Increase in efficiency of formation structure process of the modified gypsum by carbonation

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Abstract. The attention of leading scientists in the field of materials science is paid to the influence of moisture on the properties of disperse systems. It is noted that when the dispersed system is found for a long time in conditions of high humidity, moisture, after the formation of adsorption layers of maximum thickness, gradually accumulates in the gaps between the grains and is retained there by surface tension forces. It is established that the shrinkage of concrete products with a decrease in humidity at the time of its structure formation occurs due to an increase in the capillary contraction forces with a decrease in the thickness of the water interlayers.

The introduction of the carbonate component into the composition of raw mixtures of composite products leads to changes in the character of the process of structure formation in gypsum systems, which requires the optimization of curing conditions. However, the issues of the effect of environmental humidity on the hydration of composite astringents based on semi-aquatic gypsum and carbonate additives, as well as on the formation and hardening of composites based on them, remain insufficiently studied.

The paper presents the results of studying the dependence of the processes of structure formation in gypsum and composite gypsum-lime binders. The effect of curing modes and forced carbonization on the strength of composites obtained on the basis of a gypsum binder and a modifying additive is shown.

The research used high-strength gypsum GVVS-16 of the Samara gypsum plant for samples obtained by injection molding technology. As an additive, the lime was used for the Uglovsky limestone plant in the Novgorod region. Samples were kept for 7, 14 and 28 days in air-dry and wet conditions. In addition, the samples were exposed to carbon dioxide for 6 days at a temperature of (20 \pm 2) ° C. A comparative analysis of the obtained materials on the strength and density was carried out according to the results of testing the samples by standard methods. Based on the results of the studies, the influence of the material composition of the modified astringent, the regimes of hardening and saturation with carbon dioxide on the process of structure formation and the physical and mechanical characteristics of gypsum materials was established.

Thus, when modern modifying complexes are introduced into the gypsum binder, it is necessary to establish the optimum moisture regime. It should promote hardening of the
material and reducing deformations in the structure of the hardening stone. The results of the studies show the combined effects of the addition of calcium hydroxide, forced carbonization, and optimal conditions for hardening. Optimal conditions of hardening contribute to the formation of a more dense structure of gypsum stone. Consequently, the physical and mechanical properties of the modified composite structure increase, the durability of the materials being designed.

1. Introduction
The researchers consider various ways to improve the quality of gypsum products and expand the scope of their use. The use of modern modifying complexes is reflected in the processes of hydration and hardening of composite and modified gypsum materials. Regulation of the patterns of structure formation can allow to reduce energy intensity and to increase the properties and durability of gypsum products.

The effect of moisture on the properties of disperse systems is shown in the works of Pokrovsky, E. Freycinet, V.V. Mikhailov, V.V. Belov, E.I. Shmitko et al.

Thus, in [1, 2], the effect of moisture on the structure formation of mineral binders and their properties on strength, density, connectivity, as well as on the molding properties of raw mixtures on their basis was considered. It is noted that when the dispersed system is found for a long time in conditions of high moisture, humidity, after the formation of adsorption layers of maximum thickness [3], it gradually accumulates in the gaps between the grains and is retained there by surface tension forces. Regularities in the formation of the structure of dispersed-granular systems, depending on the regimes of hardening and, first of all, moisture regimes at different stages of structure formation are shown in [4, 5, 6, 7]. It was established in [4, 5] that the shrinkage of concrete products with a decrease in humidity at the time of its structure formation was due to the fact that when the liquid evaporates, the thickness of the water interlayers decreases, resulting in considerable capillary contraction forces, which leads to a decrease in the volume of the concrete stone in whole. The influence of humidity and the presence of carbon dioxide in the protective layer of concrete on the strength and durability of port facilities was considered in the survey of structures of berthing facilities [7].

Adding to the composition of raw mixtures of non-combustible composite products of the carbonate component, as the examples of studies [8, 9, 10, 11] indicate, lead to changes in the character of the process of structure formation in gypsum systems [10], and, consequently, requires the optimization of hardening regimes. Also, problems of carbonization hardening of calcareous binders are described [12]. However, the issues of the effect of environmental humidity on the hydration of composite astringents based on semi-aquatic gypsum and carbonate additives, as well as on the formation and hardening of composites based on them, remain insufficiently studied.

2. Materials and methods
The research used the high-strength gypsum GVVS-16 (tabl. 1) of the Samara gypsum plant for samples obtained by injection molding technology. As an additive, the lime (tabl. 2) was used for the Uglovsky limestone plant in the Novgorod region. Samples were kept for 7, 14 and 28 days in air-dry and wet conditions. In addition, the samples were exposed to carbon dioxide for 6 days at a temperature of (20 ± 2) °C. A comparative analysis of the obtained materials on the strength and density was carried out according to the results of testing the samples by standard methods.

| Properties | Requirements |
|------------|--------------|
| The degree of milling, the remainder on a sieve with the dimensions of the cells in the light 0.2 мм, %, | no more |
| Average values | 1 |

**Table 1. Properties of the Samara high-strength gypsum.**
The ultimate strength of the specimen-beads at the age of 2 hours, MPa
ultimate compressive strength flexural strength
not less than not less than 16 6

Setting time, min:
Start end
not earlier not later 4.5 20

Content of metal impurities in 1 kg of binder
no more 10

Table 2. Properties of the Uglovka lime.

| Properties                    | Requirements GOST 9179 | Average values |
|-------------------------------|------------------------|----------------|
| Active CaO+MgO, %             | not less than 80       | 85.72          |
| CO₂, %                       | no more 5              | 3.7            |
| non-extinguished grains, %    | no more 11             | 9.70           |
| Time of blanking for the GOST,min | no more 8             | 4              |

3. Research results
In this work the research of conditions of curing on properties of composite materials has been conducted. Compositions on the basis of the hemihydrate of calcium sulfate and the modifying additives have been used.

The structure of compositions for extra-strong gypsum has been determined by manifestation of efficiency in earlier executed researches.

As these additives show the properties in the system of gypsum in various conditions of curing it has been investigated.

The results of studies of composite materials based on hemihydrate of calcium sulfate and a calcareous additive using different conditions of hardening are shown in Fig. 1, 2.

The comparative analysis of density for samples on the basis of gypsum, on the basis of gypsum with lime additive, on the basis of gypsum with additive of lime and carbonation has been carried out.

The parameters of average density (Fig. 1) were obtained with hardening in wet conditions. The parameters of the strength (Fig. 2) were obtained with hardening in wet conditions.

The moisture regime maintained in the production of the gypsum composites is a factor that has a significant effect on the physical and mechanical characteristics and structure of the resulting composite. If, in the case of control samples, dry curing conditions are the most favorable conditions (Fig.3), in the case of lime-additive formulations and the use of forced carbonization, higher strength values are characteristic for samples hardened in wet conditions (Fig. 2).
Figure 1. Effect of hardening conditions and composition on the average density of compositions based on semi-aqueous gypsum.

Figure 2. Effect of hardening conditions on the strength of compositions based on semi-aqueous gypsum.

Lime additive promotes change of conditions of curing. It is explained by properties of the alkaline environment. In the alkaline environment the polarity of molecules changes and process of crystallization goes more actively (Fig.4).

Carbonation in damp conditions is most effective. The gypsum modified stone has higher rates of strength and density.
The microstructure of the gypsum modified stone in comparison with pure gypsum has more dense structure. Formation of crystals of calcium hydroxide and a calcium carbonate changes an inward extension of gypsum system.

4. Conclusions
The composition of raw mixtures, as studies have shown, reflects the nature of the structure formation and determines the optimal regimes for hardening gypsum compositions of hydration hardening. Forced carbonization and humidity of the environment increases the strength and density of the gypsum modified structure, pores the pores, improves the quality of construction products.

Thus, when modern modifying complexes are introduced into the gypsum binder, it is necessary to establish the optimum moisture regime. It should promote hardening of the material and reducing deformations in the structure of the hardening stone. The results of the studies show the combined effects of the addition of calcium hydroxide, forced carbonization, and optimal conditions for hardening.

Optimal conditions of hardening contribute to the formation of a more dense structure of gypsum stone. Consequently, the physical and mechanical properties of the modified composite structure increase, the durability of the materials being designed.

Figure 3. Microphotography of the structure of gypsum stone.

Figure 4. Microphotography of the structure of gypsum composite.
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