Modification of the structure of the stabilized basalt fiber

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Abstract. The study of thermophysical, physical-mechanical and acoustic characteristics of coarse continuous basalt fiber in the conditions of influence of operational factors and corrosion environment is carried out. It is shown that obtaining barrier materials with high thermophysical and acoustic properties is possible by creating a porous system in the material with a predetermined textural characteristic of pores of different class, purpose and combination. The influence of the porous system of coarse continuous basalt fiber on the operational properties of flexible heat and sound insulation products and materials has been studied. It is determined that the performance characteristics of flexible thermal insulation materials are in direct proportion to the degree of porosity of the constituent materials and their structural characteristics. Shown that the increase in the operating temperature of these materials, sound and thermal resistance is determined by the chemical and mineralogical composition of the source materials and their structural characteristics. The influence of the mechanism of selective leaching of coarse continuous basalt fibers on their textural characteristics and the zone of operating temperatures is studied.

Introduction. The requirements of regulatory documents on thermal protection of buildings and structures have led to a steady trend to create new materials that ensure the sustainable operation of structure and equipment in conditions of intense exposure to destructive factors of external influence. Such materials are subject to a set of (sometimes mutually exclusive) requirements that must combine: physical and mechanical, chemical, hygienic, thermophysical, decorative and other properties of materials. In this regard, there was a need to create materials. Which at low average density, high strength is able to withstand significant temperature loads, the impact of extreme natural and operational factors.

The development of modern technology necessitates the creation of materials that are characterized by low average density, able to withstand the effects of high temperatures and aggressive environments. One such material is mineral fibers based on erupted rocks. The raw materials for their production are non-deficient, widespread in Ukraine the main rocks of magmatic origin - basalts and their structural analogues - diabases, amphiboles and others. The relatively low melting point makes it possible to use these rocks for the production of mineral fibers in a simplified scheme, directly with the loading of rock into the smelting unit, which ensures high efficiency of the product, stability of process parameters and no harmful load on the environment.
The development of construction production to increase the requirements for structural and thermophysical characteristics of buildings requires the creation of materials that in their properties should significantly exceed existing ones.

In this regard, there is a need to create products that have a low average density, high strength characteristics that can withstand temperature loads, the impact of aggressive environments.

One of the materials that meet the above requirements are concretes based on continuous basalt fiber. In addition to high technical performance, their lower cost should be taken into account, compared to other types of materials for reinforcement. On elasticity it prevails over steel.

The main difference of basalt concrete is its high strength at all types of stress and the ability to withstand large deformations. The relative deformation of basalt concrete, without the formation of cracks can reach 0.7,...0.9%, which is much higher than that for conventional concrete.

Basalt fibers of the VRV and STV type from the basalt of the Usachkovsky, Talne, and Yakova Dolyna deposits were used for research.

When processing basalt fiber of a certain chemical and mineral composition with solutions of certain chemical reagents, it is possible to obtain porous siliceous fibers with high technical characteristics and performance properties. In terms of chemical composition, they consist in the vast majority of modifications of silica. Therefore, the question of durability and stability in aggressive environments of porous basalt fiber, given that the wall thickness of its framework is extremely small and can reach only a few dozen angstroms, is of paramount importance and requires detailed research.

The paper considers one of these aspects, namely the stability of the modified basalt fibre in complex chemical solutions that simulate the composition of the pore liquid in real conditions of solidification of the material.

Basalt fibers, in contrast to glass fibers have a high tendency to crystallization, higher temperature resistance and chemical resistance. Depending on the temperature and heating time, the content of oxides in them changes significantly. Thus, when heated above 600 °C, the beginning of the transition of FeO to Fe₂O₃ is observed. When heating basalt fibers to 450 ... 500 °C there is a slight decrease in mass, which is due to the loss of chemically bound water, and with subsequent heating - an increase in mass, which is associated with the addition of oxygen in the oxidation of ferrous iron to trivalent. The chemical resistance of heat-treated fibers to water and alkali is practically unchanged, as these fibers in the initial state have a high resistance in these media. Acid resistance of heat-treated basalt fibers increases with increasing temperature and reaches its maximum at 800 °C. There is an increase in corrosion resistance of heat-treated basalt fiber in an alkaline environment.

As can be seen from Fig. 1, the decrease in the strength of basalt fibers after heat treatment is insignificant. On average, the decrease in the strength of basalt fiber is in the range of 16 ... 24% and in any case has a much smaller value compared to glass fibers.

![Figure 1. Dependence of strength of mineral fibers on heat treatment temperature. 1- basalt fiber; 2 - glass fiber; 3 - mineral wool](image-url)
The study of the chemical stability of different types of basalts - vitreous, recrystallized, original, porcelain, it was found that vitreous basalt, which has not been subjected to heat treatment above the transition temperature, is destroyed by acid solutions. After leaching of the glass basalt, a pure porous silica skeleton of the fiber remains.

Thus, the leaching of all types of basalt fibers can be explained by the structural ratio of different phases and the position of a number of oxides, which are in the siliceous skeleton of the fiber. These phenomena are confirmed by theoretical statements about the leading role of the method and the degree of supercooling of the starting material and the state and temperature at which the fibers of a certain chemical and mineralogical composition were fixed.

An overview of the problem status

The aim of the research was to obtain porous coarse continuous basalt fibers with elevated operating temperature.

An important area in the production of mineral fibers is the use of rocks as a one-component raw material. In the technological process of obtaining the working melt it is possible to exclude the stages of adjustment of mineral and chemical composition of raw materials, silicate formation and lighting, which significantly increase the complexity of production and, consequently, lead to a significant increase in the cost of finished products. It is known that basalts, diabases, amphibolites, andesitic, diabase and pyroxene porphyrites, andesitobasalts and others can be used as one-component raw materials for the production of mineral fibers. The fibers obtained from this raw material are not only not inferior to traditional glass and mineral fibers, but in a number of properties far outweigh them. In the table 1.

| №  | Fiber material | Density, kg/m³ | Tensile strength, MPa 10³ | Young modulus, MPa 10³ | Elongation at tension, MPa 10³ |
|----|----------------|----------------|---------------------------|------------------------|------------------------------|
| 1  | Steel fiber    | 7.8            | 0.8… 2.15                | 200                    | 3… 4                         |
| 2  | Asbestos       | 2.6            | 0.91… 3.1                | 68                     | 0.6                          |
| 3  | Fiberglass     | 2.6            | 1.05… 3.85              | 70… 80                | 1.5… 3.5                    |
| 4  | Carbon         | 2.0            | 2.0                      | 245                    | 1.0                          |
| 5  | Basalt         | 1.1… 1.6      | 4.0… 12.0               | 184… 210              | 1.2… 1.8                    |

This is the basis for the intensive development of the production of heat and sound insulation products using mineral fibers. Table 2 shows the comparative characteristics of the main technical characteristics of thermal insulation materials using mineral fibers.

| №  | Indicators | BTSH (10mm) | HSP (20mm) | BTSH (30mm) | SHAON (15mm) | SHAON (15mm) |
|----|------------|-------------|------------|-------------|---------------|---------------|
| 1  | Operating temperature, ºC | 700  | 700    | 1150        | 400           | 400           |
| 2  | Thermal conductivity, VT/mK | 0.055 | 0.055  | 0.055       | -             | -             |
| 3  | Linear density, tex | 25  | 60     | 100         | 56-79         | 200-240       |
| 4  | Sorption hydration | 2  | 2      | 16          | -             | -             |
| 5  | Density, kg/m³ | 450 | 200    | 190         | -             | -             |

As can be seen from the data given in table 1.2 heat-insulating products (TZIV), for the production of which basalt fibers were used have an unconditional advantage over other types of TZIV based on mineral fibers and, moreover, based on fibers made of polymeric materials. But at the same time as meeting the growing needs of industry in the production of thermal insulation materials come to the fore...
requirements to improve their performance, including such as operating temperature, thermal conductivity, density and others. It should be noted that basalt fibers and materials based on them have high thermal and insulating properties, as well as structural properties. In terms of temperature resistance, basalt fibers and products based on them significantly outperform similar indicators of heat and sound insulation products based on glass and mineral fibers.

Analyzing the structure, mineral and chemical composition of the fibers, it is possible to conclude that there are common features in all thermal and sound insulation materials, which impose certain restrictions on improving their performance. Thus, a common feature of all heat and sound insulation materials is the use for their production of fibers of dense structure with mineralogical and chemical composition, which is similar to the raw material, which predetermines the honey performance. Therefore, one of the ways to increase the performance of products based on inorganic mineral fibers is to modify the structure of the fiber, as well as adjust its chemical and mineralogical composition in the direction of increasing the operating temperature and thermal insulation properties of the fibers. In this direction, the possibility of replacing fibers with a dense structure in thermal insulation materials with basalt fibers with a three-dimensional microporous structure and with an adjusted mineral and chemical composition was considered. The research was carried out on thickened continuous fibers made from basalt raw materials of the Usachkivske, Yanova Dolyna (Rivne region) and Khayla-Choprak (Donetsk region) deposits. The chemical composition of basalt raw materials of these deposits is given in table 3.

Table 3. Chemical composition of basalt raw materials of different fields (% wt)

| №  | Field             | SO₂ | TiO₂ | Al₂O₃ | Fe₂O₃ | FeO  | MgO  | CaO  | Na₂O  | K₂O  |
|----|-------------------|-----|------|-------|-------|------|------|------|-------|------|
| 1  | Kryvyi Rih        | 54.6| 0.2  | 13.3  | 1.9   | 9.0  | 5.56 | 4.44 | 2.09  | 1.31 |
| 2  | Berestovetskoe    | 49.03| 2.85 | 12.59 | 3.88  | 10.15| 5.47 | 9.54 | 2.34  | 0.66 |
| 3  | Selchivske        | 55.6| 0.66 | 19.4  | 7.54  | 7.54 | 3.84 | 7.91 | 1.86  | 1.56 |
| 4  | Yanova Dolina     | 48.8| 2.75 | 15.0  | 8.47  | 6.39 | 5.13 | 8.34 | 1.5   | 0.75 |

Results

As can be seen from the results of the experiments shown in tables 1-3 the lowest value of the viscosity is a solution of basalt charge of basalts with a high content of iron compounds (in oxide and oxide form), manganese compounds and alkali metals. These materials include basalts of Hein-Chokhrak field of Donetsk region and vice versa basalts of field Yanov Dolina of Rivne region, which contain high content of compounds of aluminum, titanium and calcium show the highest values of melt viscosity. Accordingly, the melting temperatures of the basalt charge of these deposits are inversely related (1390°C for Hein-Chokhrak field of Donetsk region and 1540°C for the field of Yanova Dolina, Rivne region). The temperatures of the upper and lower limits of crystallization of melts of basalts of different deposits are in the range of 1165… 1295°C and also depend on their chemical composition and structural characteristics of the rock. X-ray phase analysis of samples of basalt melt (melting point 1540°C, holding time 0.5 hours), showed the presence of augite and magnetite.

Experiments to determine the cooling rate of basaltic melt of different deposits Fig. 1. showed that melts with a high content of iron and alkali metal compounds (curves 2, 3.) have a significantly lower cooling rate compared with solutions (curve 1) in which the content of iron and alkali metal compounds is limited to 8…11% and 0, respectively 8…1.4%.
Figure 2. The rate of cooling of the melt of basalt rocks and their structural analogues
1. Melts with a low content of compounds of iron and alkali metals;
2. Melts with high content of iron compounds;
3. Melts with high content of iron and alkali metal compounds

These features of the cooling rate of the basalt melt of different deposits can be explained by a decrease in the temperature transparency of melts with a high content of iron and alkali metal compounds. Thus, the most important properties of basalt melts, which provide the possibility of forming a continuous coarse fiber to obtain the specified characteristics are the viscosity of the melt and its crystallization properties.

Determination of the stability of the obtained continuous coarse basalt fiber in a corrosive environment was determined by the method of its treatment with solutions of different chemical nature at a temperature of $95 \pm 5^\circ$C.

Conclusions
According to the obtained results, porous basalt fiber with the texture of the specified parameters can be obtained using basalts of certain deposits. Technological processing of basalt fiber, in this case, is carried out with the help of reagents and with parameters that ensure the formation of a silica skeleton of a certain structure. This provides a porous quartzite fiber with high operating temperatures, which significantly exceeds the operating temperature of basalt fibers.

References
[1] Iler R K 1979 The Chemistry of Silica (New York: John Wiley & Sons) p 896
[2] Fournier R O 1985 Behavior of silica in hydrothermal solutions Review in Economic Geology 2 45-60 https://doi.org/10.5382/Rev.02.03
[3] Allègre C-J, Michard G 1974 Introduction to Geochemistry (Springer, Dordrecht) https://doi.org/10.1007/978-94-010-2261-3
[4] Abrahayman AV 1963 Study of the process of leaching of vitreous basalts Glass and ceramics 7
[5] Christensen V, Jensen S, Guldborg M & Kamstrup Ole 1994 Effect of Chemical Composition of Man-Made Vitreous Fibers on the Rate of Dissolution in Vitro at Different pHs Environmental health perspectives 102 Suppl 5 83-86 doi: 10.1289/ehp.94102s583.