

Метадами комплексного термічного аналізу та інфрачервоної спектроскопії досліджено процеси взаємодії кремнійорганічних сполук з карбонатними і силікатними нерудними матеріалами. Визначено втрати маси карбонатів і силікатів, просочених кремнійорганічними сполуками, в результаті дериватографічних досліджень. Проаналізовано ІЧ-спектри карбонатів і силікатів, оброблених силіконатами і гідроліза- том етилсилікату

Ключові слова: нерудні матеріали, карбонати, силікати, кремнійорганічні сполуки, ІЧ-спектроскопія, ДТА, ДТГ, ТГ

Метадами комплексного термического анализа и инфракрасной спектроскопии исследованы процессы взаимодействия кремнийорганических соединений с карбонатными и силикатными нерудными материалами. Определены потери массы карбонатов и силикатов, пропитанных кремнийорганическими соединениями, в результате дериватографических исследований. Проанализированы ИК-спектры карбонатов и силикатов, обработанных силиконатами и гидролизатом этилсиликата

Ключевые слова: нерудные материалы, карбонаты, силикаты, кремнийорганические соединения, ИК-спектроскопия, ДТА, ДТГ, ТГ

THERMAL ANALYSIS AND IR-SPECTROSCOPIC RESEARCH INTO INTERACTION BETWEEN ORGANOSILICON COMPOUNDS AND NONMETALLIC MATERIALS

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1. Introduction

Natural stone carbonate and silicate materials are used in construction at all stages of building the facilities. Limestone, dolomite, tuff, sandstone, shell rock are applied in the exterior facing of buildings and for laying of walls.

Constant contact between the surface of nonmetallic materials and aggressive environmental factors cause a gradual deterioration of operational and decorative properties as a result of corrosion processes. Solving this problem is possible by the introduction of organosilicon compounds, resistant to natural factors and chemically aggressive agents, into materials and structures [1].

Impregnation of organosilicon compounds of different classes through porous natural stone is a complicated diffusion process. The latter includes the stages of absorption, wetting, diffusion and filling the pores, which proceed in different sequence and combinations and depend on the physical-chemical properties of the matrix and the impregnating compositions [2].

In this regard, it is of scientific and practical interest to study the interaction between nonmetallic materials and hydrophobizing substances. An analysis of peculiarities of their interaction by modern methods of thermal analysis [3] and IR-spectroscopy [4] are essential for determining the

most effective combination of building materials with impregnating substances.

2. Literature review and problem statement

In order to protect the masonry facades, building surfaces from moisture and weather conditions, different organosilicon preparations are applied. It is known, for example, that aqueous compositions of oligomeric siloxanes and alkyl silanes are used for the hydrophobization of building non-metallic materials [5]. Along with the chemical, they also employ a non-thermal treatment of materials [6]. Specific properties of the treated materials are achieved due to the processes of interaction between substances and the structure of materials, chemical conversion, etc.

Non-metallic materials possess complex structure, characterized by the existence of phase transitions during thermal treatment [7]. A comprehensive thermal and infrared analysis is run to determine the mechanism of influence of auxiliary substances on the properties of nonmetallic building materials, for example, kaolinite [8], limestone [9, 10]. However, the mixtures of building substances are mostly examined. A thermal analysis is conducted to detect influence of amide additives on the cement hardening process-

es [11]. Authors of article [12] investigated by the method of differential-thermal analysis the effect of complex action of calcium-containing components and SAS on the speed of structure-forming processes in cement and the properties of artificial stone based on it. Paper [13] examined the processes of cement carbonization. Research into carbonate and silicate nonmetallic materials – natural stone – is of fragmented character.

3. The aim and tasks of the study

The aim of present research was to determine the thermal stability of carbonate and silicate nonmetallic materials depending on the type of organosilicon compound used in the impregnation. This will allow us to find out which of the impregnating substances contribute to the most complete interaction between the non-metallic building materials. The data obtained in turn are relevant when choosing the facing materials, resistant to environmental factors of different climatic zones.

To achieve the set aim, the following tasks were to be solved:

- to determine if chemical interaction occurs in the course of impregnating the nonmetallic materials with organosilicon compounds, and, if it does, to identify its mechanism;
- to establish if there is a physical fixation of organosilicon compounds at the surface of carbonate and silicate nonmetallic materials;
- to find out which of the applied organosilicon compounds provides for the largest and the lowest strength with nonmetallic materials;
- to define with which nonmetallic materials (silicate or carbonate) the organosilicon compounds interact most strongly and establish the extent of weight loss by the impregnated silicates and carbonates.

4. Materials and methods for examining the peculiarities of interaction between organosilicon compounds and carbonate and silicate non-metallic materials

4.1. Examined materials that were used in the experiment

The set tasks were solved by using silicate and carbonate nonmetallic materials treated with solutions of organosilicon compounds. We selected the samples most widely used in the construction industry: tuff and sandstone among the silicates, limestone and shell rock among the carbonates.

As the organosilicon compounds, we chose potassium and sodium siliconates (potassium methyl silicate, sodium ethyl silicate, sodium phenyl silicate) and hydrolyzate of ethyl silicate. Specified compounds demonstrated the most positive results for improving mechanical strength and reducing water absorption as a result of impregnation of porous nonmetallic materials [14].

4.2. A procedure for conducting comprehensive thermal analysis and infrared spectroscopy

The peculiarities of interaction processes between non-metallic materials were examined by using independent methods of physical-chemical analysis, in particular a comprehensive thermal analysis and infrared spectroscopy.

A study into the character of bond between organosilicon compounds and non-metallic materials was carried out on the derivatograph Q-1500D by the Paulik-Paulik-Erdey system (Hungary), which allows joint registration of integral (T) and differential (DTA) heating curves, integral (TG) and differential (DTG) curves of mass change at linear rise in temperature. Extrema on the DTG curve correspond to the maximum speed of mass change that makes it possible to determine the actual temperature of the process. In addition, the use of derivatographic analysis provides for the possibility to divide thermal effects [3].

The method of IR spectroscopy is based on the analysis of radiation absorption by a substance in infrared region of the spectrum associated with the excitation of valent and deformational oscillations in molecules. It allows determining the presence in substance in particular structural or functional groups of atoms and their relative content [4, 7]. The research is carried out using the spectrophotometer IR-75 Specord (made by Carl Zeiss AG – Zeiss AG, Germany) on tablets with spectrally pure KBr.

5. Results of comprehensive thermal analysis and IR-spectroscopy

Data on thermal analysis of carbonates (limestone, shell rock), represented in the form of DTG and DTA curves, demonstrated that there were no considerable changes in mass or processes with heat release or absorption in the composition of starting materials at heating to temperatures of 1223 K (Fig. 1). Endothermic effects at the mentioned temperatures are associated with the results of calcium carbonate dissociation.

The treatment of carbonates with potassium methyl silicate and ethyl silicate hydrolyzate leads to certain changes in their behavior when heated. As far as endoeffect at 1223 K is concerned, its shift should be noted into the region of lower temperatures by 15–25 K for limestone and by 20–100 K for shell rock. In this case, potassium methyl silicate demonstrates a more intensive catalytic action on the dissociation of calcium carbonate. Explaining this fact is possible by the presence of alkali metals in the composition of the latter.

The presence of organosilicon compounds in the composition of limestone is also accompanied by the occurrence of exothermic effects at 753 K for potassium methyl silicate and at 623 K for ethyl silicate hydrolyzate. The existence of these effects is caused by the destruction of methyl and ethyl radicals, respectively.

Of the largest interest in terms of establishing the mechanism of interaction between the specified organosilicon compounds and carbonates is the occurrence of endoeffects for the impregnated limestone in the temperature range of 373–543 K for silicate and 363–500 K for hydrolyzate. Their occurrence is obviously caused by the release of water, which has different strength of binding to the surface of limestone and was formed in the interaction between the latter and organosilicon compounds. The DTG and DTA curves of the starting material do not show the indicated endoeffects.

The behavior of the impregnated shell rock under the influence of heat is similar to that described above. A slight difference is only in the quantitative parameters of the described processes. Thus, the maximum of exoeffects in the

destruction of methyl and ethyl radicals is shifted toward lower temperatures by 15 and 20 K, respectively.

The intensity and area of endothermic effects associated with the removal of water are by 20–30 % less compared to the impregnated limestone.

The peculiarities in thermograms of the original silicate materials (sandstone and tuff) are the lack of any significant effects associated with a change in their heat capacity and mass (Fig. 2).

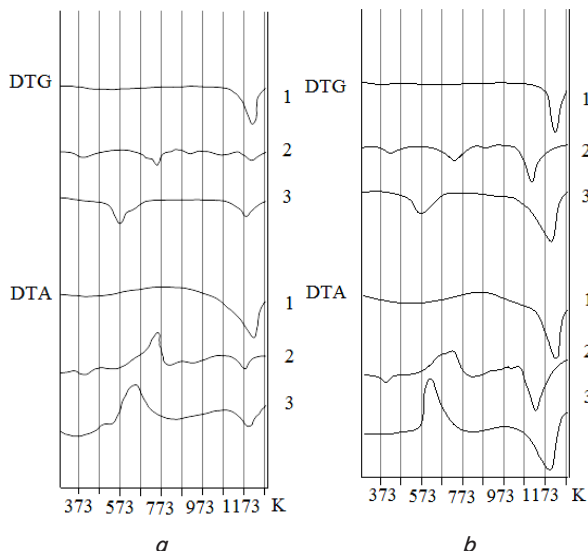


Fig. 1. Thermograms of carbonates: *a* – limestone; *b* – shell rock; 1 – original state; 2 – treated with potassium methyl silicate; 3 – treated with ethyl silicate hydrolyzate

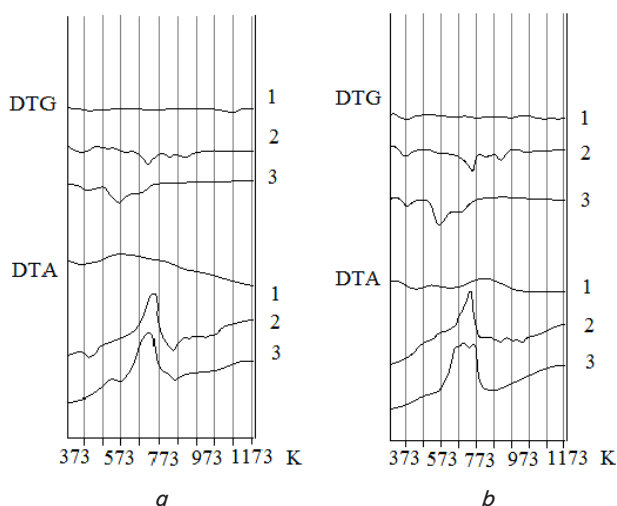


Fig. 2. Thermograms of silicates: *a* – sandstone; *b* – tuff; 1 – original state; 2 – treated with potassium methyl silicate; 3 – treated with ethyl silicate hydrolyzate

The treatment of sandstone and tuff with potassium methyl silicate and ethyl silicate hydrolyzate is accompanied by the occurrence of significant esothermic effects at 730 and 650–773 K, respectively. In this case, worth noting is the considerable area of exoeffect in the case of combining Tuff with ethyl silicate hydrolyzate. Similar to the previous case, these effects are related to the cleavage of ethyl and methyl radicals, respectively. A general tendency for thermal stability in the oxidizing environment is maintained. In the

first case, however, the process of decomposition occurs at higher temperatures. A wide range of removal of radicals C₂H₅ from the structure of impregnated tuff may be predetermined by somewhat more intensive interaction with the surface of the latter.

Endoeffects, caused by the removal of water, are observed in the temperature range of 373–390 K when potassium methyl silicate is employed. In the case of ethyl silicate, they are shifted into the region of temperatures 500–560 K. It indicates its stronger bond with the surface of silicates in comparison with potassium methyl silicate.

It was therefore decided to conduct a thermal analysis of the examined nonmetallic materials treated with sodium ethyl silicate and sodium phenyl silicate, which also belong to the silicates and differ by radicals. The results obtained when using all the examined silicates relative to carbonates confirmed the patterns received earlier in the behavior of the latter when heated (Fig. 3). In addition to the mentioned endoeffects at 1153–1173 K, related to the dissociation of calcium carbonate, the DTA and DTG curves demonstrate exo- and endothermic effects. Exoeffects in the temperature range of 813–833 K are caused by the cleavage of organic radicals in the composition of silicates. In this case, their thermal stability decreases in a series: potassium methyl silicate > sodium phenyl silicate > sodium ethyl silicate.

The endoeffects linked to the removal of water from the structure of impregnated carbonates are observed at temperatures of 283–303 K. Strength of its bond, judging by the temperatures of these effects maxima, can be represented as follows: sodium phenyl silicate > potassium methyl silicate > sodium ethyl silicate.

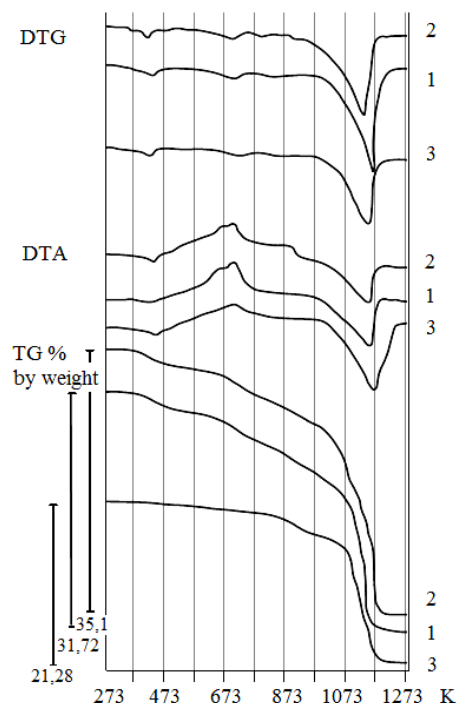


Fig. 3. Thermograms of carbonates treated with organosilicon compounds: 1 – potassium methyl silicate; 2 – sodium ethyl silicate; 3 – sodium phenyl silicate

Similar patterns were noted in the derivatograms of silicates, impregnated with silicates. In this case, worth noting is the shift in maxima of exoeffects associated with

the cleavage of organic radicals of siliconates, by 20–40 K in the direction of higher temperatures (Fig. 4). A similar pattern, but with a less difference in temperatures, is observed for the endothermic effects of water removal. Noteworthy is an increase in the intensity and area of these effects. This indicates a larger amount of water that can form in the process of interaction between siliconates of alkaline metals and silicates, and its stronger bond with the non-organic matrix.

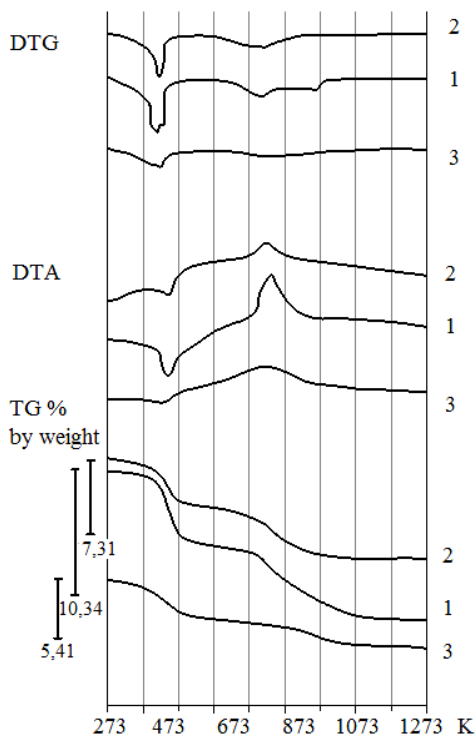


Fig. 4. Thermograms of silicates treated with organosilicon compounds: 1 – with potassium methyl silicate; 2 – with sodium ethyl silicate; 3 – with sodium phenyl silicate

The total loss of mass of the impregnated silicates is 5.4–10.3 % versus 26.1–30.3 % in carbonates.

Method of infrared spectral analysis is characterized by high sensitivity and makes it possible to respond to minimal changes in the chemical composition of examined materials. Results obtained by using such an independent method allowed us to obtain additional information about the peculiarities of interaction between siliconates of alkali metals and non-organic matrices.

The IR-spectra of the starting carbonate are characterized by the existence of intensive absorption bands in the region of 1410–1450 and 860–880 cm^{-1} responsible for the valence oscillations of the CO_3^{2-} anion (Fig. 5).

A treatment of calcium-containing material with siliconates of potassium and sodium is characterized by certain changes in the infrared spectra. There occur the absorption bands in the range of 2900–3000 cm^{-1} , characteristic for valence oscillations of the C–H bond. The intensity of absorption bands increases at 3400–3500 cm^{-1} (valence oscillations of adsorbed water) and 1000–1100 cm^{-1} (valence oscillations of the Si–O–Si bond). At the same time, the intensity of those absorption bands decreases that are inherent to the oscillations of anion carbonate.

The occurrence of new bands at 2900–3000 cm^{-1} and an increase in the intensity of bands in charge of the oscillations

of bonds between silicon and oxygen, allow us to state the fixation of siliconates in the composition of carbonates.

Simultaneous increase in the adsorbed water and decrease in the intensity of absorption bands, characteristic for the anion CO_3^{2-} , may testify to the interaction between the reaction-capable groups that formed in the process of silicate hydrolysis and active centers of the carbonate surface.

A structure of IR spectrum of the starting silicate (on the example of tuff as a more multicomponent by oxide content) displays a more complex character compared with calcium carbonates. We noted absorption bands, characteristic of valence oscillations of the bridging bonds Si–O–Si (1020, 980 cm^{-1}) and Si–O–Al (780, 740 cm^{-1}). In addition, there are absorption bands responsible for the deformational oscillations of bonds Si–O–Al (526, 560 cm^{-1}) and Si–O (453 cm^{-1}) (Fig. 6).

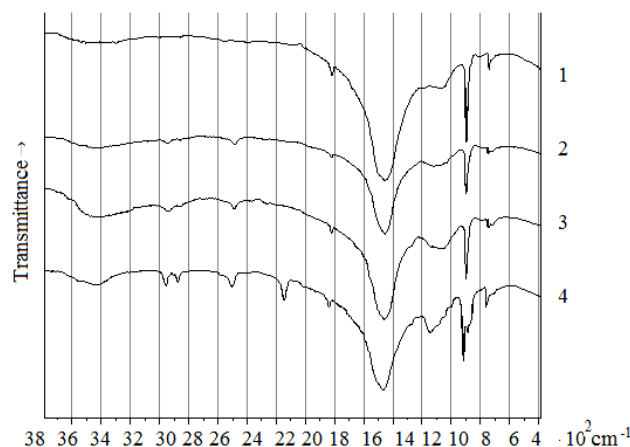


Fig. 5. IR spectra of carbonates treated with siliconates: 1 – untreated; 2 – with potassium methyl silicate; 3 – with sodium ethyl silicate; 4 – with sodium phenyl silicate

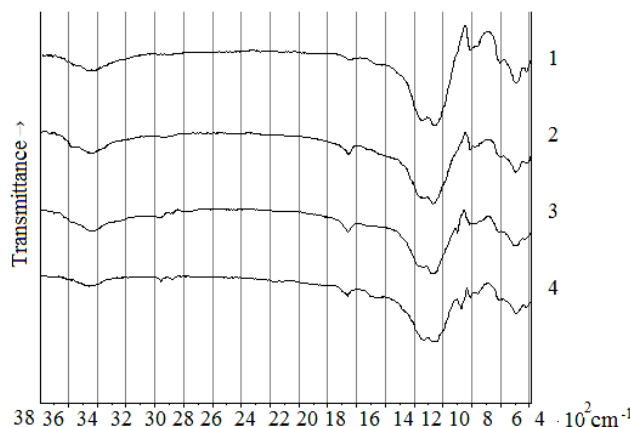


Fig. 6. IR spectra of silicates treated with siliconates: 1 – untreated; 2 – with potassium ethyl silicate; 3 – with sodium methyl silicate; 4 – with sodium phenyl silicate

Along with the structure-forming bonds, IR spectra contain absorption bands, characteristic of oscillations in the adsorbed water (3400–3450 cm^{-1}) and hydroxyl groups (820 cm^{-1}).

A treatment of tuff with siliconates of alkali metal has common attributes with carbonates in the occurrence of absorption bands at 2900–3000 cm^{-1} (valence oscillations of the C–H bonds). At the same time, we should note some individual features. This is, first of all, the occurrence of absorp-

tion bands at 1440 and 1630 cm^{-1} , predetermined by the deformational oscillation of the C–H bond and adsorbed water, respectively. There is an ambiguous change by 0.7–1.3 times in the intensities of the bands at 3400–3450 cm^{-1} (valence oscillations of adsorbed water) compared to the starting material. An expansion is observed in the range of bands responsible for the valence and deformational oscillations of bonds between silicon and oxygen up to 1150 cm^{-1} .

Of particular interest for discovering the mechanism of interaction between siliconates of potassium and sodium and the silicate surface is the absorption bands at 820 cm^{-1} . In the course of their treatment with siliconates, we registered a decrease in its intensity by 1.5 times for potassium methyl silicate and sodium ethyl silicate. It decreases even larger (by 2.25 times) for sodium phenyl silicate.

6. Discussion of results of examining the nonmetallic materials impregnated with organosilicon compounds

When heating the starting carbonate and silicate non-metallic materials to temperatures of 1223 K, there are no significant changes in mass and processes with heat release or absorption.

Minor endothermic effects of limestone and shell rock at the mentioned temperatures are caused by the dissociation of calcium carbonate. A treatment of these carbonate non-metallic materials with potassium methyl silicate and ethyl silicate hydrolyzate leads to a catalytic action on the dissociation of calcium carbonate. That is why the endoeffect at 1223 K shifts to the region of lower temperatures (by 15–25 K for limestone and by 20–100 K for shell rock).

A treatment of carbonate and silicate nonmetallic materials with organosilicon compounds is accompanied by the occurrence of endothermic and exothermic effects.

Exothermal effects are associated with the cleavage of radicals in organosilicon compounds. These effects are observed when limestone is treated with potassium methyl silicate at 753 K and by ethyl silicate hydrolyzate at 623 K, for shell rock – 738 and 603 K, for sandstone and tuff – 730 K and 650–773 K, respectively.

The tuff impregnated with ethyl silicate hydrolyzate is characterized by the wider range of removal of radicals – C_2H_5 . This may be due to their more intensive interaction compared to other non-metallic materials.

The occurrence of endothermic effects is caused by release of water, which formed as a result of interaction between nonmetallic materials and organosilicon compounds. These effects are observed when limestone is treated with silicate – in the temperature range of 373–543 K, with hydrolyzate – 363–500 K. The intensity and area of endothermic effects in the case of shell rock are 20–30 % less. For the silicate non-metallic materials treated with potassium methyl silicate, the endoeffects manifest themselves in the temperature range of 373–390 K. And for the silicates treated with ethyl silicate hydrolyzate – at 500–560 K, which also indicates its more robust interaction with the surface of silicates in comparison with potassium methyl silicate.

When using siliconates that differ by radicals and cations, located next to the silicon atom, we also registered exothermic and endothermic effects. The strength of bond between organosilicon non-metallic compounds and non-metallic materials decreases in the series sodium phenyl

silicate > potassium methyl silicate > sodium ethyl silicate. The interaction between siliconates of alkali metals and silicate non-metallic materials is characterized by a stronger bond than that in the case of carbonate materials.

Data on IR spectroscopy of the impregnated nonmetallic materials also attest to the physical–chemical interaction between carbonates and silicates and organosilicon compounds. The fixation and interaction of siliconates in the composition of carbonates is evidenced by the occurrence on IR spectra of new bands at 2900–3000 cm^{-1} , an increase in the intensity of bands responsible for oscillations in the bonds between silicon and oxygen. This is also confirmed by an increase in the adsorbed water and decrease in the intensity of absorption bands characteristic of anion CO_3^{2-} . A treatment of tuff with siliconates of alkali metals is also characterized by the occurrence of absorption bands at 2900–3000 cm^{-1} responsible for the valence oscillations of the C–H bonds. There is also an expansion in the range of bands responsible for the valence and deformational oscillations of bonds between silicon and oxygen. There appear the bands that are caused by deformational oscillations in the bond between C–H and adsorbed water.

The indicated peculiarities allow us to conclude that in the structure of silicates and carbonates there occurs both a physical fixation and a chemical interaction between siliconates of potassium and sodium.

7. Conclusions

An analysis of data on the processes of interaction between siliconates of sodium and potassium and the surface of carbonates and silicates allows us, with a high degree of reliability, to state the following.

1. Chemical interaction between the enumerated objects occurs by the poly-condensation mechanism of functional reaction-capable groups of siliconates with active centers of the surface of carbonates and silicates. This is confirmed by the emergence in the composition of treated non-metallic materials of various forms of adsorbed water. Adsorbed water is absent in the starting materials and can only be a byproduct in the course of interaction reactions by the mechanism of poly-condensation.

2. As a result of treatment of nonmetallic materials, we do not exclude a physical fixation of organosilicon materials at the surface of non-organic substrates.

3. The strength of bond between organosilicon compounds and non-metallic materials decreases in a series of sodium phenyl silicate > potassium methyl silicate > sodium ethyl silicate, in other words, the largest strength is provided by sodium phenyl silicate, and the lowest one – by sodium ethyl silicate.

4. The strongest bond between organosilicon compounds and non-organic matrix is observed in the case of silicate non-metallic materials. The total loss of mass of the impregnated silicates is 5.4–10.3 % versus 26.1–30.3 % in carbonates.

Obtained data on the peculiarities of interaction between organosilicon compounds and carbonates and silicates should be taken into account in the analysis of formation of properties of the impregnated nonmetallic materials. Impregnating these materials can improve the level of their stability during operation under the influence of environmental factors that cause destruction of materials.

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