Efficient heat-insulating material based on technogenic anhydrite

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Abstract. Physical and mechanical properties of the heat-insulating composition based on high-strength anhydrite binder with expanded perlite sand as a lightweight aggregate have been studied. The study has evaluated the influence of two poring components, air-entraining additives and aluminum powder suspension, on the main characteristics of the composition: the compressive strength of the sample, its average density, thermal conductivity, and water absorption. The studies have shown that adding an air-entraining agent in an amount of 1.2% by the weight of dry fluoroanhydrite significantly influenced the decrease in the average density (up to 37%) of the material. The developed composition with a lightweight aggregate based on expanded perlite sand and an air-entraining additive can be used in construction as an efficient heat-insulating material, including for filling cavity walls during frame construction.

1. Introduction

The main task of modern building materials science is to increase the use of recycled materials in the production of building materials to improve the environmental situation in places of industrial dumping and to reduce the cost of the finished product. A cheap replacement of natural gypsum is waste from various industries, such as phosphogypsum [1-4], red gypsum [5, 6], gypsum formed during flue gas desulphurisation [7, 8], and fluoroanhydrite produced during the production of hydrofluoric acid. Despite the environmental friendliness of gypsum, its use in construction remains quite narrow. Most often it is used in the form of internal plasters, gypsum boards, and blocks for partitions. However, the potential use of gypsum is much wider. Gypsum blocks can also be used as external bearing elements with proper hydrophobization [9, 10]. Another promising method of application is the development of porous gypsum compositions, which can be obtained as a foamed or expanded gypsum solution, in which porous structure is formed by chemical additives [11, 12] or using lightweight aggregates [13, 14].

To achieve the set objective, while studying foamed gypsum mixtures [11], aluminium sulphate was used as a gas-forming additive. The average density was 694 kg/m³, and the compressive strength 0.63 MPa. The expanded gypsum with ammonium bicarbonate had a bulk density of 756 kg/m³ and a compressive strength of 0.35 MPa.

Study [12] provides information on the development of porous gypsum materials with an average density of 200 to 700 kg/m³. The composition with a density of 500 kg/m³ provided a thermal conductivity of 0.16 W/m·K and a compressive strength of 0.7 MPa.
Article [15] provides a solution for the production of lightweight gypsum composites based on a high-density matrix with expanded perlite as an ultralight aggregate. The binder was made on the basis of gypsum waste formed during flue gas desulphurisation. A liquid acid agent obtained from aluminum sulfate and dissolved in water citric acid was used as the acid gas-forming component [16]. 20% perlite being added to the mass of gypsum, the average density of the material decreased to 300 kg/m$^3$, the thermal conductivity coefficient to 0.08 W/mK, while the compressive strength decreased to 0.3 MPa. 5% perlite being added to the mass of gypsum, the average density of the material was 547 kg/m$^3$, the strength was 2 MPa and the thermal conductivity was 0.12 W/mK.

The objective of this study was to reduce the average density and thermal conductivity of the fluoroanhydrite composition with expanded perlite sand as a lightweight aggregate to the values that meet the requirements for thermal insulation materials. Earlier studies of fluoroanhydrite compositions with expanded perlite sand content from 45% to 85% by the volume of dry matter showed that it is impossible to reduce the average density without using additional components - when the content of perlite is 85%, the average density decreases only to 660 kg/m$^3$ while the compressive strength of the sample at the age of 7 days falls to 0.75 MPa. It has been experimentally proved that a further increase in the content of expanded perlite is impractical since the samples are destroyed during demolding. Therefore, in order to further reduce the density of the material, poring agents, aluminum powder and an air entraining agent, were added to the composition.

2. Materials and methods

The produced compositions were based of high-strength anhydrite binder prepared in accordance with work [17], 75% expanded perlite sand being added by the volume of dry matter as an ultra-light aggregate.

For producing a high-strength binder, powdered fluoroanhydrite was used, which is a waste product of hydrofluoric acid produced by “HaloPolymer”. To activate the processes of structure formation of fluoroanhydrite, 3% aqueous solution of sodium phosphate Na$_3$PO$_4$ was used.

The chemical composition of fluoroanhydrite [18] is given in Table 1.

| CaO  | SO$_3$ | CaF$_2$ | SiO$_2$ | Al$_2$O$_3$ | Fe$_3$O$_5$ |
|------|--------|---------|---------|-------------|-------------|
| 35.0-36.5 | not less than 45 | 2.2-5    | 2.6-3.4  | 0.5-0.7    | 0.2-0.95    |

The conducted dispersion analysis of ground fluoroanhydrite using a SALD-7500nano Shimadzu laser analyzer showed that the average particle diameter is 10.5 μm (Figure 1). It is necessary to note the presence of a nanodispersed component in the composition of fluoroanhydrite with the average particle size of 140 nm.
Figure 1. Dispersion analysis of ground fluoroanhydrite.

Expanded perlite sand (GOST 10832-2009) with a bulk density of 98.9 kg/m\(^3\) was used in the experiment. The chemical composition of expanded perlite sand is given in Table 2.

|    | SiO\(_2\) | Al\(_2\)O\(_3\) | K\(_2\)O | TiO\(_2\) | CaO + Mg\(_2\)O + Fe\(_2\)O\(_3\) |
|----|-----------|-----------------|--------|---------|-------------------------------|
| %  | 73        | 15              | 4.7    | 5.0     | 2.3                           |

Dispersion analysis (Figure 2) showed that the average particle size of the expanded perlite sand is 65 μm, up to 72% of the particles of the expanded sand have sizes up to 100 μm.

Figure 2. Dispersion analysis of expanded perlite.
Aluminum powder suspension and Poralan STA air-entraining additive produced by the Czech company Stachema were used as poring agents. In order to ensure uniformity of the mixture and uniform distribution of the additive in the composition, the aluminum powder suspension was prepared on the basis of surfactant in a ratio of 1 part of powder to 10 parts of surfactant.

Mass proportions of the main components:
- water 48%
- fluoroanhydrite 41%
- expanded perlite sand 11%

Poring components were added to the composition consisting of high-strength fluoroanhydrite binder and expanded perlite sand. In order to ensure better adhesion, expanded perlite sand was added to a previously prepared solution based on fluoroanhydrite mixed with a 3% aqueous solution of sodium phosphate Na₃PO₄. Such a sequence makes it possible to harden the composition due to the physicochemical interaction between the binder matrix and the surface of the expanded perlite particles, which is confirmed by analyzing the microstructure of the sample with a perlite content of 45% by the volume of dry matter performed on the MIRA3 TESCAN microscope at the AdMaS Technical University of Brno (Figure 3a). Figure 3b shows chemical interaction of the binder at the interphase boundary between perlite and the fluoroanhydrite matrix with the appearance of needle-like new formations [19].

Figure 3. a) Microstructure of the interface at 10000-fold magnification b) Physical and chemical interaction of the binder matrix with the surface of the expanded perlite at 40000-fold magnification.

The resulting mixture was put in molds of 40x40x160 mm and hardened in the air. In the process of hardening, the structure of the composition was formed due to the hydration of fluoroanhydrite with the formation of a binding matrix based on calcium sulfate dihydrate. Test samples of the compositions were carried out in accordance with the requirements of GOST 23789-2018.

3. Results and discussions
To study the physical and mechanical properties, the following samples were prepared:
1 - composition with 75% expanded perlite, without additives;
2 - composition with 75% expanded perlite with aluminum powder suspension in an amount of 0.1% by the weight of dry fluoroanhydrite;
3 - composition with 75% expanded perlite with an air entraining additive in the amount of 1.2% by the weight of dry fluoroanhydrite.

The results of physical and mechanical tests are given in Table 3.

| Composition | Flexural strength, MPa | Compressive strength, MPa | Density kg/m³ | Thermal conductivity W/mK. | Softening coefficient Cₛ | Water absorption % |
|-------------|------------------------|---------------------------|---------------|----------------------------|--------------------------|-------------------|
|             | 7 days | 28 days | 7 days | 28 days |                      |                          |                  |
| 1           | 0.553  | 1.417   | 1.325   | 2,732    | 873                     | 0.228                    | 0.42              | 36.4             |
| 2           | 0.534  | *       | 0.711   | *        | 587                     | 0.131                    | 0.44              | 82.2             |
| 3           | 0.597  | *       | 0.912   | *        | 546                     | 0.127                    | 0.50              | 96.5             |

*Indicators were not determined for technical reasons.

As seen from Table 3, adding a suspension of aluminum powder allowed to reduce the average density of the composition by 33%, the tensile strength of the sample practically being not changed, and the compressive strength of the sample decreased by 46%. Using air-entraining additives allowed to reduce the average density of the composition by 37%, and the compressive strength of the sample at the age of 7 days decreased by 31%, which is not critical for a heat-insulation material.

Analysis of the microstructure of the samples with an electronic USB microscope (Fig. 4) made it possible to establish the presence of large pores (up to 2 mm) in the composition without additives. Aluminum powder being added, large pores are not observed, and there is an increase in the number of small pores (0.2-0.5 mm), which leads to the material shrinkage during the hardening process. This causes microcracks and reduced strength. Air-entraining additive being used, the number of small pores also increased. In this case, the pores are distributed more evenly than with aluminum powder, microcracks are absent.

![Figure 4. Microstructure of samples at 50-fold magnification](image)

Thus, we can conclude that the most effective solution to the problem of reducing the average density of the fluoroanhydrite composition with expanded perlite sand was the use of Poralan STA air-entraining agent. Its use allows to obtain a heat-insulating composition with the following parameters: the average density is 546 kg/m³, the thermal conductivity coefficient is 0.127 W/mK, the compressive strength on the 7th day is 0.912 MPa.
Conclusion
The developed fluoroanhydrite composition with a lightweight aggregate based on expanded perlite sand and Poralan STA air-entraining additive can be used in construction as an effective heat-insulating material, including for filling cavity walls during frame construction. It fully meets the requirements for the values of physico-mechanical parameters imposed on heat-insulating materials and complies with the task of expanding the field of application of industrial wastes in building materials science.

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