Gypsum composites with glass granules

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Abstract. The article explored the possibility of reducing the average density of self-reinforced gypsum composites. Gypsum matrix and glass hollow granules leads to the appearance of a synergistic effect. It manifests itself in the formation of a compacted gypsum reinforced matrix, which is filled with microspheres. This provides a modified gypsum stone with high technical indicators. The volume of use of glass hollow granules is increasing every year, including in the construction industry. This material, unique in its properties, provides very high compressive strength, low water absorption, low heat conductivity, high chemical resistance, and radio transparency for its composite materials. The method of obtaining this light filler is a combination of complex physicochemical and hydrodynamic processes that occur during the formation of hollow balls from microparticles of glass melt. Creating effective composites based on glass micro granules as a component in the molding of gypsum products opens up new possibilities for designers and technologists. This will significantly expand their scope.

1. Introduction

In the building materials market, a need arose for decorative materials that are used for volumetric space decoration, the so-called 3D products - panels, tiles, stone, etc., which are made on the basis of polymers with the addition of crushed pressed plant materials: bamboo, cane, cellulose, much less often - on the basis of gypsum binder and mineral or organic fillers (sawdust, shavings, other plant and industrial waste, including agriculture, 1 soft industry, etc.). Gypsum materials and products based on them are environmentally friendly, have good heat and sound insulation, as well as a number of other unique properties [1-5]. For example, due to the peculiarities of the structure, they work as a natural air conditioner, regulating indoor air humidity. However, for the production of composite gypsum products, special binders and (or) additives [6-9] are required, which significantly increases the cost of production and complicates the technology for their production [10-13].

Modification of the composite with inexpensive sulfate or sulfoaluminate additives (modifiers) promotes the formation of calcium hydrosulfoaluminates reinforcing the gypsum matrix. In a disperse system based on hemihydrate of calcium sulfate, at the level of the mineral matrix, by controlling the crystallization of the substance during hardening, it is possible to form needle crystals of calcium hydrosulfoaluminates, which will strengthen the structure of gypsum [9]. Thus, the use of a complex additive based on aluminum sulfate makes it possible to increase the strength of gypsum materials by more than 80% [9, 10]. But it is interesting not only to increase the strength of the material [12, 13], but
also to reduce its density, and hence its weight, in order to meet the modern needs of the construction business.

It is known that reinforcing a gypsum matrix with crystals of a dispersed modifier of nanometer size can not only strengthen the structure of the stone, and, consequently, increase the physical-mechanical properties of the gypsum matrix and materials based on it, but also give them enhanced performance due to the transition of calcium sulfate dihydrate into less soluble compounds [14].

Moreover, when choosing the type of additive, it is necessary to take into account that the introduced additive should have a similar structure and chemical composition to the reinforced matrix, as noted by many authors [16]. The reinforcing substance must have a large number of surface-active centers. At these centers, dissociative adsorption of water molecules will occur, which should lead to an increase in the number of free charge carriers. As a result, there will be an acceleration of the formation of the structure of the gypsum conglomerate and an increase in its strength [15].

In order to increase the operational characteristics of gypsum stone used to obtain 3D products, and their quality, the possibility of introducing microfillers into self-reinforced compositions based on calcium sulfate hemihydrate to reduce the weight of decorative materials was studied in the work.

Hollow glass microspheres are white color dry powder consisting of tiny bubbles with a diameter of 20–160 μm and the wall thickness less than 1–2 μm. The glass composition and almost regular shape of microspheres provide a very high compressive strength, low water absorption, low heat conductivity, high chemical resistance and radio-transparency. Good adhesion of the HGM towards binders makes it possible to create composites on their basis with a unique complex of properties. All the above factors defined a wide variety of application for the HGM.

Technology for the HGM manufacture is a combination of complex hydrodynamic, physical and chemical processes taking place in the course of forming of hollow bubbles from micro-particles of glass melt by blowing. For realization of these processes, the scientists of NPO Stekloplastic have developed special fine-dispersion multi-component glass powders capable to form micro-particles of predetermined volume in melted state.

Strength of the microspheres is estimated by the value of hydrostatic pressure at which not more than 10 % HGM fail. It is natural that microspheres with a greater weight, and thus with thicker walls, are stronger. Composites based on HGM have opened new possibilities for designers and industrial engineers.

The main objective of the study was to study the dependence of the technical characteristics of the obtained self-reinforced composites on the percentage of filler. The formation of the hardened structure of gypsum composites is due to the use of complex mineral additives [15, 16]. The introduction of a binder mineral complex can contribute to the formation of non-shrinking or expanding compositions. After crystallization, they can have high strength, medium density, and water resistance [17–20].

2. Methods

The following raw materials were used for preparing gypsum stone: gypsum binder grades G 5 B II, according to GOST (Russian State Standard) 125-2018, lightweight filler, aluminum sulfate and air lime. Quicklime ground lime of the Uglovskiy lime plant according to GOST 9179 corresponds to grade 1 and is classified as slowly extinguishing. The content of hydrated water in quicklime does not exceed 2 %. Glass micro filler in the form of hollow granules - spheres with sizes ranging from 0.1 μm to 50 μm was obtained under the conditions of NPO Glass Plastic, Tver Region.

The characteristics of gypsum are presented in table 1. Qualitative indicators of lime are shown in table 2. The main indicators of micro-filler MS - VP - A9 (TU 6-48-91-92 with changes 1-7) are given in table 2, Fig. 1.

The composition of the complex additives was assumed constant according to the results of previous studies [16].

Investigations of the physical and mechanical properties of self-reinforced gypsum stone with the addition of micro-filler were carried out on standard beam samples with dimensions 40.0 x 40.0 x 160.0 mm and cylinder samples with a diameter of 20 mm and (or) 50 mm at the age of 7 days after hardening.
in normal conditions. The tests were carried out according to the requirements of the norm - GOST 23789 – 2018 Gypsum binders. Test methods.

Table 1. The characteristics of plaster B16 B3 according to GOST 125.

| Parameter                                                                 | Value  |
|---------------------------------------------------------------------------|--------|
| The degree of grinding according to the residue on a sieve with a mesh size of 0.2 mm, %, not more than | I      |
| The tensile strength of beam samples at the age of 2 hours, (MPa), with compression not less than | 5.0    |
| The tensile strength of beam samples at the age of 2 hours, (MPa), with a bend of at least | 6.0    |
| Setting time, beginning not earlier, min                                   | 4.5    |
| Setting time, end no later than, min                                       | 20.0   |
| Volume expansion, %, no more than                                          | 0.15   |
| Impurities insoluble in hydrochloric acid, %, no more than                 | 1.0    |
| The content of metal impurities in 1 kg of gypsum, mg, no more than        | 8.0    |

Table 2. The characteristics of lime.

| Indicators          | Requirements GOST 9179 | Averages |
|---------------------|------------------------|----------|
| Active CaO+MgO, %   | No less 80             | 85.54    |
| CO₂, %              | No more 5              | 4.3      |
| Overburn, %         | No more 2              | 0.98     |
| Sieve residue:      | Up to 15               |          |
| 0.2 mm              |                         | 0.16     |
| sieve 0.08 mm       |                         | 3.24     |
| Hydration moisture, %| No more 2              | 1.26     |
| GOST extinguishing time, min   | No more 8             | 4'08"    |

Table 3. The Hollow glass microspheres MS – VP - A9. The properties.

| The properties                      | Units | Value |
|-------------------------------------|-------|-------|
| Compressive strength (10% fracture rate) | MPa   | 25    |
| True Density of Microspheres       | kg/m³ | 370   |
| Volume fill factor                 | %     | 65    |
| Humidity, mass fraction            | %     | 0.11  |
| Buoyancy, volume fraction          | %     | 100   |

Figure 1. Electron micrograph microspheres.
The experiments to determine the compressive strength (fig. 2) and average density were carried out in the laboratories of the Department of Production of Building Products and Structures of Tver State Technical University.

3. Results and Discussion
The results of studies of the strength and density of a self-reinforced composite on the content in its composition of a glass micro filler (glass spheres) are presented in fig. 3, 4.

The strength of the self-reinforced composite decreases in the range of changes in the content of the additive from 0 to 30 % by an average of 5 MPa at different values of the water-solid ratio W/S (fig. 3).

The average density of the gypsum composite with an increase in the amount of filler also decreases monotonically in the entire studied range from 0 to 30 % (fig. 4). The decrease in density in the studied range of changes in the percentage of filler is an average of 384 kg/m³.

![Figure 2. Compression tests of self-reinforced gypsum samples.](image)

![Figure 3. The effect of glass filler on the strength of self-reinforced composites.](image)
A comparative analysis of the structural quality coefficients of gypsum composites showed that the maximum value of the coefficient (fig. 5) corresponds to the composition without filler (0 %) and the smallest water-solid ratio in the studied range (W/S = 0.6). With the introduction of glass spheres, the highest indicator of the structural quality coefficient corresponds to the maximum content of glass micro-filler with a minimum water-solid ratio (W/S = 0.6).

The strength characteristics of the gypsum composite when using a glass granules are similar in comparison with aluminosilicate [3]. In the case of using glass material, the strength value for a composition with a filler content of 30 % is 11 MPa. For a ceramic foam filler, the value is 10.89 MPa. However, the density of the material is 20 % less.

**Figure 4.** The effect of glass filler on the density of self-reinforced composites.

**Figure 5.** Comparative analysis of the coefficient of structural quality of a self-reinforced composite using filler.

On fig. 6 shows the microstructure of the resulting composite. An analysis of the microstructure of the self-reinforced gypsum composite shows that a compacted structure of gypsum stone is formed, which is mainly represented by tabular dihydrate crystals in combination with ettringite whiskers. The combination of fiber-reinforced ettringite gypsum matrix and glass hollow granules leads to the
appearance of a synergistic effect. It manifests itself in the formation, along with a compacted gypsum reinforced matrix, of a composite with a micro-additive uniformly distributed throughout the volume, filling the voids between the formed crystals. Studies of the hardening composite found that in the presence of a micro dispersed filler, the process of hydration of gypsum is activated. In addition, there is a change in the habit of gypsum crystals. This is consistent with the data of E.V. Tkach [7] and other authors.

4. Conclusions
Thus, the use of glass micro-filler in self-reinforced composites makes it possible to obtain gypsum material with higher physical, mechanical, construction and technical characteristics. Their use allows you to save costs and resources at all stages of the life cycle of construction production by providing less weight lightweight elements. They are also more convenient during transportation, installation and during any reconstruction.

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