Modified gypsum-cement-pozzolanic composites reinforced with polypropylene fibers

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Abstract. The paper shows the effectiveness of the use of a polyfunctional complex modifier for a gypsum-cement-pozzolanic binder (GCPB), which allows reducing the water requirement of the mixture by 35%, increasing the flexural strength of gypsum-cement-pozzolanic composites (GPPC) by 28%, and 25% for compression. The results of experimental studies of the effect of polypropylene fibers on the basic physicomechanical properties of a central processing center are presented. The performed studies have shown high efficiency of polypropylene fibers of the type VSM-II-6 for dispersed reinforcement of the central industrial park. The maximum increases in the values of the flexural strength (by 41.2%) and compression (by 20%) are achieved with their volume content in the amount of 1%. It should be noted that the introduction of the studied fibers with a length of more than 6 mm did not lead to the expected result, which is due to the formation of a heterogeneous structure of the GPPC

Introduction

Products based on gypsum-cement-pozzolanic composites are widely used in construction as a universal building material (dry construction mixtures, gypsum plasterboards, facing tiles for interior and exterior). Along with a lot of positive technical properties, materials and products based on gypsum-cement-pozzolanic binders have considerable brittleness, which is especially true when using thin-walled sheet products, as well as high water absorption, which limits their use in humid environments. To eliminate these drawbacks, various mineral and chemical additives, as well as reinforcing materials, are introduced into the GCPB composition.

The physicomechanical properties of the GPPC depend on the composition of the binder, its activity, water binding relationship, hardening conditions, etc. The main technological factor designed to ensure the possibility of combining the gypsum binder with Portland cement in a single binder composition is the introduction of active mineral additives (tripoli, flask, etc.).

The most typical active mineral additives (AMD) - tripoly, kaolin, blast furnace slag, aluminosilicate, selected in accordance with the procedure described in [1], reduce the concentration of calcium hydroxide in hydrating gypsum-cement mixture only after 4 days of hydration. This effect is caused by hydrolysis of the hydration products of clinker minerals, which are not capable of binding
their own calcium hydroxide. As a result, they cannot eliminate the negative interaction with the gypsum substance at the stage of a structured formation. In this regard, the expansion of the system occurs, caused by the formation of ettringite. Thus, the introduction of the gypsum-cement chemical composition leads to the implementation of experimental experimental studies [2,3].

Mineral supplements of the type metakaolin [4,5], ferrosilicon, thermally activated clay [4], microsilica [5], and white soot have a completely different quality. They are characterized by extremely high dispersion, chemical activity and reactivity. This is due to their relatively low required content in the composition of the gypsum-cement mixture [6].

It should be noted that the short setting times for GCPB greatly complicate the processes of forming articles based on it, including gypsum-fiber sheets (GFS). In this regard, it is necessary to consider the features of regulation of the setting time and hardening of the GCPB, analyze chemical modifiers (plasticizing and water-repellent additives) of the gypsum-cement matrix and GFS on its basis to improve their performance and durability.

In the production of materials and products based on GCPs, a wide range of modifying additives is used, such as additives for regulating the kinetics of initial structure formation and hardening, plasticizing additives (PA), water-repellent additives (WRA). At the same time, the nomenclature of modifying additives for cement binders is much wider than for gypsum binders and building materials based on them. It should be noted that the work of modifying additives largely depends on the composition of the binder, the quantity and quality of the compounds formed during the hydration of the binder [7], as well as the alkalinity of the medium.

In [8], the effectiveness of using citric acid to slow down the setting of recycled gypsum plaster (β-hemihydrate calcium) was shown. It was found that citric acid reduces the compressive strength of samples and their hardness. In [9], the effectiveness of the use of superplasticizers based on sulfonated melamine formaldehyde resins for the modification of calcium β-hemihydrate is shown. Introduction in the amount of 0.6% leads to an increase in the strength of the samples by 69%, acceleration of hydration processes, leads to the formation of a denser structure, which increases their water resistance. In [10], it was shown that the use of complex additives containing carbon nanotubes and ultrafine additives leads to an increase in physicomechanical characteristics, a change in the qualitative composition of hydrate tumors, as well as a change in their morphology and size of crystalline hydrates. At the same time, the effectiveness of complex additives should be ensured by the synergistic effect of the interaction of the components of the additive.

In previous studies [11,12], we developed a multifunctional complex modifier, including the Best-GFS regulator for setting and hardening, GP Odolit-K, and DG Ethyl silicate-40, for gypsum-cement-pozzolan mixtures. The effect of the synergistic interaction of the components of the developed complex modifier can significantly improve the water resistance of products based on HRC, their limits of bending and compression strength. In addition, the use of this modifier leads to a lengthening of the dates of the beginning and end of the mixture setting, which will simplify the technological processes of manufacturing and installation of products based on GCPB [13]. In this regard, this multifunctional complex modifier was adopted by us to modify the FIR in these studies.

As is known, dispersed reinforcement of binders based on various compositions allows to increase many of the most important physical and mechanical characteristics: compressive and flexural strength, fracture toughness, crack resistance, etc. [14-16]. The matrix in the reinforced compositions gives the product the necessary shape, creates a monolithic material. Combining numerous fibers in a single whole, the matrix allows the composition to perceive various kinds of external loads (tension, compression, bending, shear, etc.). At the same time, the matrix itself participates in the creation of the bearing capacity of the composition, ensuring the transfer of forces to the fibers [17]. For the calculation of composite materials, in particular concrete, diagram methods [18] are used, which allow a more complete assessment of the stress-strain state of the calculated cross sections taking into account the physical nonlinearity of materials [19].

The use of basalt and glass fibers for the reinforcement of gypsum-cement-pozzolan compositions is limited due to the available data on their low resistance to chemical corrosion in the
medium of the gypsum-cement-pozzolanic stone [20,21]. It should be noted that the solution to this problem is possible by modifying the surface of these fibers [22].

In [23], the effect of polyvinyl acetate and polypropylene fibers on the properties of gypsum composites was studied. It was shown that polyvinyl acetate fibers can significantly accelerate the process of hydration of the binder, increase the flexural strength and impact strength of gypsum composites (compared to polypropylene fibers). It should be noted that the length of the fibers studied in the work was 6-12 mm with their volume fraction in the composition of the gypsum composite up to 1.2%. In this regard, it is of interest to study the effect of fibers of greater length and content on the material properties.

Technical characteristics of various types of fibers, which are used for dispersed reinforcement of products, are given in [16]. Polypropylene fibers according to this classification can be attributed to low-modular, synthetic, since the relative elongation at break is 10-25%, tensile strength 400-770 MPa, average fiber diameter 20-22 μm, length 6, 12, 18, 24, 32 mm and more. Such characteristics of polypropylene fiber provide high impact strength and flexural strength of a composite material.

High technical indicators, chemical resistance and low weight of polypropylene fibers cause a considerable interest in their research as a dispersion-reinforcing material for the GPPC. Of particular interest is the study of the influence of the length and volume content of fibers on the basic physical and mechanical properties of modified gypsum-pozzolanic systems, which can be used in the manufacture of a wide range of building products.

The purpose of the research is to study the effect of polypropylene fibers of various lengths and content in the composition of the gypsum-cement-pozzolanic mixture on the physicomechanical properties of modified GPCC.

Materials and Methods

To carry out experimental studies, the following materials were adopted:

- a) knitting:
  - construction gypsum G6BII produced by LLC Arakchinsky gypsum, produced according to GOST 125-79;
  - Portland cement Belgorod cement plant PTs500 D0, produced according to GOST 10178-85;
- b) modifying additives:
  - AMD - metakaolin produced according to TU 5729-098-12515988-2013, with hydraulic activity of at least 1000 mg / g.
  - SE "Odolit-K", produced by LLC "Service-Group" according to TU 5745-01-96326574-08;
- regulator of setting and hardening terms “Best-TB” produced by LLC “Innovative Technologies”;
- Homogeneous mixture of oligoethoxysiloxanes "Ethyl silicate-40" produced by JSC Khimprom, Novocheboksarsk according to TU 2435-427-05763441-2004.
- c) fibers:
  - polypropylene fibers of the mark VSM-II, 6, 12, 18, 24 and 32 mm long, produced according to TU5458-001-82255741-2008. Specifications are shown in Table 1.

| Name                              | Indicators                        |
|-----------------------------------|-----------------------------------|
| Material                          | High Modulus Thermoplastic Modified Polymer |
| The average fiber diameter, microns | 20-22                             |
| Fiber length, mm                  | 6, 12, 18, 24, 32                 |
| Tensile strength, MPa             | 550                               |
| Elongation                        | 20%                               |
| Modulus of elasticity, MPa        | No less 10000                      |
The number of single fibers, ppm / kg | 300-600
Fiber surface area, m² / kg | 150
Melting point, °C | 160

d) drinking tap water that meets the requirements of GOST 23732.

Preparation and testing of samples GPPC. At the first stage, to obtain GCPB, its components were mixed in a dry form with a gypsum: cement: AMD ratio of 76: 20: 4. At the second stage, the rheological properties of GCPB with and without a complex modifier were investigated. The content of polyfunctional complex modifier was 1.5% by weight of the binder. At the third stage, in order to evenly distribute polypropylene fibers in the gypsum-cement-pozzolan matrix, they were fused in the calculated amount of mixing water in the presence of a modifying additive. At the next stage, the components of the gypsum-cement fiber mixture were mixed for one minute, followed by molding the samples.

Tests of samples after their hardening for 28 days in an air-humid environment were carried out on standard beam specimens with dimensions of 4x4x16cm, from a molding mixture of normal thickness according to the method described in GOST 23789-79.

Optical studies of samples of the gypsum-cement-pozzolanic stone were carried out using a Philips XL-30 scanning electron microscope. Optical studies were conducted to study the morphology of hydrated tumors, the surface structure of the studied gypsum-cement compositions and changes in them.

Results and Discussion

The introduction of a polyfunctional complex modifier into the GCPB structure made it possible to reduce its water demand by 35% and to increase the setting time by 19 minutes. At the same time, the flexural strength increases by 28%, and by 25% during compression. The microstructure of the initial and modified gypsum-pozzolanic matrix was studied using scanning electron microscopy with the analysis of the elemental composition of the studied compositions at the indicated characteristic points. Electronic images of the samples are presented in Fig. 1-4.
Analysis of the elemental composition of the initial matrix at the indicated points (Fig. 1, 2) allows us to conclude that there are needle-like inclusions of ettringite \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O})\). Electron microscopic images with the elemental composition of the modified GPCP (Fig. 3, 4) indicate the presence in it of the needle forms of calcium monosulfate \((3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 12\text{H}_2\text{O})\), as well as chains of low-base hydrosilicates \((3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O})\), what caused the formation of a more homogeneous crystalline structure and a decrease in the porosity of the modified samples as compared with the initial composition and an increase in their physicomechanical characteristics.

The effect of the volume content of polypropylene fibers of different lengths on the flexural and compressive strength limits of the centrally applied control centers is shown in Fig. 5 and 6.

The following regression equations have been obtained, which characterize the effect of the studied fibers on the flexural strength of the GPPC, the reliability of which is 0.81-0.98:

- \(R_{\text{flex}}(1) = -33.872x^2 + 74.291x + 97.831\);
- \(R_{\text{flex}}(2) = -17.646x^2 + 38.044x + 100.96\);
- \(R_{\text{flex}}(3) = -15.027x + 27.894x + 101.85\);
- \(R_{\text{flex}}(4) = -9.072x + 12.811x + 103.23\);
- \(R_{\text{flex}}(5) = -25.091x + 18.673x + 101.06\).
The effect of the volume content of polypropylene fibers on the relative compressive strength of the GPPC with a length of: 1 - 6 mm; 2 - 12 mm; 3 - 18 mm; 4 - 24 mm; 5 - 32 mm

The following regression equations were obtained, which characterize the effect of the studied fibers on the flexural strength of the GPPC, the reliability of which is 0.82 - 0.99:

\[ R_{\text{comp}}(1) = -18.045x^2 + 38.117x + 100.78; \]
\[ R_{\text{comp}}(2) = -10.174x^2 + 20.833x + 101.68; \]
\[ R_{\text{comp}}(3) = -6.5806x^2 + 12.523x + 101.5; \]
\[ R_{\text{comp}}(4) = -2.5211x^2 + 1.4998x + 101.75; \]
\[ R_{\text{comp}}(5) = -18.909x^2 + 12.327x + 100.44; \]

As can be seen (Fig. 5, 6), the introduction of polypropylene fibers into the composition of the gypsum-cement-pozzolan mixture, depending on the length and their volume content, has a different effect on the flexural strength of the GPPC. The most effective fiber showed a length of 6 mm. So, depending on their dosage in the composition of the mixture, the flexural strength increases by 10 - 41.2%, when compressed by 5 - 20%. Keeping the fibers with a length of 12 mm to a lesser extent increases the tensile strength of the GPPC when bending (6.7 - 20%) and compression (3 - 11%).

The introduction of fibers of 18, 24 and 32 mm in length with an increase in their content in the composition of the mixture leads to their uneven distribution, difficulty with mixing and the formation of an uneven structure of GPPC. This, in our opinion, causes a decrease in the strength of the samples with an increase in their content in the mixture. The increase of the flexural strength (up to 15%) and compression (up to 6%) is achieved with relatively low dosages of fibers (0.25 - 0.5%).

Conclusions
1. Analysis of literature data indicates the effectiveness of the use of complex chemical additives for the modification of gypsum-based binders, which, due to the effect of the multifunctional interaction of the components, have greater capabilities in regulating the processes of formation of the structure and properties of finished products. In this regard, a complex modifier was adopted for the modification of GCPB on the basis of “Best-TB” regulator of setting and hardening, “Odolit-K” hyperplasticizer and “Ethylsilicate-40” water-repellent additive.
2. Analysis of the elemental composition of the initial gypsum-cement matrix allows to conclude that there are inclusions of ettringite in it. (3CaO*Al₂O₃*3CaSO₄*32H₂O). Electron-microscopic images with the elemental composition of the modified gypsum-pozzolanic matrix indicate the presence of acicular forms of calcium monosulfate (3CaO*Al₂O₃*3CaSO₄*12H₂O), as well as chains of low-base hydrosilicates (3CaO·2SiO₂·3H₂O), what causes the formation of a more homogeneous crystalline structure and a decrease in the porosity of the modified samples as compared...
with the initial composition and an increase in their physicomechanical characteristics.

3. It has been established that one of the effective ways to solve problems aimed at improving the performance properties of products based on gypsum binder is their disperse reinforcement. Analysis of the experience of using various types of reinforcing fibers made it possible to identify polypropylene fibers, as one of the most effective for disperse reinforcement of products based on GPPC.

4. The completed studies have shown high efficiency of polypropylene fibers of the type VSM-II-6 for dispersed reinforcement of GPPC. Thus, the maximum increase in the values of the flexural strength (by 41.2%) and compression (by 20%) is achieved with their volume content in the mixture in an amount of 1%.

5. It should be noted that the introduction of the investigated fibers with a length of more than 6 mm did not lead to the expected result. In our opinion, this is due to the formation of an inhomogeneous structure of GPPC. In addition, the introduction of silicone modifier could reduce the adhesion strength of the fibers with the matrix. Therefore, the influence of the organosilicon modifier and the technology of introducing fibers into the gypsum-cement-pozzolanic mixture is of interest for further research.

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