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Water-resistant gypsum compositions with man-made modifiers

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Abstract

The work has studied the structure and properties of gypsum compositions modified with the manmade modifier based on metallurgical dust and multi-walled carbon nanotubes. The results show that changing the structure of solid gypsum leads to the increase in bending and compressive strength by 70,5% and 138% correspondingly, the water resistance increasing and the softening factor reaching 0,85. Modifying gypsum composition with complex additive leads to the formation of amorphous structures based on calcium hydrosilicates on the surface of primary gypsum crystallohydrates that bond gypsum crystals and reduce the access of water.

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Keywords: gypsum, metallurgical dust, multi-walled carbon nanotubes, water resistance, calcium hydrosilicates, X-ray analyze, microstructure.

1. Introduction

The physical and mechanical characteristics of solid gypsum depend on the crystal morphology of calcium sulfate dihydrate, and are also determined by the number and strength of their contacts [1], these properties of the structure are due to the raw material quality and the impurities [1,2]. In addition, the production technology of

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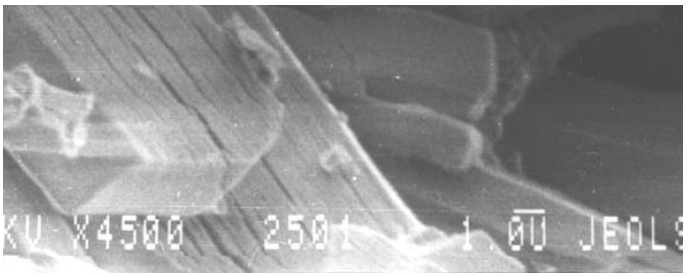
gypsum binder, its specific surface area, the size and shape of crystals, the presence of defects and the surface quality of raw materials also influence gypsum products [1]. Insufficient strength, low water-resistance and high



creep at load are predetermined by the crystal structure and the increased solubility of gypsum (Fig. 1).

Fig. 1. Distortions of the structure of calcium sulfate dihydrate crystals caused by its thermal damage (segregation associated with the removal of crystallohydrate water from gypsum).

Finely dispersed additives in the binder composition may affect the hydration process and regulate the morphology and size of new crystallohydrate formations [3,4], increasing the interfacial contact area in setting gypsum. The effectiveness of finely dispersed modifiers will depend on their chemical composition and dispersion degree.

According to the research by E.V. Korolyov [5,6] the modifiers that affect the structurization of mineral matrices can be divided into chemical additives, surfactants, complex additives with electrolytes, surfactants, nanoscale minerals, primary nanomaterials based on metal oxides, carbon nanosystems, sols of various compounds.

One of the main ways to improve the performance of calcium sulphate binders is using the additives that hydrate and form insoluble products increases its solubility and decreases the water resistance of solid gypsum as well as accelerate the hydration reaction [4,7].

Water resistance of gypsum composition is conventionally increased by the simultaneous adding of Portland cement or ground granulated blast furnace slag and the active mineral additives comprising amorphous silica [8, 9]. Improving the physical and mechanical characteristics of the binder is connected with the formation of slightly soluble fine-grained low-basic calcium hydrosilicates in the structure of solid gypsum that bind gypsum crystals protecting their surface from water influence and leading to the formation of a dense matrix that conglomerates the structure of solid gypsum.

Gypsum-cement-pozzolanic binders and concretes based on them have a new quality level of technical and technological properties, as well as better performance in comparison with the conventional gypsum materials [8-10]. However, the widespread use of these materials is hindered with a sophisticated production technology, the dependence of the properties on the mineralogical Portland cement composition and the activeness of additives.

Today, special attention is paid to the use of man-made materials in order to improve physical and technical properties of conventional binders. This contributes to solving the issues of saving energy and resources, and improving the ecological situation [8,11].

For example, the use of ultrafine aluminous mixture [12] (metallurgical wastes with mainly Al_2O_3) leads to the formation of amorphous structures on the surface of gypsum crystals coating the crystallohydrate surface and leading to an increase in the water resistance of gypsum matrix.

A number of researchers [13,14] suggested using a complex hydraulic additive comprising ceramsite dust (20-30%), ground blast furnace slag (up to 30%), lime and superplasticizer. This additive provides a dense, durable and water-resistant structure of artificial stone based on gypsum binder. At that, improving the physical and mechanical characteristics of the composite material at the optimum amount of additives leads to the formation of hydration matrix consisting of the products of interreaction of silica, aluminum and iron.

At the same time the authors [15] developed a water-resistant gypsum composition comprising lime, microsilica and aluminum sulfate as modifiers which, being added, lead to the formation of calcium hydrosilicates of various basicity coating the calcium sulfate dihydrate crystals and preventing their elutriation.

The gypsum composition modified with bog iron ore mainly comprising iron oxide has a higher softening coefficient of up to 0.55 and the compressive strength increased by 10% in comparison with the low-grade G-3 plaster [16]. Adding the modifier provides the directed control of the hydration process of calcium sulfate hemihydrate which causes interreaction of calcium sulfate dihydrate and the components of the additive. This is confirmed by IR-spectra of the composition and ultimately causes changes in the gypsum matrix structure.

Thus, producing water-resistant gypsum compositions requires the use of finely dispersed additives that foster the formation of slightly soluble compounds coating the calcium sulfate dihydrate crystals, linking them and forming a dense and solid matrix of the material. At that, the developed solutions are complex multicomponent systems comprising expensive modifiers (such as Portland cement, microsilica).

The authors of this paper have developed the ways to protect gypsum structure from the adverse environmental factors by means of carbon nanotubes in combination with metallurgical dust. Their adding leads to profound changes in the structure of solid gypsum [17].

The studies of the properties and the structure of solid gypsum, metallurgic flue dust being added [18,19] showed the effectiveness of this modifier which increases the binder properties.

The studies were conducted of the joint effect of metallurgic flue dust and multi-walled carbon nanotubes on the structure and properties of solid gypsum. The previous studies [20] determined the optimal concentration of a nano-dispersed additive as 0.005%. Modifying binding matrices with multilayer carbon nanotubes (MWCNTs) dispersion has improved the physical and mechanical properties of gypsum composites due to the structuring of new formations, the morphology of which primarily depends on the uniformity of carbon nanotubes distribution in the volume of setting binding matrix.

This paper continues the study of the effect of complex fine additives on the hydration and setting of gypsum binder in order to improve its performance properties. The study shows the results of the joint influence of steel flue dust and multi-walled carbon nanotubes on the structure and properties of solid gypsum.

2. Materials and Methods

2.1. Materials

The research used as a binder normally setting gypsum of the average fineness degree of G-4 grade produced by Prikamskaya Gypsum Company, LTD (Perm) and meeting GOST 125-79.

The ultrafine additive used was metallurgic flue dust from steel production in Izhstal, JSC, Izhevsk. Chemical composition of metallurgical dust: Fe_2O_3 – 54%, MgO – 14%, CaO – 12%, SiO_2 – 6%. The impurities (the total amount to 14%) are chromium compounds (III), aluminum, manganese and zinc compounds.

a) b)

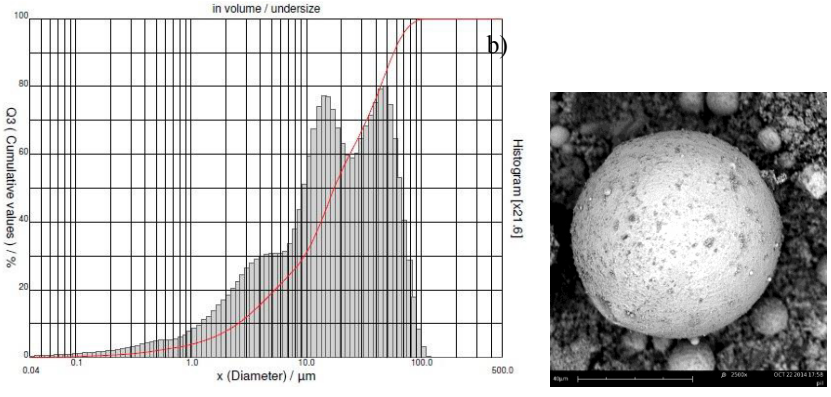


Fig. 2. Dispersion analysis of flue dust (a), microstructure of flue dust (b).

The given dispersion analysis (Fig. 2 a) shows that the average particle size of the additive was 20-30 microns, more than 50% of the additive particles of less than 18 microns. Particle shape is mainly spherical (Fig. 2 b).

The experiments used an aqueous dispersion of multilayer carbon nanotubes produced with high-speed mixers dispersed in the medium of carboxymethylcellulose. The analysis with a laser analyzer showed the presence of the particles of carbon nanostructures of the average particle size of 230 nm up to 20% of the total volume in the aqueous dispersion (except the particles in the micrometer range). The analysis of MWCNT dispersions revealed their stability within 7 days after preparation.

2.2. Methods

The ready dispersion of carbon nanotubes has been mixed with the required amount of water or with the required amounts of water and metallurgical dust and after that introduced into the gypsum binder. The optimal quantity of water has been taken from the binder mass to obtain the gypsum dough with normal density. The correlation of the components of forming mixtures is given in Table 1. The components have been mixed manually within 2-2.5 minutes.

Table 1. Sample compositions.

Sample compositions / Components	Reference sample	Sample with carbon nanotubes and metallurgical dust
Gypsum, %	100	99,395-99,895
Metallurgical dust, %	–	0,2-0,6 (by 0,2)
Carbon nanotubes, %	–	0,005
Water-gypsum ratio, %	60	60

Standard steel molds with sizes 40×40×160 mm have been used to obtain the gypsum samples. The gypsum samples were kept in a mold for 20-30 minutes followed by the mechanical strength tests. The samples were stored at the temperature of 20 ºC for 14 or 28 days at the normal humidity conditions.

The strength tests of the samples were conducted on a hydraulic press GMP-100 with the limit load of 100 kN and the loading speed of 0,5 MPa/sec according to the requirements of the standard. The final test results were the average values calculated from the results of three successful measurements.

Calorimetric tests were carried out to determine the influence of the additives on the heat release during the binder hydration. The compositions of binder and additives were studied with Macesta calorimeter having Thermochron thermal recorder.

The analysis of the chemical composition of metallurgical flue dust was performed by Axios mAX X-ray, an X-ray fluorescence spectrometer (PANalytical) by conducting wave length dispersion analysis.

The dispersion analysis of metallurgical dust and MWCNT was conducted by laser analyzer CILAS 1090.

The microstructure of the samples was analyzed by scanning electron microscopes JSM 7600F (JEOL) and ESEM XL-30 (FEI/Philips) using the electron beam accelerating voltage of 4 kV. The elemental analysis of new formations was performed by X-ray microanalyzer attached to the scanning electron microscope of ESEM XL-30. The electron beam accelerating voltage of 15...25 kV was used during microanalysis.

3. Results and Discussion

In our previous works [17,18] have been shown that the simultaneous adding of metallurgical dust and carbon nanotubes to the gypsum binder in optimal concentrations of 0.2% and 0.005%, respectively, leads to the increase values of compressive and bending strength of the 7-day samples by 70.5% and 138.3%, correspondingly (Fig. 3).

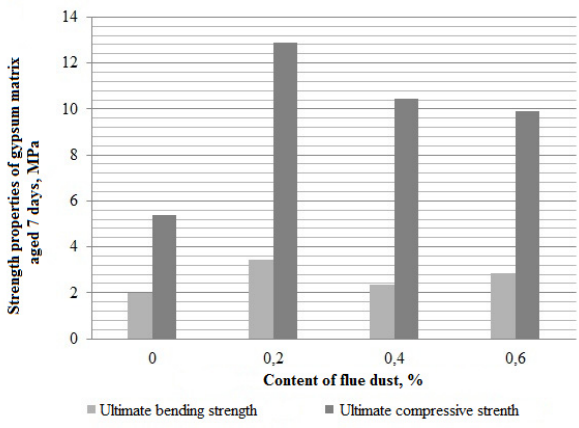


Fig. 3. Strength of gypsum matrix, flue dust and carbon nanotubes being added simultaneously.

A significant increase in the physical and mechanical characteristics is associated with the synergistic effect of the joint action of the modifiers: carbon nanotubes act as crystallization centers on the surface of which an ordered dense structure with the block crystals packing is formed. At the same time, the presence of hydrating components in flue dust helps to the formation of an amorphous phase on the surface of gypsum crystals (Fig. 4 b, d). The microstructure (Fig. 4 a, b) of the reference sample significantly differs from the modified matrix. The somewhat similar was done in works [13,21], the authors of which created the conditions for such amorphous coatings of gypsum crystallohydrates blocking the direct effect of water on the structure of gypsum binding matrices.

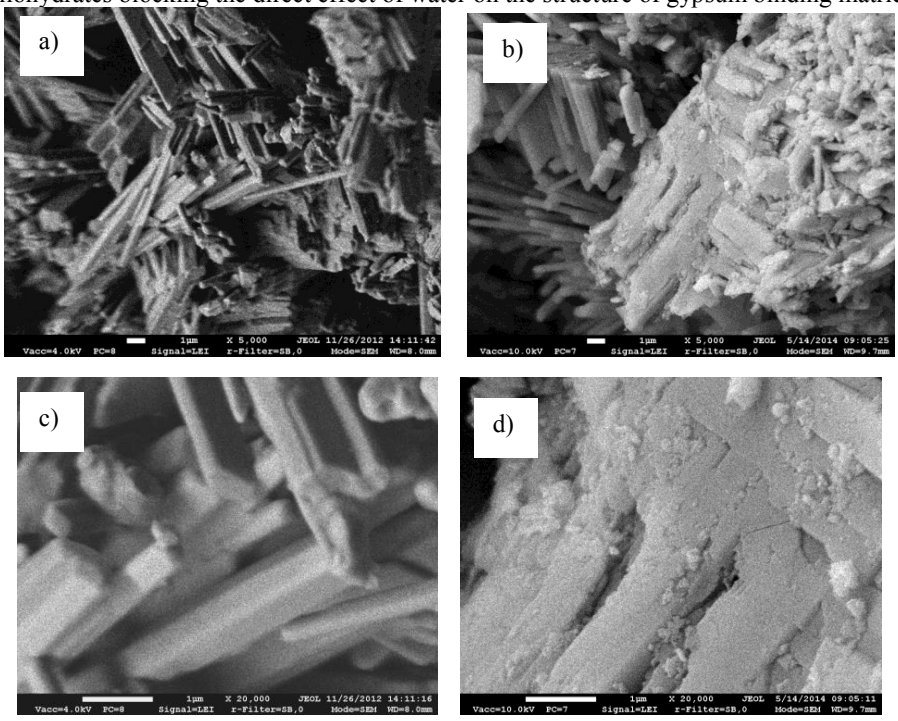


Fig. 4. The microstructure of gypsum matrix [16]: the reference sample magnified ×5000 (a) and × 20000 (c); the composition having modifiers added together, magnified ×5000 (b) and × 20000 (d).

It is assumed that the growth of calcium sulfate dihydrate crystals is limited by forming an amorphous phase around them, which leads to the increased interfacial surface area, lower porosity, more durable contacts and improved physical and mechanical parameters. The amorphous component on the surface of gypsum crystals is likely to reduce the "wedging" effect of the water layers reducing the water resistance of gypsum materials.

To determine the effect of modifiers on the hydration processes of gypsum compositions the colorimetric tests have been conducted. These tests have determined the dependence of mortar temperature on setting time, the values being measured every 2 minutes (Fig. 5).

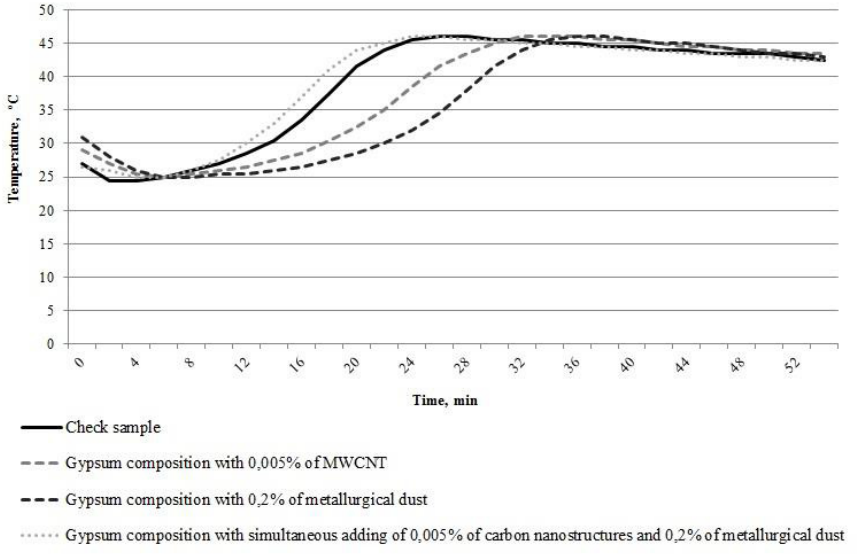


Fig. 5. Dependence of the plaster hydration speed on the modifying additive type.

The hydration process of gypsum is related to the dissolving of hemihydrate calcium sulfate followed with the crystallization of calcium sulfate dihydrate and is accompanied by considerable heat release. Gypsum binder being mixed with water, the temperature rises due to the hydration, and further small decrease of temperature is caused by the dissolving of calcium sulfate. The process of setting and formation of gypsum crystallohydrates from the oversaturated solution is an exothermic process accompanied by a slow rise of temperature. The released heat compensates the temperature drop associated with the dissolution of new portions of hemihydrate calcium sulfate. The above steps are clearly visible on the diagram of the control structure (Fig. 5) that reflects the temperature changes of the solution depending on the hydration time of hemihydrate gypsum.

The modifiers of multi-walled carbon nanotubes (MWCNT) and metallurgical dust being added separately, the hydration process slows down and the temperature effect shifts in the formation process of crystalline structure of the gypsum composition. An aqueous dispersion of multi-walled carbon nanostructures being added in the composition, this effect can be due to the presence of carboxymethyl cellulose, a surfactant in the additive composition which is adsorbed on the binder surface and retards the formation of crystallohydrates. Using metallurgical dust increases the pH value of the medium due to the presence of metal compounds that retard the hydration of plaster [2]. At the same time, MWCNTs and metallurgical dust being added simultaneously, the hydration processes accelerate due to their synergistic effect. Perhaps, the acceleration of the gypsum composition hydration is the result of blocking the surface of active metal oxides with carboxymethyl cellulose from MWCNT dispersion. Due to this process, carbon nanotubes intensify the hydration process increasing its speed.

The conducted tests of the modified composite materials determined the water absorption to range from 29.2 to 27.1%, which is slightly higher than the one of the reference sample (25.9%). The softening coefficient of the gypsum matrix increases significantly from 0.4 of the reference sample to 0.85 of the modified composition.

The enhanced water-resistant properties of the gypsum with metallurgical dust are associated with new formations based on iron hydroxides formed in the hydration process.

X-ray microanalysis of the surface of new formations was conducted at the gypsum compositions with the optimum content of modifiers (Fig. 6, 7).

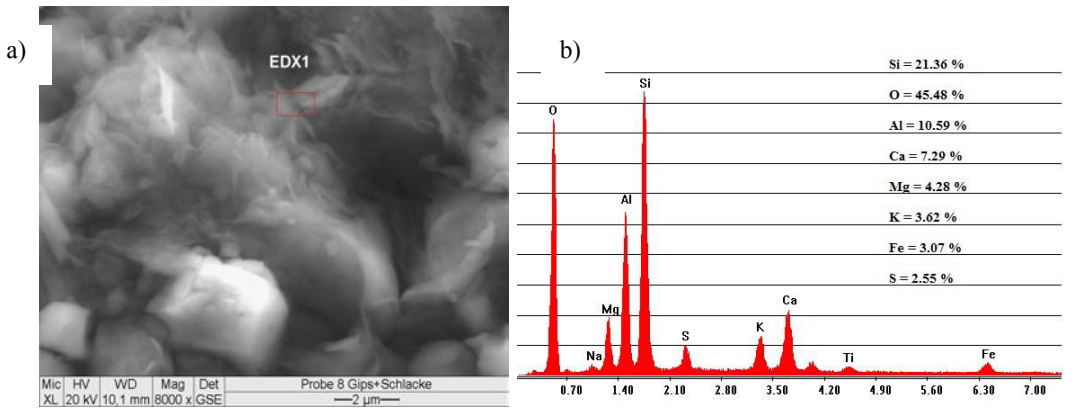


Fig. 6. The microstructure of modified gypsum matrix (a), the results of X-ray microanalysis of the modified matrix (b).

The analysis of the amorphous phase on the surface of calcium sulphate dihydrate crystallohydrates showed the content of silicon, oxygen, aluminum, magnesium and calcium compounds that occur in slightly soluble low-basic calcium and aluminum hydrosilicates on the surface calcium sulphate dihydrate crystals.

In the gypsum matrix structure there is a layer of new hydrate formations on the surface of the spherical particles of metallurgical dust (Fig. 7a). These formations do not appear on the surface of fresh dust (Fig. 2b), which leads to the conclusion that the additives are actively involved in the process of hydration. According to the conducted X-ray microanalysis (Fig. 7b), their composition may comprise calcium hydrosilicates, hydroferrites and hydroaluminates.

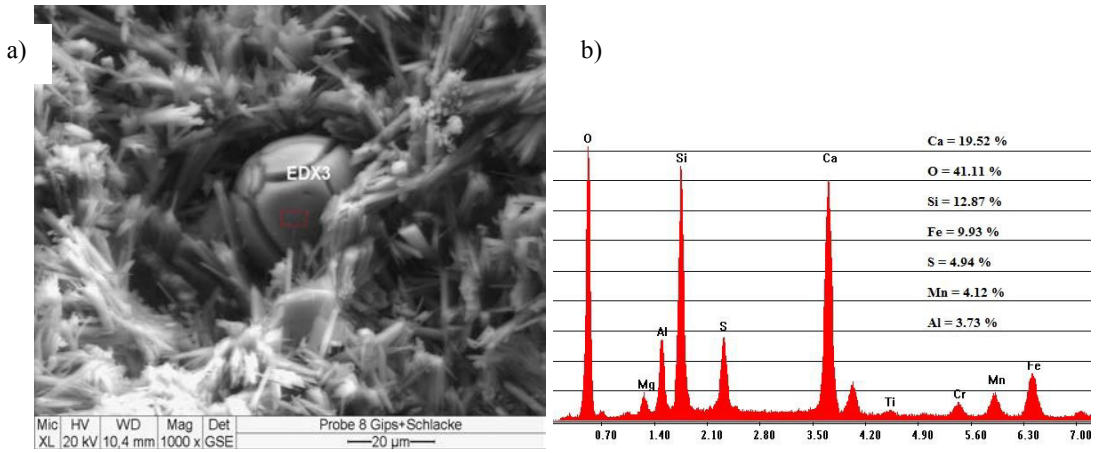


Fig. 7. The microstructure of the modified gypsum matrix (a), the results of X-ray microanalysis of the additive surface (b).

Thus, the conducted X-ray microanalysis confirmed the formation of compounds in the structure of the material that bind calcium sulphate crystallohydrates while increasing the interfacial surface area, which ultimately enhances the physical and mechanical properties of the gypsum composition.

4. Conclusion

The simultaneous adding of ultra- and nano-dispersed additives to gypsum compositions will improve the bending and compressive strength characteristics by 70.5% and 138%, respectively, increase the water resistance of the material due to the synergistic effect of the modifiers. The integrated use of metallurgical dust and carbon nanosystems leads to profound transformation of the matrix structure: carbon nanotubes being gypsum crystallization centers, influence the formation rate of seed crystals, at that, the hydration products of metallurgical dust causes the following changes between the primary gypsum crystals the amorphous phase is formed consisting of slightly soluble compounds based on calcium and aluminum hydrosilicates binding the gypsum crystals in large block aggregates and protecting from water. Thus, ultra- and nano-dispersed additives being added simultaneously, a dense structure of solid gypsum is formed with the increased strength of contacts, which enhances the physical and mechanical properties.

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