of penetration, the type, and its optimal amount, contributes to the improvement in durability of buildings. It should be noted that nanotechnologies are one of the key areas in the field of construction. The use of hydrophobizing substances that contain nanoparticles could

increase the indicator of frost resistance and durability of the brickwork [11, 12].

Therefore, it is a relevant task to study the design of hydrophobized nano-liquids to ensure the enhanced operational properties of brick structures.

2. Literature review and problem statement

The main factors that affect the durability of buildings are the aggressive environmental factors, which lead to materials destruction, reduced durability, deterioration of the operational properties of fencing structures [13, 14]. Ceramic brick remains one of the main building materials used to construct buildings and structures. At present, ceramic face brick is widely used to provide decorative and aesthetic properties to buildings as a facing wall material. Paper [15] reports results of research into an artificial stone, which indicate its enhanced porosity. During operation, this results in the penetration of moisture both to the surface and deep layers of the brickwork, destroying it, especially when exposed to reduced positive and negative temperatures.

On the other hand, a study [16] established that there occurs the process of washing out salt from the ceramic brick, thereby taking it to the surface of the material. This also leads to the loss of the aesthetic appearance of a building. A technique to overcome these difficulties could be the treatment of surface with hydrophobized substances, protecting the brick structure from atmospheric influences, reducing the probability of destructive processes. This is the approach used in studies [17, 18]. However, when modifying ceramic bricks with hydrophobized substances based on acrylic polymers, its technical characteristics improve, in particular, the rates of water absorption and capillary diffusion decrease, while consumer properties are compromised. As it is known from study [19], hydrophobized substances that include silicone, silane and siloxane-based polymeric compounds are characterized by high efficiency. The size of particles of the hydrophobized compounds affects the depth and rate of penetration into the structure of a material. It should be noted that silicone resins are characterized by the largest particle size, which is approximately 100 times larger than the particles of siloxanes. Investigation [20] has established that such substances do not form a homogeneous film, do not cover all pores and microcracks, and, therefore, they cannot completely prevent the migration of water and provide the required frost resistance. However, it should be noted that the waterproof film formed at the surface of a material, which, during operation under conditions of alternating temperatures, deforms, does not ensure the required durability, namely frost resistance and high stability of the structure.

The application of hydrophobized compounds based on organosilicon compounds is common. At the same time, study [21] shows that the organosilicon compounds, especially polyorganosiloxanes, do not provide for the required performance properties of a material in comparison to other polymers. In order to overcome this problem, authors of paper [22] studied the effectivity of the modified composition of such hydrophobized substances. Nano-liquids are used to effectively protect surfaces at the nano- and sub-micro-level, which make it possible to reduce permeability coefficient and improve waterproofness of a brick structure. The unique properties characterize the nanopowder of aluminum oxide Al_2O_3 , which plays a decisive role both in the production of

ceramic materials and as a filler in nanocomposites to improve their properties.

Despite the practical significance of such results, the operational properties of the brickwork with the use of ceramic facing bricks, modified by nano-liquids, were not sufficiently considered. Therefore, there are reasons to believe that the lack of certainty about the effect of hydrophobized nano-liquids with the addition of Al_2O_3 nanopowder on the operational properties of ceramic brick necessitates undertaking a research in this direction.

3. The aim and objectives of the study

The investigation that we conducted aimed to improve the operational properties of brick building structures by modifying the surface of a ceramic brick with hydrophobized substances, particularly, a nano-liquid.

To achieve the set aim, the following tasks have been solved:

- to determine the impact of different classes of hydrophobized substances on the physical-technical and operational properties of ceramic bricks;
- to investigate the effect of a nano-liquid containing nano- Al_2O_3 on water absorption and capillary pull of the ceramic brick using a method of mathematical planning of the experiment;
- to establish the effect of hydrophobized substances on the operational properties of the brickwork, in particular capillary pull, weather resistance, frost resistance, and salt-ing-out resistance.

4. Materials and methods to study the impact of modified substances on the operational properties of the ceramic brick

4.1. Examined materials and equipment used in the experiment

The research was conducted using ceramic hollow brick made by TzOV “Evroton”, with an average density of $1,317 \text{ kg/m}^3$, a strength grade of M100, water absorption is 16.5 %. Film-forming polymethylphenylsiloxane (PMPHS) and an acrylic polymer (AP) were used as hydrophobizing substances. To improve the operational properties of the brickwork, a nano-liquid with a permeable complex action was developed, containing the nanosized crystalline powder based on Al_2O_3 the size of 30... 0 nm. The nanocrystalline powder contains about 90 % of active Al_2O_3 .

A nano-coating is a colloidal solution of nanoparticles containing pure polymethylphenylsiloxane varnish, aluminum oxide, and a nanocrystalline powder based on the active aluminum Al_2O_3 . A nano-liquid was obtained by dispersing the components (pure polymethylphenylsiloxane varnish, aluminum oxide) and a nanopowder based on the active aluminum Al_2O_3 . When conducting the research, the nano-liquid was applied at the surface of the brick structure using a roller.

Granulometric composition of the nanopowder was determined using the laser analyzer Mastersizer 3000 (Great Britain). Microstructure of the surface of the ceramic brick was examined using the raster electron microscope REM 106I (Ukraine).

4. 2. Procedure for determining the indicators of sample properties

To determine the water absorption rate, a non-destructive analysis in line with the Karsten's method (RILEM Test Method II.4) was used, according to ASTM E 514 and in accordance with DSTU B V.2.7-126:2011 [23].

Atmospheric resistance of the ceramic face brick was determined by alternating wetting and drying over 100 cycles. The samples were considered to be weather resistant if, after 100 cycles of humidification and drying, the strength did not decrease by more than 25 %. Stability of the ceramic brick against salting-out was tested according to DSTU B V.2.7-171:2008 [24]. The samples were immersed in distilled water while maintaining the water level constant. The surface of the samples above the water was blown with air at a temperature of (20 ± 2) °C and a relative air humidity of (60 ± 10) % for at least 3 hours a day. After 7 days of testing, the presence of salt efflorescence at the surface of the brick was determined visually.

Determining the frost resistance of ceramic bricks was conducted in accordance with DSTU B V.2.7-42-97 [25]. Assessment of frost resistance was conducted based on the external physical appearance (degree of damage) and the loss of strength for compression and the loss of mass in accordance with the requirements of acting normative documents.

When studying the effect of a nano-coating on the properties of the brick, the method of orthogonal central composite planning was applied.

5. Results of studying the indicators of properties of the modified ceramic brick

We established during experimental study that the ceramic brick is characterized by high porosity (21.9 %), water absorption (16.5 %), water absorption at capillary pull $(2.2 \text{ kg/m}^2\cdot\text{h}^{0.5})$. In the course of investigating the salting-out, we observed salt efflorescence at the surface of the ceramic brick after 7 days. In order to improve the properties of the ceramic brick, the hydrophobizing substances were applied to the surface of the ceramic article. Thus, when applying the hydrophobizing agent PMPHS, porosity decreases from 21.9 to 17.4 %, water absorption – from 16.5 to 13.6 %, water absorption at capillary pull – from 2.2 to $1.98 \text{ kg/m}^2\cdot\text{h}^{0.5}$. At the same time, when applying the hydrophobizing agent AP, porosity decreases to 16.5 %, water absorption – to 7.09 %, water absorption at capillary pull – to $0.68 \text{ kg/m}^2\cdot\text{h}^{0.5}$ [15].

The results of experimental tests have shown that for the modified ceramic brick, the surface of which is treated with PMPHS, frost resistance increases by 15 cycles compared to the untreated brick (F50). At the same time, when treating the surface of brick with AP, frost resistance increases by 20 cycles. Using an electron microscopy method, it was found that after alternating freezing and thawing the surface of the brick treated with the PMPHS-based hydrophobizing agent demonstrates the intensive formation of microcracks (Fig. 1). This is also confirmed by studying water absorption – the

indicator increased by 42 %. As regards the brick, modified by AP, cracks at the surface of the sample formed locally, with less opening, which led to an increase in water absorption by 28 %. This indicates that the examined coatings cannot be used to protect brick structures that operate under high humidity and external aggressive factors because of the low water resistance caused by the washing out of components.

To improve the operational properties of ceramic brick, we examined the effect of hydrophobizing substances containing a nanocrystalline powder employing a method of mathematical planning of the experiment. Experimental study into the effect of nano-liquids on the properties of the ceramic brick was conducted in accordance with the plan of a two-factor three-level experiment. The variables selected were the content of pure polymethylphenylsiloxane varnish ($X_1=30; 35; 40$ %) and the amount of Al_2O_3 nano powder ($X_2=0; 0.5; 1.0$ % by weight) (respectively, the content of fillers: aluminum oxide and ferrum oxides was 55...65 %). As a result of processing the plans and the corresponding experimental data using the method of least squares, the water absorption regression (Y_w) and capillary pull (Y_{wk}) regression equations were constructed, which adequately describe the dependence of indicators, as the optimization criteria of the system, on the variables.

$$Y_w = 2.11 - 0.03X_1 + 0.017 X_2 - 0.067 X_1^2 - 0.117 X_2^2 - 0.150 X_1 X_2;$$

$$Y_{wk} = 1.15 - 0.325X_1 - 0.60 X_2 - 0.175 X_1^2 + 0.100 X_2^2 - 0.012 X_1 X_2.$$

Based on the graphical interpretation of the derived mathematical models (Fig. 2), it was established that the optimal region for the introduction of nano- Al_2O_3 is within 0.4...0.8 %.

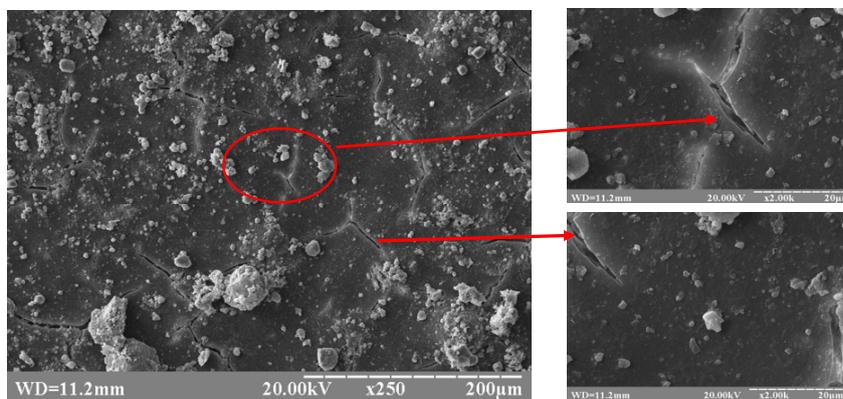


Fig. 1. Microcracks at the surface of the brick treated with the PMPHS-based hydrophobizing agent

When treating the surface with a nano-liquid (amount of nano- Al_2O_3 is 0.8 %), water absorption decreases to 1.2–1.6 %, the rate of water absorption at capillary pull – to $0.08\text{--}0.12 \text{ kg/m}^2\cdot\text{h}^{0.5}$. We established, by applying a method of defectoscopy using the Karsten tube (Fig. 3, c), that the surface of the ceramic brick, modified by a nano-liquid, is characterized by the lowest water absorption (0.002 ml/cm^2) after 2 hours of aging-fall, whereas for the brick covered with AP – 0.03 ml/cm^2 (Fig. 3, b), and without a coating – 0.15 ml/cm^2 (Fig. 3, a). The kinetics of change in water absorption, using the Karsten tube, over 6 hours of testing are shown in Fig. 4.

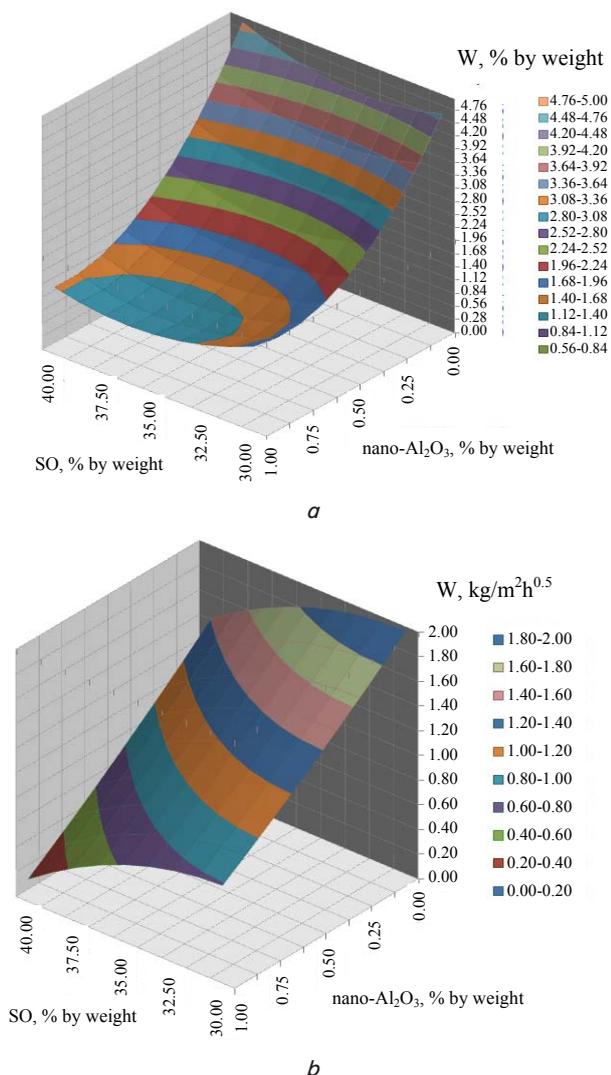


Fig. 2. Isoparametric diagrams of change: *a* – in water absorption; *b* – in water absorption at capillary pull

Based on these results, we can state the presence of an interesting pattern that is associated with the formation of the surface microstructure. Specifically, when applying the method of electron microscopy, it was established that the surface of sample of the ceramic brick without a coating is non-uniform, with projections and capillary micropores (the size of 10–15 microns) (Fig. 3, *a*). When the surface of the sample is impregnated with the nano-liquid, the structure is leveled and compacted through the penetration of nanoparticles inside the material (Fig. 3, *c*). Effectiveness of the application of a nano-fluid is predetermined by the free energy of the surface, as well as by the colmatation of the surface with particles of nano-Al₂O₃ in the composition of the hydrophobizing substance. In this case, the pulling up of water-soluble salts from the brickwork is blocked. Generalization of this fact can be formulated in the form of the following postulate: “Treatment with a nano-liquid provides structures with a uniform and denser character by creating a composite cross-linked structure with new phases, which reduces indicators of water absorption and increases the atmospheric and frost resistance of the brick structure”.

The study into atmospheric resistance has established that after 100 cycles of alternating wetting and drying of the uncovered ceramic brick, the loss of strength was 15.2%. In this case, the examined samples demonstrated crack formation with a width of opening of 2...3 mm. At the same time, for the ceramic brick, the surface of which was covered with PMPHS, the loss of strength decreased to 7.9%, and that of the AP covered – to 6.8%. It should be noted that the surface of the treated samples also revealed cracks.

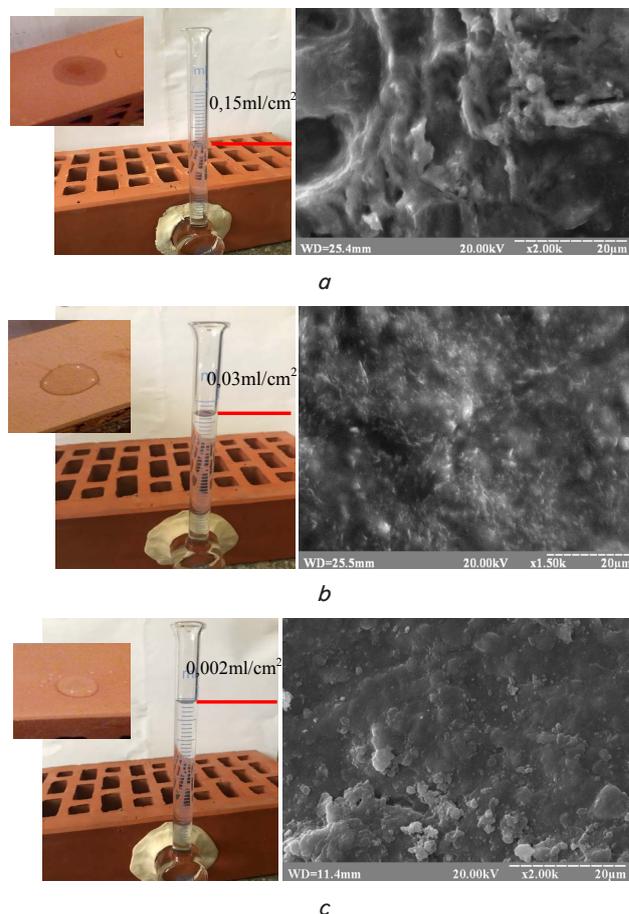


Fig. 3. Water absorption of ceramic brick using the Karsten tube: *a* – without a coating; *b* – AP; *c* – nano-liquid

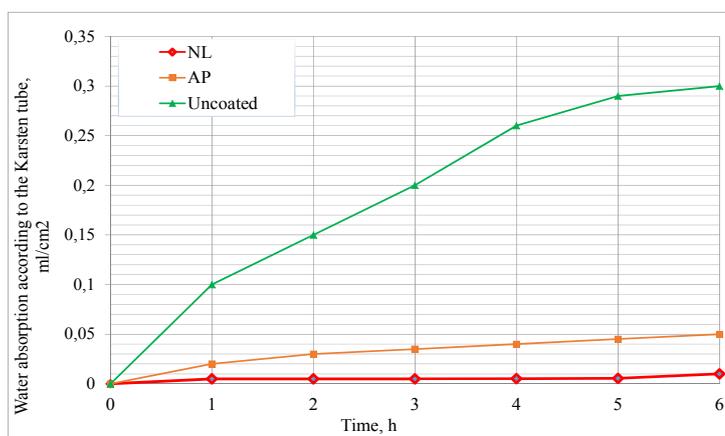


Fig. 4. Kinetics of change in water absorption using the Karsten tube

As can be seen from Table 1, for the ceramic facing brick, covered with a nano-liquid, when studying the atmospheric

and frost resistance, the loss of strength, respectively, is 2.9 and 1.8 times lower than that of the reference sample; the frost resistance in this case increased by 50 cycles and reached the mark F100.

Table 1

Physical-technical properties of the ceramic brick treated with a nano-liquid

Properties	Units of measurement	Results	
		Reference sample (untreated)	Sample treated with a nano-liquid
Water absorption	%	16.5	1.2
Capillary pull	kg/m ² h ^{0.5}	2.2	0.08
Atmospheric resistance – loss of strength	%	15.2	5.1
Frost resistance:			
– loss of strength	%	19.0	10.5
– loss of weight	%	8.6	3.9

The brick masonry, covered with the developed nano-liquid, is characterized by improved protective properties – reduced water absorption and capillary pull, increased atmospheric and frost resistance. This will make it possible to receive a building structure with improved operational properties, especially under conditions of high humidity and alternating temperatures.

6. Discussion of results of studying the impact of the modifying substances on the ceramic brick's properties

When determining the effectiveness of hydrophobizing additives PMPHS and AP for the process of water absorption and capillary pull, as it follows from the results, it is logical to reduce these indicators. This is predetermined by the formation of a waterproof film at the surface of the ceramic face brick, which slows down the penetration of water. It should be noted that the application of such hydrophobizing additives with the formation of the film is not very effective, especially under the influence of alternating temperatures – following the alternating freezing and thawing, the surface of the treated brick demonstrates intensive formation of microcracks. In this sense, interpretation of the results of electron microscopy, shown in Fig. 1, is of a special interest, confirming the establishment of the described fact. This indicates that the formation of a hydrophobizing film does not ensure sufficient frost resistance, since the surface of the coating demonstrated microcracks after the test, which lead to a decrease in the operational properties of the brickwork.

A special feature of the proposed solutions is the optimization of hydrophobic coatings with the use of nano-Al₂O₃, which was selected as a variable factor (X₂=0; 0.5; 1.0 % by

weight) in the mathematical planning of the experiment. It follows from the results obtained (Fig. 2) that the brick treated with a hydrophobizing agent that does not contain nanopowder is characterized by the highest indicators of water absorption (4.78 %) and capillary pull (1.96 %). In this case, the treatment of surface with a hydrophobizing agent containing nano-Al₂O₃ (from 0.15 to 0.8 % by weight) ensures a significant reduction in the studied parameters. This is predetermined by the colmatating and penetrating action of Al₂O₃ nano-fibers with the formation of a composite cross-linking structure by newly-formed phases, which reduces the water absorption indicators (Fig. 3, 4) and increases the atmospheric and frost resistance (Table 1) of the brick structure.

However, it is impossible to ignore practical data from papers [8, 14] whose authors also describe the significance of the effect of hydrophobizing coatings based on Al₂O₃, that contain mineral fibers. The obtained data indicate that such coatings lead to a decrease in the water absorption indicators; in this case, the results of atmospheric and frost resistance studies are not sufficient. This means that taking this fact into consideration opens up a possibility for effective regulation of the operational properties of a brick structure using the developed protective compositions of nano-liquids that contain the active nano-Al₂O₃ with a penetrating effect.

Such conclusions can be considered useful from a practical point of view, as they make it possible to reasonably approach determining the required type of a modifying substance and its effect on the operational properties of brick building structures.

7. Conclusions

1. The conducted experimental study has established that the use of hydrophobizing substances provides ceramic bricks with water-repellent properties, although it forms a hydrophobic film at the surface, in which microcracks are formed under the impact of external climatic factors.

2. By using a method of mathematical planning of an experiment, we developed formulations for the hydrophobizing nano-liquids containing the Al₂O₃ nanopowder. It was established that the optimum region for the introduction of nano-Al₂O₃ is in the range of 0.4...0.8 %.

3. Modifying the surface by a nano-liquid containing 0.8 % of Al₂O₃ nanopowder ensures a decrease in the indicators of porosity and water absorption without the formation of a film. In this case, frost resistance increases by 50 cycles; efflorescence formation at the surface of the sample is not observed. Give this, it can be argued that the nano-liquid significantly influences a change in the character of the structure of the ceramic brick surface in order to provide protection for the brick building structure and to enhance its operational properties.

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