Ecologically pure gypsum composites modified by microfillers

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Abstract. The use of micro-fillers in order to reduce the weight of gypsum products and at the same time increase their operational properties is a problem that today requires an urgent solution. The study of the effect of modifying micro-fillers on the properties of gypsum stone allows increasing the competitiveness of many modern innovative products and improving their quality. The inclusion of a ceramic component in the gypsum binder foam raw material mixture affects the properties of the modified composite structure. The optimal values of the content of foam additives and water for mixing gypsum binder are determined. The structure, technical characteristics of composites, and their quality are primarily provided by the addition of ceramic foam. However, it allows adjusting the optimal water content of the raw mixes. Micro-fillers can, apparently, be considered as an effective additive for obtaining bulk products for internal work, as well as for gypsum casting.

1. Introduction
Modern construction technologies, both in the developed countries of the world and in Russia, are directed at the general use of gypsum binders. They provide comfortable and safe living. In addition, the technology for their production, operation and disposal fully meets the protection of the natural environment. However, gypsum materials offered by the market require improved performance.

At present, to obtain building composite binders and materials with improved properties, mineral additives and various micro- and nanofillers are widely used to reduce the weight of products, which greatly expands the scope of innovative gypsum products [1-7]. Research projects on the use of mineral filler are very interesting. Such fillers are used for microreinforcing the structure of building materials [1, 2, 3]. Moreover, the influence of filler additives is noted not only on the physical and mechanical [5, 6, 7], but also on the operational properties of the products [1, 3, 6].

More known methods for producing modified composites based on cement binder. So, to reduce the average density and improve the technical parameters of mineral compositions with wood fiber additives, silica dust and nanosized particles of shungite and silica were additionally introduced [8]. The wood-mineral composition with cement has an average density of 747 kg / m³, the compressive strength of the wood-mineral stone reaches 2.3 MPa, but high water absorption by mass is 86%. With the introduction of shungite into nanoscale particles, it was possible to reduce the average density to 707 kg / m³, and the water absorption by weight to a record value of 27%. Interestingly, the compressive strength also increased, but not significantly - up to 2.7 MPa.

With the introduction of the additive with nanosized particles of silica, it was possible to further reduce the average density to 670 kg / m³, and to increase the compressive strength to 3.5 MPa, however, the water absorption by weight increased to 65%.
With the introduction of additives with nanosized particles of silica and silica fume, it was possible to reduce the average density to 610 kg/m$^3$, the water absorption by mass was 62%, and the compressive strength increased to 6.2 MPa.

With the complex use of additives with nanosized mineral microparticles-activators, it was possible to obtain a wood-cement composition with an average density of 610 kg/m$^3$, water absorption by mass of 62%, and compressive strength of 6.2 MPa [8].

Known studies of cement compositions, which show that a very good pozzolanic reactivity without expansion when hardening a cement stone is manifested by dispersed glass powder obtained by grinding glass to a grain size of the order of 300 microns [9, 10]. In addition, to reduce the probability of disruption due to the reactivity of alkaline silica, Byars etc. [11] in his studies proposed the introduction of additional cementitious material. It can be fly ash, silica powder, etc.

The pozzolanic effect of fly ash on the properties of mineral composites with glass microparticles is described in other works [12]. Fly ash from the burning of oil palm waste (POFA) acts as a source of silica. Alumina components, in the presence of water, form silicate and aluminate hydrates upon interaction with Ca(OH)$_2$ [13]. In addition, limiting the grain size of ground glass and ash from the burning of oil palm wastes helped the reactivity to achieve higher strength. The reaction that occurs during the hydration process is as follows.

However, there are not so many studies in the field of modification of gypsum binders with micro-fillers as in the field of cement binders. Of interest are the works performed by Yu.G. Meshcheryakov, S.V. Fedorov, etc. [14].

Compositions of self-hardening gypsum composites with improved water resistance characteristics have been developed. The compositions include microdispersed microfillers - amorphous silica, quartz, as well as industrial by-products. But the investigated additives mainly increase the density of gypsum. Research in the field of lightweight gypsum materials with microdispersed additives [15], contributing to an increase in strength [16–19] and at the same time to a decrease in average density, is not enough.

In the work, the possibility of obtaining modified gypsum composite with improved physical and mechanical parameters, and primarily with reduced weight, was investigated. This will allow more efficient use of gypsum composites in order to solve the problem of energy conservation in the field of construction technology.

2. Methods
As initial components, gypsum binders of the Samara gypsum plant were used. Ceramic foam granules based on industrial waste produced in Russia were used as additives.

In order to study the physicomechanical characteristics of the gypsum composite, beam samples 40 × 40 × 160 (mm) in size were used, which, after hardening under normal conditions, were tested at the age of 3 days in accordance with the requirements of GOST 23789.

Variation of additives was determined by the research program.

To optimize the composition of gypsum composites and study the effect of foam ceramics on the strength of artificial gypsum, a two-factor experiment was used, where the water content of the mixture and the percentage of granules were taken as variable parameters. The limits of variation of the studied factors and parameter values are given in tables 1, 2, 3.

### Table 1. Limits of variation of factors (3 days hardening).

| Matrix | $X_1$ | $X_2$ | $X_3$ | $X_4$ |
|--------|-------|-------|-------|-------|
|        |       |       |       |       |
The choice of intervals of factors is given in table 3. It is due to the results of previous studies. In this study, the water content varied from 0.34 to 0.38 %. The content of reinforcing additives in the composition of the composite ranged from 0 to 10% by weight of a gypsum binder. The results of studies of the dependence of the strength and density of the modified gypsum material on the content of the additive are shown below in figures 1, 2.

3. Results and discussion

As a result of the experiment, an equation is obtained that describes the combined effect of the input parameters on the compressive strength of the obtained hardening systems:

\[
Y_1(R_c) = f(X_1, X_2) = 46.225 - 0.6262X_1 + 0.4158X_2 + 1.4363X_1^2 - 2.395X_2^2 - 3.17X_1X_2, MPa
\]

where \(Y_1\) – the compressive strength for gypsum systems on the 3rd day of hardening.

### Table 2. Limits of variation of factors (3 days hardening).

| Matrix | \(X_1\) | \(X_2\) | \(R_c, MPa\) |
|--------|--------|--------|-------------|
| 1      | –      | –      | 42.96       |
| 2      | +      | –      | 46.1        |
| 3      | –      | +      | 46.71       |
| 4      | +      | +      | 40.27       |
| 5      | –      | 0      | 48.17       |
| 6      | +      | 0      | 47.72       |
| 7      | 0      | –      | 41.05       |
| 8      | 0      | +      | 45.62       |
| 9      | 0      | 0      | 45.39       |

### Table 3. Limits of variation of factors (3 days hardening).

| Matrix | \(X_1\) | \(X_2\) | \(\rho_b, kg / m^3\) |
|--------|--------|--------|----------------------|

3
Based on the calculations, the dependences of the strength of gypsum stone on the percentage of foam granules and the water content of the raw mix are shown in figure 1.

\[
Y_2(X_1, X_2) = 1570.527 - 17.18X_1 - 33.81X_2 + 10.78X_1^2 - 30.375X_2^2 + 25.482X_1X_2, \text{kg/m}^3
\]

where \(Y_2\) – the average density of gypsum systems on the 3rd day of hardening.

Based on the calculations, the dependences of the average density of gypsum stone on the percentage of foam granules and the water content of the raw mix are shown in figure 2.

The microstructure of foam ceramic granules and of the modified gypsum stone is shown in figure 3.
Figure 2. The effect of reinforcing additives on the density of gypsum samples at the age of 3 days.

The strength of samples tested at the age of 3 days with a water content of 0.34-0.35 increases. Then the pattern of the addiction changes. With a water content of 0.37-0.38, the tensile strength decreases with increasing percentage of water, as shown in figure 1. The maximum strength in the studied interval corresponds to 0% of the granules and the water content of 0.37, the minimum - 0.38 when the content of granules in amount of 10%.

A slightly different pattern of the dependence of density on the content of foam granules. It is shown that at a water content of 0.34, the density is little dependent on the content of the granules. However, with an increase in water content to 0.38, the average density begins to decrease. The minimum density of the modified gypsum stone is 1525.41 kg / m³.
Figure 3. The microstructure of foam ceramic granules and of the modified gypsum stone with the addition of foam ceramic granules.

An analysis of the obtained research results shows that microdispersed modification leads to a decrease in the density and strength of the material with an increase in water content to 0.38.

The decrease in the strength of gypsum stone is explained by a decrease in the number of contacts in the initial system, and, consequently, the number of fusion bridges in the resulting structure, which is consistent with the data [4].

With the introduction of additives in an amount of 10%, the compressive strength of the gypsum composite decreases from 48 to 41 MPa. The different pattern of the strength dependences is apparently due to excess surfactants in the composition of the raw mix.

The lowest density value of the modified gypsum stone is achieved when the content of the additive is 10% by weight of the gypsum binder and amounts to 1525.41 kg / m$^3$ in accordance with Figure 2, the ultimate strength of the stone is reduced by 14%. The dependence of the average density on the amount of modifying additive is similar in pattern to the compressive strength for an aqueous content of 0.38.

Foam granules have a well-developed internal porous structure. The structure of the modified stone obtained by hydration of a gypsum binder with the addition of ceramic foam is characterized by well-formed gypsum crystals located in different planes. These structural features of the granules and compacted modified gypsum stone are reflected in the material properties. First of all, on the strength and density of the composite.
4. Conclusions
Thus, the studies confirm the positive effect of the additive on the density of gypsum material. Modification of gypsum stone with a mineral additive will reduce the density and increase the durability of thin-walled gypsum products. Therefore, this can increase the demand for the material by ensuring their high quality.

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