Effect of soot pigment additive on properties of composite gypsum binder

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Abstract. The results of studies to increase strength and water resistance of gypsum materials due to the hydraulic complex, pozzolanic and ultradispersed additives are presented in the paper. The astringents compositions, consisting of gypsum, cement, microsilica, ultrafine carbon additive of universal pigment concentrate are developed. The average particle size of the carbon black is 150-180 nm. The addition of soot contributes to the hardening processes intensification of the gypsum cement-pozzolanic binder (GCPB) and leads to the formation of a more homogeneous and finely dispersed phase binders’ structure. The additive use allowed the authors to improve the mechanical properties of the gypsum cement-pozzolanic binder and to increase the water resistance by the composite compacting structure. The compositions of lightweight concrete and light plaster solutions were developed on the basis of gypsum binder compositions.

1. Introduction
The wide use of gypsum-based materials is limited by their insufficient water resistance, which is accompanied by creep increasing and significant decrease in strength.

To increase the water resistance of gypsum products, the following methods are used:

- decrease in the set gypsum solubility;
- change in the capillary-porous structure of gypsum stone in order to reduce water absorption and water permeability;
- surface hydrophobization, which prevents water saturation of gypsum products [1].

The first two methods increase the products water resistance throughout the volume, and their reliability does not depend on accidental damage to the surface.

In order to implement this task, various additives are used, but the most effective are those that simultaneously reduce the gypsum solubility and the permeability of gypsum stone [2].

It is known [3] that gypsum binders, depending on the value of the coefficient softening $C_S$, are divided into:

- non-waterproof - $C_S <0.45$;
- average water resistance - $0.45 < C_S <0.6$;
- increased water resistance - $0.6 < C_S <0.8$;
- water resistant - $C_S > 0.8$. 
2. Relevance of the Study

The development of effective gypsum materials is impossible without their modification. Properties of gypsum products (water resistance, strength, etc.) are determined by the binder state and structure. Various additives significantly influence the course of hydration and the formation of the mineral astringents structure: they change the size and shape of the crystals, the interphase surface state, the porosity, and so on.

In the 60's of the 20th century, the studies to obtain strong and waterproof gypsum binders with active mineral additives were conducted. They lead to the stabilization of the gypsum cement system, but at that time the effect of the additives was insufficient.

In this connection, the studies of the recent years have proposed to increase the strength properties and water resistance of gypsum binders in the process of modern complex hydraulic, pozzolanic additives and ultradisperse parts introducing [4,5].

Recently, the technologies for the directed regulation of the building materials structure and properties using carbon nanosystems have been intensively mastered. The additives of ultrafine particles have high surface energy and chemical activity, so they have the strongest influence on the formation of the mineral binders’ structure. The introduction of carbon nanotubes into the composition of gypsum binding dispersants leads to their indices’ strength increase and the formation of a strong, dense structure [6,7].

One of the factors hampering the use of carbon nanotubes in building materials is the high cost associated with unprofitable production, underdeveloped markets, and the complexity of their use in practice.

The purpose of this work was to improve water resistance, strength characteristics and structure of composite gypsum binder with carbon additive in the ultrafine particles form of industrial production. Improvement of the composites structure based on gypsum cement-pozzolanic binder (GCPB) was carried out due to the introduction of man-made waste ultra-low concentrations from the soot production.

3. Results of the research

Building gypsum of G4-G5 grade medium fineness of grinding and portland cement CEM I of 42.5B grade were used for the preparation of composite binder. The quantitative content of gypsum and portland cement varied between 55-75% and 5-35%, respectively.

A man-made product of metallurgical production was used as a pozzolanic additive, which is obtained during the smelting of ferrosilicon by microsilica MC-85 in an amount of 10-15%.

A carbonaceous additive of a coloring paste on a water basis, a pigment universal concentrate (soot) was used as ultradisperse particles. The dried pigment (Figure 1) is represented by dense aggregates of 5-15 microns aggregated particles, which is probably connected with the use of surface-active additives in the coloring paste.

Figure 1. Photomicrograph of soot pigment.
The analysis of the soot pigment dispersion with the use of a laser particle analyzer shows that the non-aggregated particles size varies from 130 to 250 nm, and the average size is 150-180 nm (Figure 2).

Figure 2. The distribution of pigment particles (soot) in size.

The soot pigment was introduced in 0.001 to 0.005% amount by dry weight based on the binder weight. This additive is not expensive and scarce, as the process of preparing a composite binder does not require special technologies, because the water-dispersed pigment is added to the mixing water and is easily distributed into the composition.

In addition to mineral additives, a plasticizing additive was used in 0.1% to 0.5% amount by the binder weight. Optimum consumption of plasticizer was - 0.3%.

To study the effect of the additive on the binder strength properties, 4x4x16 sm samples in size were made from a normal density test.

Preliminary study was made of the soot additive effect on the gypsum binder strength without additives. It was found that the introduction of soot in the gypsum composition does not affect its strength characteristics. Gypsum samples, modified with cement, microsilica and soot, were kept under normal conditions, followed by mechanical testing at the age of 28 days.

It was established that the introduction of a carbon ultradispersed black additive in 0.004% amount of the composite binder weight (gypsum cement + microsilica) made it possible to increase the strength by 58% and increase the coefficient softening ($C_s$) by 30% (Table 1), compared to the binder without additives, thus obtaining a water-resistant gypsum cement-pozzolanic binder.

Table 1. Compositions and physical - mechanical characteristics of composite astringents.

| No | Composition of binder (%) | Compressive strength 28 days, (MPa) | Coefficient softening $C_s = \frac{R_{sat}}{R_{dry}}$ |
|----|---------------------------|-------------------------------------|-----------------------------------------------|
| 1  | G* 100 PC - - - - 4,7 1,6 | 0,34 |
| 2  | 65 25 MS - - - - 10,4 6,7 | 0,65 |
| 3  | 65 25 10 0,3 0,004 16,4 13,9 | 0,85 |

Note: * G - gypsum, PC - Portland cement, MS - microsilica, PA - plasticizing additive.

X-ray phase analysis of solidified composite astringents was performed: a) gypsum-cement (gypsum + cement); b) gypsum cement-pozzolanic (gypsum + cement + microsilica); c) gypsum cement-pozzolanic with soot addition.

Diffractograms analysis shows that in a process of microsilica additives adding; microsilica and ultradisperse soot no new reflexes appear in comparison with the control composition, but the
intensities of neoplasms reflexes increase. It can be considered that the addition of microsilica increases amount and variety of calcium hydrosilicates in the composite binder.

It can be assumed that GCPB increase in water resistance is due to the binding of free calcium hydroxide with microsilica, and the carbon additive, being a crystallization center, contributes to the formation of a greater amount of low-basic calcium hydrosilicates, which prevent the ettringite formation.

The snapshots analysis of the gypsum cement-pozzolanic (a) and carbon black-modified astringent (b) photomicrographs, shown in Fig. 3, showed the compaction of the structure in the last sample due to the denser packing formation of the double-gypsum crystals and low-basic calcium hydrosilicates.

Figure 3. Microstructure of gypsum cement-pozzolanic binder: a) a control sample;b) with a carbon additive

4. Practical significance
It is established that carbon ultradisperse additive plays the role of crystallization centers, changing the direction and speed of physicochemical processes in the hardening gypsum cement-pozzolanic binder. As the complex modification result of the construction gypsum, a water-resistant (softening factor of more than 0.8), a gypsum cement-pozzolanic binder of the GCPB grade 150 was obtained.

Based on waterproof gypsum cement-pozzolanic binder with ultradisperse soot addition (composition No. 3 table 1), the compositions of light fine-grained concretes on porous aggregates were developed. Keramzit sand of 2.5 - 5 mm fractions and perlite sand of 0.315-2.5 mm fractions were used as aggregates. Contains of compositions and test results are given in Table 2.

Composition No. 1 based on keramzit sand meets the requirements for wall stones, slabs and partitions. Composition No. 2 (based on perlitic sand) can be used for warm plasters [8].

The obtained results allow us to classify concretes and mortars based on gypsum cement-pozzolanic binders modified with soot to an increased water resistance group (0.6 < C_s <0.8).

Table 2. Compositions and results of fine-grained gypsum-concretes tests.

| No | GCPB (kg/m³) | Aggregate (kg/m³) | Water (kg/m³) | Density (kg/m³) | R_comp 28 days (MPa) | Coefficient thermal conductivity, \( \lambda \), W/(m°C) |
|----|--------------|------------------|--------------|----------------|---------------------|------------------------------------------|
|    | Keramzit     | Perlite          | in dry condition | in water-saturated |                      |                                           |
| 1  | 600          | 475              | -            | 425            | 1160                | 7.8                                      | 0.74                                      | 0.31                                      |
| 2  | 600          | -                | 220          | 500            | 920                 | 2.7                                      | 1.9                                       | 0.70                                      | 0.27                                      |
The microstructure of the GCPB filled with perlite is shown in (Figure 4). Particles of perlite granules with point zones of the filler surface interaction with binding matrix crystals are clearly seen. Defects of perlite granules (cracks, chips) cause the relatively low strength of products. On the other hand, the achieved average density and thermal conductivity in the process of a pearlite filler use meet the requirements for warm plaster materials.

![Microstructure of a composite filled with pearlite sand: a) general view; b) the contact zone of the GCPB – perlite.](image1)

**Figure 4.** Microstructure of a composite filled with pearlite sand: a) general view; b) the contact zone of the GCPB – perlite.

The photomicrographs of the GCPB solidified, filled with keramzit, show a close contact between the binder and the aggregate (Figure 5), which leads to the strength increasing in the lightweight concrete.

Thus, the introduction of a carbonic ultradisperse additive into the gypsum cement-pozzolanic binder composition allowed to improve its mechanical properties and to increase the water resistance by compacting of the composite structure [9].

![Microstructure of the composite filled with keramzit sand: a) general view; b) contact zone of GCPB – keramzit.](image2)

**Figure 5.** Microstructure of the composite filled with keramzit sand: a) general view; b) contact zone of GCPB – keramzit.
5. Conclusion

It is shown that the introduction of an ultradispersed carbon additive into the GCPB composition contributes to the intensification of curing processes and leads to the formation of a more homogeneous and finely dispersed phase structure of binders.

These results are achieved due to the formation of a denser pore materials structure based on a gypsum cement-pozzolanic binder modified with ultradispersed soot particles. The results of concretes physical and mechanical tests on the basis of the developed binder, keramzit and perlite sand allow us to conclude that the obtained parameters level corresponds to the requirements for wall products and warm plaster compositions.

References

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