Influence of technological factors on the properties of building materials on the basis of expanded alunitized high-silica mountain rocks

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Abstract. The influence of technological factors in the production of building materials on the basis of expanded alunitized high-silica rocks on their physical-mechanical and thermal-technical characteristics is determined. It is determined that the production of wall materials with high physical and mechanical and thermophysical characteristics, as well as the ability to obtain products with certain predetermined geometric dimensions, are determined by a set of initial indicators, both properties of raw materials and processes, as well as a certain sequence of individual elemental operations. It is shown that the production of wall materials with high physical and mechanical and thermal characteristics can be achieved by reproducing in the volume of the material of a porous system of closed type with homogeneous, evenly distributed throughout the material pores. The influence of the nature of pores and their textural characteristics of alunitized highly siliceous rocks on the performance properties of building materials has been studied. It is shown that the extension of the service life of these materials without reducing their basic physical and mechanical, thermal and thermal-technical indicators directly depends on the porosity coefficient, the values of their textural values and the nature of the pores. The influence of technological factors on the process of pore formation of alunitized highly siliceous rocks, their textural characteristics and stability of parameters during operation under the influence of aggressive environmental factors are considered. It is determined that the increase in the operating temperature of materials created in compliance with these principles is determined by the morphology and structural characteristics of the source materials by their chemical and mineralogical composition, as well as the influence of process parameters.

1. Introduction

Modern requirements of documents of state structures in the field of construction show a steady tendency to increase the requirements for thermal protection of buildings and structures in conditions of intensive exposure to aggressive environmental factors. The necessity of maintaining the declared properties is also emphasized: physical-mechanical, thermophysical, decorative -finishing, acoustic and other characteristics of materials during all term of operation under the condition of complex influence of external aggressive factors. These trends necessitated research, both scientific and chemical - technological in nature to create new types of materials for use in the external structures of buildings and structures. These materials should have low average density and at the same time increased physical and mechanical characteristics, and also to provide invariability of the properties during all term of operation at simultaneous influence of aggressive factors of external environment (corrosion, thermal, mechanical, atmospheric factors, etc.). One of such materials is construction products based on swollen alunitized high-silica rocks. The starting materials for their production are non-scarce, quite widely and evenly distributed in the world rocks - alunite ores, alunitized rocks and their structural analogues (jarosite and others). In addition to high technical performance should take into account their lower cost, compared with other types of structural thermal insulation materials, the
environmental friendliness of both the materials themselves and the process of their production. The main active ingredient, which determines the technological, Alunite is a natural mineral that has the general formula $\text{Am}(\text{XO}_n)\text{pZg}$ at $m:p=2:1$. Chemical formula of alunite - $\text{KSO}_4\text{Al}_2(\text{SO}_4)_3\cdot 2\text{Al}_2\text{O}_3\cdot 6\text{H}_2\text{O}$. Alunite belongs to the group of basic sulfates. All its structural analogues are characterized by the phenomenon of isomorphic substitution by anions and cations, as well as the formation of solid solutions. But the most widespread in nature are structural analogues of alunite - jarosite (sodium form of alunite and mixed K-Na form of alunite (1,2). The hardness of alunite is 4.5…5, density 2.6…2.82 (pure varieties), alunitized rocks - 2.39…2.89 t/m$^3$. At room temperature, alunite is almost insoluble in water, low-concentration acids, ammonia, but easily soluble in alkalis, and hydrofluoric acid. At 1000$^\circ$C it acquires limited solubility in hydrochloric and nitric acids, at 2000$^\circ$C it is completely soluble in concentrated hydrochloric acid (1).

Alunite is a fairly widespread mineral in the world, which forms strong and extended layers of alunite and alunite-kaolin rocks. Alunite deposits and their structural analogues are located in Ukraine, USA, China, Italy and many other countries. The content of alunite deposits is usually in the range of 10…70%. Typical impurities of alunite ores are: quartz, kaolin, dikit, pyrophyllite, opal, chalcedony, iron oxides and others. When heated, alunite consistently undergoes a number of structural transformations that make significant changes in its physical-mechanical, chemical and textural characteristics. According to the results of X-ray structural and differential thermal analyzes (Figure 1…3) the first irreversible structural transformations in the crystal lattice of alunite begin at temperatures of 350$^\circ$C and up to 475…480$^\circ$C the disordered state of matter remains. The dehydration region is in the range of 490…600$^\circ$C. Increasing the temperature to 750$^\circ$C leads to the formation of $\text{KSO}_4\text{Al}_2(\text{SO}_4)_3$. Further increase in temperature leads to the formation of potassium sulfate and alumina. The results of X-ray diffraction analysis also confirm the process of destruction of the crystal lattice and the formation of the amorphous phase, which is confirmed by the increase in the value of the continuous background.

2. Problem status overview
The aim of the research was to determine the parameters and sequence of elemental operations in the technological process of manufacturing porous building materials with predetermined geometric dimensions, as well as to determine the influence of technological parameters on the formation of pore structure of alunitized high-silica rocks. A study of the impact on the process of pore formation of the chemical and mineralogical composition of raw materials and their relationship with the parameters of the technological process. The formation of the cellular structure of building materials on the basis of alunitized high-silica rocks is due to the process of chemical interaction of alunite with the accompanying silica components of the source materials under thermal loading. Changing the chemical composition of alunite as the main mineral of this process.

Table 1 Chemical composition of potassium alunite under thermal loading.

| №  | Burning temperature, $^\circ$C | $\text{K}_2\text{O}$ Content,% | $\text{Al}_2\text{O}_3$ | $\text{SO}_3$ | $\text{H}_2\text{O}$ |
|----|-------------------------------|-------------------------------|-----------------------|----------------|------------------|
| 1  | 95                            | 10.16                         | 28.01                 | 29.14          | 26.08            |
| 2  | 200                           | 11.80                         | 28.64                 | 45.41          | 2.19             |
| 3  | 400                           | 10.60                         | 36.98                 | 38.81          | 13.53            |
| 4  | 800                           | 17.80                         | 63.90                 | 16.96          | 0.00             |
| 5  | 1000                          | 17.80                         | 64.12                 | 16.91          | 0.00             |
| 6  | 1200                          | 18.12                         | 64.90                 | 16.04          | 0.00             |
| 7  | 1400                          | 18.40                         | 63.68                 | 15.45          | 0.00             |

This process is the main in the multi-stage process of obtaining the cellular structure of the studied materials with predetermined textural characteristics. The formation of aluminosilicate melt in the material, under thermal load on the material samples and its properties (viscosity, surface tension forces and other characteristics) allow to regulate the formation of the pore system and, most importantly, to ensure the formation of its predetermined textural characteristics. This makes it
possible to use in the production of cellular building materials rocks with a low content of directly alunite, which provides an expansion of the raw material base due to substandard ores and leads to a sharp reduction in production costs. Obtaining building materials with specified properties is possible by choosing the optimal ratio, in terms of the problem, alunite and siliceous component of raw materials at which the maximum intensity of gas evolution will occur at the time of formation of aluminosilicate melt with design characteristics. It should also be noted that the technological parameters of this main process are significantly influenced by minor impurities that are present in the raw materials, namely - clay minerals, impurities of carbonates and iron oxides.

3. Results

As a result of temperature loading (heating of initial materials, depending on the set purpose, to temperature 1000… 1400°C) fine-porous material with vitreous walls of which pores are within 5…8 mm, average density 1500…1700 kg/m³ turns out. The presence in alunited rocks of foreign impurities in the form of silica inclusions, clay, carbonate materials and inclusions of iron, titanium and other chemical elements makes significant changes in the main process of pore formation. In this case, it is possible to obtain fine-grained material with a low average density in the range of 500…700 kg/m³. This allows the use of low-quality alunite ores for the production of fine-grained and cellular building materials in the form of backfill insulation. In this case, the use of expanded alunited rocks has undeniable advantages over traditional expanded clay with increased strength, fire resistance, resistance to aggressive environments and durability. Both highly enriched samples of alunite ores and natural samples of alunite-containing rocks of various deposits located both on the territory of Ukraine and other countries were used for research. The results of chemical and mineralogical analyzes of the studied samples are given in table 2.3.

| № | Material name       | SiO₂  | Al₂O₃ | SO₃  | Fe₂O₃ |
|---|---------------------|-------|-------|------|-------|
| 1 | Alunitized rock №1  | 86.31 | 4.92  | 3.76 | 0.98  |
| 2 | Alunitized rock №2  | 68.16 | 11.08 | 11.34| 2.50  |
| 3 | Substandard alunite ore | 80.2 | 18.26 | 7.8  | 0.6   |
| 4 | Alunite ore         | 31.93 | 28.58 | 28.5 | 9.07  |

Table 3 Mineral composition of alunite ores and alunited rocks.

| № of sample | Name of the material      | Alunite,% | Quartz,% | Oxidation,% | Carbo-Nati,% | Clay materials,% |
|-------------|--------------------------|-----------|----------|-------------|--------------|-----------------|
| 1           | Alunitized breed №1      | 8.7       | 76.1     | 0.9         | 0.7          | 9.6             |
| 2           | Alunitized breed №2      | 28.9      | 54.8     | 1.4         | 2.9          | 11.2            |
| 3           | Substandard alunite       | 36.1      | 42.6     | 3.6         | 2.4          | 12.7            |
| 4           | Alunite ore              | 47.4      | 32.4     | 6.2         | 5.1          | 2.4             |

The thermal load according to the set mode occurred in the temperature range 1250…1500°C. As a result of determination of physical and mechanical characteristics of the samples received after firing the optimum ratio of the basic minerals of initial materials at which the most significant effect is reached is defined. The interval of concentrations of components of alunited rocks outside which leads to change of dynamics of gas formation and viscosity of aluminosilicate melt and, as a result or decrease in coefficient of swelling of material, or even leads to process of shrinkage is established. It was found that samples with an alunite content within 16…38% provide a stable cellular structure at a temperature load above 1280°C. In the process of thermal loading SO₃ is removed, the average density decreases. The process of formation of the cellular structure is also influenced by the presence of other
impurities. The results of determining the physical and mechanical characteristics of the swollen samples after thermal loading are given in table 4.

Table 4 Physical-mechanical properties of swollen samples of alunite-containing high-silica rocks.

| №  | Name of the material                  | Burning temperature, °C | Average density, kg/m³ | Water absorption, % | Clamping strength, MPa |
|----|-------------------------------------|-------------------------|------------------------|---------------------|------------------------|
| 1  | Alunitized breed №1                 | 1290                    | 840                    | 15.8                | 14.1                   |
| 2  | Alunitized breed №2                 | 1340                    | 560                    | 16.2                | 11.6                   |
| 3  | Substandard alunite                  | 1290                    | 510                    | 17.9                | 10.8                   |
| 4  | Alunit ore                           | 1360                    | 410                    | 19.4                | 8.3                    |
| 5  | Expanded clay (control sample)      | 1290                    | 640                    | 27.4                | 4.6                    |

Heat resistance of materials based on swollen alunitized rocks is high, which is determined by the significant temperature of its formation. On the other hand, high temperature is a significant negative factor in the technological process, which leads to a decrease in technical and economic indicators of production and the deterioration of the competitiveness of the material. Therefore, the identification of ways to reduce the temperature of the thermal load is a priority way to improve the technology of obtaining materials of cellular structure on the basis of alunitized high-silica rocks.

As can be seen from the above indicators, the main factor that determines the formation of the cellular structure is an aluminosilicate melt capable of holding gaseous products of thermal destruction of alunite. Thus, the process of regulating the parameters of the technological process is possible by influencing the temperature of formation of aluminosilicate melt, its viscosity, physico-chemical properties, as well as the process of thermal destruction of alunite. The decrease in the temperature of thermal destruction of alunite can be associated with a decrease in the temperature of aluminosilicate melt as a result of chemical interaction of alunite with silica on the one hand and with a decrease in the decomposition temperature of its sulfate-containing components on the other hand. These processes are significantly influenced by impurities that are part of alunitized rocks and, primarily the influence of various forms of silica, as well as carbonate components. Influence of silica content. A significant influence on the course of physico-chemical reactions on the formation of the cellular structure of the material is the presence of silica in the raw material. Different forms of silica have different effects on the textural characteristics of the pore system and on the parameters of the technological process, its total duration and cost-effectiveness of the obtained building materials. In the presence of silica in amorphous or submicrocrystalline form, the process of thermal destruction of alunite in all allotropic formations is significantly accelerated in comparison with its crystalline modifications, such as quartz. The shape of the silica also affects the temperature of formation of aluminosilicate solution during thermal loading.

Accordingly, move to the zone of lower temperatures and all subsequent processes that determine the formation of the specified textural characteristics of the cellular structure of the material. A characteristic feature of such transformations is the intensification of the formation of closed-type pores. As the temperature increases, this process accelerates to maximum values at temperatures of 1280…1320 °C.
3.1 Influence of carbonate inclusions.

It is known that under the influence of oxides and salts of alkali and alkaline earth metals intensify the processes of sintering, crystallization, as well as the formation of a porous structure. According to a number of studies (5,6), the effect of lowering the temperature of the formation of the liquid phase is determined in the presence of carbonate impurities in the raw materials. According to research, the introduction of calcium oxides in the charge in the amount of 8...19% significantly reduces the temperature of formation of the liquid phase, as well as shifts towards low temperatures the formation of closed-type pores and promotes their uniform distribution throughout the material. Therefore, the addition of carbonate components to the source materials in obtaining a cellular structure is technologically feasible and cost-effective.

4. Conclusions

According to the obtained results of determination of physical and mechanical characteristics of cellular structure of building materials on the basis of alunitized high-silica rocks and their comparison with similar characteristics of other porous aggregates (expanded clay gravel) it is possible to draw conclusions about certain advantages of the first. This gives grounds for determining the scope of use of the obtained materials as light porous building materials in the construction of buildings and structures.

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