Anhydrite and gypsum compositions modified with ultrafine man-made admixtures

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Abstract

The influence of technogenic ultrafine additives on structure and properties of binders based on calcium sulfate has been studied. The study of physical and mechanical properties of gypsum compositions modified with metallurgical dust has showed an increase in ultimate compressive strength up to 30%, ultimate bending strength – 15%, the value of water resistance of the binder did not change. 1% of metallurgical dust being added to natural anhydrite, there is a significant increase of the strength of the composition by 40%, and the water resistance of the material decreases slightly. The conducted X-ray analysis does not show the presence of any new products of hydration and intensification of hydration of calcium sulfate dehydrate. At the same time, the conducted studies of the structure of the compositions confirm significant changes in the morphology of new formations. Thus, adding ultrafine additives to natural anhydrite and gypsum leads to the formation of a dense matrix of the increased strength.

Keywords: natural unhydrite; gypsum; metallurgical dust; X-ray analysis; microstructure

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1. Introduction

Nowadays in our country and around the world more and more attention is given to the greening of production and maximum efficiency of resource usage, which is achieved by means of recycling and use of industrial wastes as binders and ultrafine admixtures. At the same time, the development of clinkerless binders like anhydrite and gypsum cement is relevant. In addition, natural anhydrite and gypsum are environmentally friendly, non-toxic materials that do not emit carbon dioxide in the process of their production.

However, the binders based on calcium sulfate have low water resistance, inadequate strength and creep under load, especially under the conditions of increased humidity [1], and, therefore, they are mainly used indoors, the main requirements being imposed on meeting the temperature and humidity conditions. The expanding of the scope of their application requires the improvement of the physical and mechanical characteristics of anhydrite- and gypsum based products.

There are various ways to increase the strength and water resistance properties of gypsum binders by means of additives which are modern industrial wastes. The researchers [2-4] have proven the efficiency of modification of binders based on calcium sulfate by various types of technogenic raw materials like wastes of wet magnetic separation of ferruginous quartzites (wastes of WMS) and screenings of quartzite sandstone grinding, Portland cement being added. The developed compositions have the compressive strength of up to 30 MPa and the softening coefficient of up to 0.8. The technogenic additives interreacting with gypsum matrix and minerals of Portland cement clinker due to the presence of lots of structural defects accelerate the process of hydration and the appearance of new formations, which ultimately leads to a strong and dense matrix.

A number of researchers [5-7] offered some water-resistant gypsum compositions using the wastes of metallurgical industry, i.e. ground granulated blast-furnace slag, lime and active mineral additives. Also a complex hydraulic additive [8] containing ceramsite dust, ground blast furnace slag, lime and superplasticizer was offered; its adding provides the formation of a dense, strong and water-resistant structure of artificial stone.

The studies of the properties and structure of gypsum stone, freshly selected metallurgical flue dust being added [9-11], have shown the effectiveness of this modifier which leads to an increase of the technical characteristics of the binder. However, no studies have been conducted of the effect of this additive on the structure and properties of composite materials based on calcium sulfate during the prolonged storage of metallurgical dust.

One of the up-to-date ways of modification is the use of ultra- and nanodispersed additives which provide the adjustment of the morphology and the size of the crystalline hydrates of calcium sulfate dehydrate [12, 13]. The effectiveness of the influence on the structure of gypsum matrix is determined by the nature, size and shape of the particles of the additives [14].

Regulation of the hydration process of unfired anhydride binders for obtaining the specified properties is possible by means of adding various hardening activators and finely dispersed additives [15]. It has been found [16, 17] that the use of oxides and hydroxides of alkali metals leads to activating the process of structure formation of anhydrite matrices providing the materials with the improved technological, physical and mechanical properties.

Thus, the analysis of the above researches aimed at improving physical and technical parameters of composite materials based on sulfate binders leads to the conclusion that one of the promising areas in this field is mixed activation of anhydrite hardening along with modification of compositions with dispersed additives, as well as modification of gypsum matrices with technogenic finely dispersed systems.
2. Materials and methods of research

2.1. Materials

The binder used is natural anhydrite of Ergachevskoe deposit (Kungurskiy district, Perm region) and normally hardening gypsum of the average fineness degree of G-4 produced by Prikamskaya Gypsum Company (Perm) and meeting GOST 125-79. X-ray diffraction analysis of natural anhydrite (Fig. 1) showed that its composition has calcium sulfate dihydrate ($d_\alpha = 7.62; 4.29; 3.8; 3.07$ Å) as well as anhydrite mineral ($d_\alpha = 3.50; 2.86; 2.47; 2.33; 2.21; 2.19; 2.09; 1.87; 1.75$ Å, etc.). The optimum hardening activator for natural anhydrite has been selected.

[Image of XRD pattern of natural anhydrite]

Metallurgical (flue) dust formed in the production of steel is used as an ultrafine additive. However, the studies present the additive which was stored for more than a year under normal conditions. The dispersion analysis of technogenic additive shows that the particle size is in the broad range from 0.1 to 100 microns (Fig.2).

[Image of dispersion analysis of metallurgical dust and microstructure of ultrafine additive]

X-ray analysis of the chemical composition of metallurgical flue dust shows that the composition of the additive has the following metal oxides: iron oxide (III) ($\text{Fe}_2\text{O}_3$) – 54%, magnesium oxide ($\text{MgO}$) – 14%, calcium oxide ($\text{CaO}$) – 12%, silica ($\text{SiO}_2$) – 6%. The impurities (1-2%) are chromium (III), aluminum, manganese and zinc oxides.
2.2. Producing samples

For producing a modifying component metallurgical dust is mixed with tempering water and a hardening activator of natural anhydrite binder, then the binder is tempered with the resulting solution. The optimal quantity of water has been taken from the binder mass to obtain the gypsum dough with normal density. The components are mixed manually for 2-2.5 minutes.

For producing gypsum and anhydrite samples standard steel molds of $40 \times 40 \times 160$ mm are used. Gypsum samples are cured for 20-30 minutes, anhydrite ones – for 24 hours, further mechanical strength being tested. The samples have been stored at $T = 20 \degree C$ for 28 days under normal humidity.

2.3. Test methods

The strength tests of the samples have been carried out on hydraulic press PGM-100 with the allowed load 100 kN and loading speed 0.5 MPa/s in accordance with the standard requirements [18]. The average values calculated by the results of three successful measurements have been taken as the final test results.

The sample microstructure has been investigated with the help of microscopes Phenom G2 Pure and JSM 7500 F produced by JEOL with the accelerating voltage 4 kV and maximum magnification up to 20000 times. The X-ray phase analysis has been carried out on diffractometer DRON-2. Cobalt has been applied as an anti-cathode.

3. Results and discussions

3.1. Physical and mechanical tests

3.1.1. Anhydrite compositions

The current state and disadvantages of the research and development of composite materials based on anhydrite being analyzed, the conclusion is drawn on the possibility of modifying the binder with an ultrafine additive with a considerable content of iron oxide. The physical and mechanical properties of anhydrite compositions with ultrafine additives and various types of activators are studied (Fig. 3).

![Graphs showing strength of anhydrite binder with different activators.](image)

**Fig.3.** Dependence of strength of anhydrite binder on the content of metallurgical dust with different hardening activators.

The above curves show that the strength characteristics of the material with sulfate activation of anhydrite binders with sodium hydrosulfite reach their maximum values (the increase in the compressive strength of the samples by 70% at the age of 14 days in comparison with the control sample) in comparison with other types of activators. In further studies, it is advisable to use sodium hydrosulfite as a hardening activator for anhydrite
compositions.

The analysis of physical and mechanical tests of anhydrite samples with metallurgical dust stored for 2 years and sodium hydrosulfite (0.8%) cured for 14 days (Fig. 4) shows that under the optimum content of additive of 1% from the mass of the binder the mechanical properties increase by 40% compared with the control sample.

![Fig. 4. Dependence of anhydrite matrix durability with the introduction of metallurgical dust.](image)

The softening coefficient of the studied composition based on anhydrite decreases, the content of metallurgical dust being increased. In the control sample it is 0.3, in the modified one at the optimum content of ultrafine additive of 1% from the mass of the binder – 0.26.

Thus, the conducted studies have shown that the optimum strength values are achieved, 1% of metallurgical dust being added to anhydrite composition. Based on these studies [19], we can assume that the strength increase is due to the formation of iron sulfate (III), which is proved by the intense red-brown coloring of the material. This salt is a strong activator of calcium sulfate dihydrate formation. Improving the mechanical properties may follow 2 mechanisms: the increase of solubility of anhydrite binder or the admixture has a structuring effect on the material’s structure, contributing to the increase of the interfacial surface area and the formation of stronger contacts.

3.1.2. Gypsum compositions

Fig. 5 presents the results of the mechanical test of gypsum binder after 28 days, metallurgical dust being added in the amount of 0% to 3% from the mass of the binder. The ultrafine additive being used in the range from 0% to 1%, no significant changes occur in the strength characteristics. The increase in compressive strength – 30% and bending strength – 15% occurs when the additive content is 1.5% from the mass of the binder. When the content of the additive in the gypsum matrix is more than 2%, mechanical properties gradually decrease. Obviously, in this case, the modifier acts as an impurity, which causes the formation of the weakened gypsum matrix on the particle surface of the additive during the setting of the composition.

The water resistance properties like water absorption and softening coefficient were determined for the studied gypsum compositions. Water absorption of the material practically does not change and is 31.9% for the control sample, 31.4% for the modified one (1.5% of metallurgical dust). The softening coefficient of gypsum cement becomes slightly smaller, the content of metallurgical dust being increased; it is 0.4 for the control sample, and 0.37 for the modified one (1.5% of metallurgical dust).
3.2. Research of the content of the composition materials

To explain the results of the physical and mechanical studies physical and chemical tests have been conducted of the samples of the compositions based on calcium sulfate at the optimum content of technogenic additives.

3.2.1. X-ray phase analysis of anhydrite compositions

The analysis of reflections on X-ray spectra (Fig. 6) revealed that when we introduce the metallurgical dust into the anhydrite matrix, the intensity of reflections in the spectrum corresponding to calcium sulfate dihydrate decreases \((d_a = 7.60; 4.28; 3.06 \text{ Å})\), and the intensities of reflections corresponding to anhydrite increase \((d_a = 3.49 \text{ and } 1.75 \text{ Å})\). This indicates that when introducing the additive we have the worse conditions for anhydrite binder solubility and calcium sulfate dihydrate hydrating.

![Fig. 5. Strength of the gypsum composition, metallurgical dust aged 28 days being added.](image)

![Fig. 6. X-ray pattern of anhydrite matrix: (a) – control sample, (b) – sample with metallurgical dust added.](image)
3.2.2. X-ray phase analysis of gypsum compositions

![X-ray pattern of gypsum matrix: (a) – control sample, (b) – sample with metallurgical dust added.](image)

The main reflections on X-ray patterns correspond with the lines of calcium sulfate dehydrate ($d_\alpha = 7.67-7.69, 4.29-4.30, 3.81, 3.07; 2.88-2.89, 2.68-2.69$). The comparison of the X-ray patterns show a line of anhydrite on the spectrum with $d_\alpha = 3.50$, metallurgical dust being added, which can be due to the worsening conditions of solvability of the binder.

The results of X-ray analysis did not show any new hydration products. Thus, increasing the strength characteristics of gypsum and anhydrite compositions cannot be associated with the increase in the content of calcium sulfate dehydrate or the formation of new hydration products.

3.3. Microstructure of compositions based on calcium sulfate

It is known that the material durability is defined not only by a number of crystalline hydrates but also by the durability and number of contacts between them [20].

3.3.1. Anhydrite compositions

An incoherent and irregular structure consisting of crystals of different morphology and size is formed in the samples without additives (Fig. 8 a) which results in considerable porosity, decrease in interface contacts and degradation of physical and mechanical characteristics.

When the ultradispersed additive is introduced, a denser finecrystalline structure is formed (Fig. 8 b) which provides the increase in contact area between the crystalline new-formations resulting in the improved durability of anhydrite matrix. Thus the formation of finecrystalline structure of anhydrite matrix with optimal additive concentration of 1% provides the growth of mechanical indexes by 40%. 
3.3.2. Gypsum compositions

The microstructural analysis of the samples without additives demonstrates (Fig. 9 a) that prismatic and lamellar crystals up to 10 μm long and up to 1 μm in diameter randomly spread in the matrix volume prevail in the structure of gypsum samples. In this case, the structure with the elevated porosity that results in decreased mechanical durability of the samples is formed. When the metallurgical dust is introduced, the prismatic crystals of different sizes prevail in the sample structure, block structures are also present (Fig. 9 b). Probably, when the ultradisperse additive is introduced, apart from the crystalline structure the conditions for the arrangement of amorphous structures which are formed in interface layers and additionally bind the crystalhydrate formations.

4. Conclusion

Metallurgical dust being added in a matrix based on calcium sulfate, less favorable conditions for hydrating. At the same time, the strength characteristics increase up to 40% for anhydrite compositions and up to 30% – for gypsum ones. This effect occurs because the additive stimulates the structuring process of matrix based on calcium sulfate. The morphology and size of crystals change, which increases the mechanical properties due to the formation of a dense structure of gypsum matrix.

References


