Structural and Thermal Insulation Materials Based on High-Strength Anhydrite Binder

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Abstract. The properties of a structural and thermal insulation composition based on a high-strength anhydrite binder based on fluoroanhydrite and expanded perlite sand have been studied. Fluoroanhydrite is a waste product of hydrofluoric acid and it is an eco-friendly material. Due to the processing of man-made anhydrite, it is possible to reduce the harm caused to nature in places of raw materials dumps, as well as significantly reduce the cost of producing new construction materials. The use of anhydrite compounds in the manufacture of products is limited with low speed setting and hardening. To activate the structure formation of the anhydrite binder, 3% aqueous solution of sodium phosphate Na₃PO₄ was used. Expanded perlite sand was used as an ultralight aggregate. As a result of the experiments, it was possible to obtain a lightweight composition possessing high strength. Studies of the microstructure and X-ray microanalysis showed new formations appearing in the interfacial zone at the border of the anhydrite binder and expanded perlite, which is confirmed by the results of the infrared spectroscopy. Also there has been noted the consolidation of the anhydrite binder structure by nanodispersed structures formed in the intercrystallite pores of the anhydrite binder. The developed composition can serve as a cheap substitute for gypsum in the production of warm plaster, gypsum boards, architectural elements by molding, tongue-and-groove slabs, wall blocks, as well as wall thermal insulation during frame construction, including for filling hollow masonry.

1. Introduction
There are some studies on using expanded perlite for insulating materials [1, 2]. In the first case, the composition comprised expanded perlite sand, a composite binder consisting of Portland cement and liquid sodium glass, in which 15% aqueous solution of sodium phosphate Na₃PO₄ was added to prevent the mixture from instantaneous coagulating. In the process of the binder hardening, a composition was formed, the colloidal phase of which bound the expanded perlite into a large-porous conglomerate with the strength sufficient for the thermal insulation material. Due to the presence of Portland cement in the composition, the strength of the binder increased over time due to the hydration of Portland cement minerals. At the same time, water for cement hydration was actively drained from colloids formed during coagulation of liquid glass, and the resulting porous medium was filled with new formations (Figure 1). This led to an increase in contact strength between all components of the composition [1]. In this case, the chemical interaction between the perlite and the binding composition was not provided; it was only of a physical nature.
In [2], the results of studies are given on the reduction of thermal conductivity of lightweight cement concrete due to adding up to 70% of perlite sand to the composition, while the thermal conductivity decreased 6.3 times. At the same time, the strength of concrete did not exceed 2.9 MPa. The paper states that the strength was additionally provided by the chemical interaction between perlite and the cement matrix, but no data confirming this conclusion are given.

Figure 1. a) Microstructure of the cement-silicate composition with expanded perlite at a 2,500-fold magnification; b) Structural formation of calcium hydrosilicates on the surface of expanded perlite particles [1]

Paper [3] presents the study of change in thermal conductivity of heat-insulating plaster depending on the concentration of perlite in the following composition: 60-70% lime, 7.5% cement, 25-40% perlite. It states that the optimal concentration of perlite is 40%, the thermal conductivity of plaster being 0.059 W/mK and the strength characteristics not given.

In addition, in the three researches presented, binders based on expensive Portland cement were used, which reduced the effectiveness of using the compositions. The aspect of ensuring the necessary strength is also not entirely clear, the composition being complicated with liquid sodium glass in the first case and nanometakaolin and flax fiber in the second case. Also, in order to improve the physical and mechanical properties of the material being developed, it is necessary to create conditions under which the binding matrix can interact with the surface of perlite sand particles.

Considering the mentioned shortcomings, a composition based on expanded perlite and high-strength anhydrite binder is suggested. For making anhydrite binder, a man-made material obtained in the production of hydrofluoric acid is used. Due to the processing of man-made anhydrite, it is possible to reduce the harm caused to nature in places of raw materials dumps, as well as significantly reduce the cost of producing new construction materials [4,5]. Anhydrite solutions and concretes are characterized with a number of positive properties, including strength, short setting time, the ability to control room humidity due to the porous structure of the composite, and environmental friendliness [6].

Based on the chemical and mineralogical composition, the use of fluoroanhydrite binders is becoming the most cost-effective in mass production of materials based on anhydrite binders instead of natural or thermally treated anhydrite [7, 8].

The use of anhydrite compounds in the manufacture of products is limited with low speed setting and hardening without using chemical additives, which are hardening activators. Therefore, the possibility of obtaining a composition based on fluoroanhydrite, which is a waste of hydrofluoric acid production, requires solving the problem of accelerating the process of its structure formation [9, 10]. To improve the physical and technical properties of anhydrite materials, hardening activators are widely used [11, 12]. Their principle of action is to accelerate the dissolution of fluoroanhydrite after its mixing with water, which in its turn leads to a forced hydration and hardening of the binder [13, 14]. Among rarely used activators of fluoroanhydrite, sodium phosphate Na₃PO₄ is known.
2. Materials and methods

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, %: SiO$_2$ -71; Al$_2$O$_3$ -14; K$_2$O -3,7; TiO$_2$ -4,0; CaO + Mg$_2$O + Fe$_2$O -1,4.

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.

For producing a high-strength binder, powdered fluoroanhydrite was used, which is a waste product of hydrofluoric acid produced by “HaloPolymer”, corresponding to TS 5744-132-05807960-98 [15]. The chemical composition of fluoroanhydrite, in %, is CaO-35,0-36,5; SO$_3$ - not less than 45; CaF$_2$-2,2-5; SiO$_2$-2,6-3,4; Al$_2$O$_3$-0,5-0,7; Fe$_2$O$_3$-0,2-0,95 [16].

The conducted dispersion analysis of ground fluoroanhydrite showed that the average particle diameter is 10.5 μm (Figure 3). It is necessary to note the presence of a nanodispersed component in the composition of fluoroanhydrite with the average particle size of 140 nm.
X-ray phase analysis of fluoroanhydrite showed the prevalence of soluble calcium sulfate $\gamma$-CaSO$_4$ (Figure 4).

On the X-ray of fluoroanhydrite, there are reflections corresponding to soluble anhydrite - CaSO$_4$ ($d_\alpha = 3.50; 2.85; 2.33; 2.21; 1.87$ Å), weak reflections of calcium sulfate dihydrate CaSO$_4$·$2$H$_2$O ($d_\alpha = 7.55; 4.26; 2.85$Å), silicon oxide SiO$_2$ ($d_\alpha = 3.35$Å), calcite CaCO$_3$ ($d_\alpha = 3.03$Å).

To activate the processes of structure formation of fluoroanhydrite, 3% aqueous solution of sodium phosphate Na$_3$PO$_4$ was used. Physical and mechanical properties of the high-strength binder based on sodium phosphate-activated fluoroanhydrite: bending strength after 28 days - 10 MPa, compressive strength after 28 days - 40 MPa, softening coefficient - 0.71, water absorption - 5.62% [17].

To determine the mineralogical composition of the source materials, an X-ray diffractometer DRON-3 was used. The distribution of particle sizes in the used materials was determined using a SALD-7500nano Shimadzu laser analyzer. The microstructure of the obtained composition was studied on a MIRA3 TESCAN microscope at AdMaS research center of the Technical University of Brno. IR spectroscopic analysis was performed on an IRAffinity-1 Shimadzu FT-IR spectrometer. The thermal conductivity was determined using an ITP-MG4-100 device (SKB Stropyribor LLC, Chelyabinsk).

The composition, % mass: fluoroanhydrite - 63.69; expanded perlite - 4.46; 3% aqueous solution of sodium phosphate - 31.85.

The process of preparing the composition included three stages: preparation of 3% aqueous solution of sodium phosphate; preparation of a binder by means of mixing fluoride hydride with 3% aqueous solution of sodium phosphate; adding expanded perlite sand into the paste, mixing until homogeneous.

The resulting mixture was put in molds of 40x40x160 mm and hardened in 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.

3. Results and discussions
The results of physical and mechanical tests are given in Table 1.
Table 1. Physical and mechanical properties of anhydrite composition

| Flexural strength, MPA | Compressive strength, MPA | Softening coefficient, C_s | Water absorption, % | Density, g/cm^3 | Thermal conductivity, W/mK |
|-----------------------|---------------------------|---------------------------|---------------------|----------------|---------------------------|
| 7 days                | 28 days                   | 7 days                    | 28 days             |                |                           |
| 1.2                   | 2.92                      | 4.29                      | 9.83                | 0              | 13.9                      | 1.17                      | 0.382                    |

The study of the microstructure of the composition found that the perlite particles have a smooth continuous shell with closed porosity (Figure 5a). The anhydrite binder consisting of lamellar crystals of calcium sulfate dihydrate has a close bond with the particles of expanded perlite (Figure 5b).

![Figure 5. a) Microstructure of the sample at 100-fold magnification; b) Fragment of the microstructure in the region of the interfacial layer at 2,000-fold magnification](image)

Analysis of the microstructure at high magnification made it possible to establish the relationship between the binder matrix and the surface of the expanded perlite (Figure 6a) with the physicochemical interaction between the particles of perlite and hydrated fluoroanhydrite. Figure 6b shows the presence of chemical interaction at the interface of the perlite particle and the fluoroanhydrite binder with the formation of erosion in the wall of the perlite particle.

At the same time, nanodispersed new formations appearing on the surface of the crystals of calcium sulfate dihydrate (Figure 6a) ensure the formation of a dense structure of the anhydrite binder, characterized by a large area of contact between the hydrate crystals of calcium sulphate.

To identify the composition of the dispersed crystalline new formations of a needle-like structure in the interfacial zone between the expanded perlite and hydrated fluoroanhydrite, an X-ray microanalysis was conducted (Figure 7). It showed the presence of Ca, Si, S, O, and aluminium Al, which suggests the formation of hydrosulphoaluminites and calcium hydrosilicates, providing an additional increase in the strength of the composition due to the chemical interaction of its components.
Figure 6. a) Microstructure of the interface at 10,000-fold magnification b) Physical and chemical interaction of the binder matrix with the surface of the expanded perlite at 40,000-fold magnification

Figure 7. X-ray microanalysis of new formations on the surface of expanded perlite particles

IR spectral analysis of the fluoroanhydrite composition confirmed the chemical interaction of calcium sulfate dihydrate with the surface of perlite particles. Thus, the binder matrix based on fluoroanhydrite activated with 3% sodium phosphate solution (Figure 8) has absorption lines corresponding to calcium sulfate dihydrate ($\nu = 1151,5; 1107,14 \text{ cm}^{-1}$).

4. Conclusions

The fluoroanhydrite composition including man-made fluoroanhydrite and expanded perlite sand has enhanced physical and mechanical properties due to the formation of a dense structure provided by the appearance of nanodispersed formations on the surface of calcium sulfate dihydrate crystals. The mentioned new formations fill the intercrystalline cavities and compact the structures of the composition. Physical and chemical interactions between the binder matrix based on calcium sulfate dihydrate and the surface of expanded perlite sand particles provide an additional increase in the strength of the composition due to calcium hydrosilicates and hydroaluminosilicates formed in the interfacial zone, which is confirmed by X-ray microanalysis and IR spectral studies. The developed composition is an effective material based on the waste of the chemical industry and can be used in the manufacture of products traditionally based on expensive gypsum binders: warm plaster, gypsum plasterboards, architectural elements, tongue-and-groove slabs, wall blocks, as well as wall insulation during frame construction, including for filling hollow masonry.
A new absorption line appears on the IR spectrum of the fluoroanhydrite composition with expanded perlite sand (Figure 9) ($\nu = 1116.78$ cm$^{-1}$), corresponding to the group Si-O-Si, which suggests the formation of calcium hydrosilicates in the interfacial layer.
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