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Role of polyfunctional admixture based on silica fume and carbon nanotubes in forming the structure of gypsum cement composition

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Abstract

One of the topical areas of regulating the structure of gypsum cement compositions is modifying the morphology with ultrafine and nanodisperse systems. The study has analyzed the possibility of changing the structure and properties of new formations of gypsum cement pozzolanic matrix by adding multifunctional admixture based on silica fume and multi-walled carbon nanotubes (MWCNTs) dispersed in a surfactant medium. The optimum content of complex admixture has been determined as 0.006% of MWCNTs and 10% volume content of silica fume as part of modified gypsum cement pozzolanic binder (GCPB) providing the increase of compressive strength by 55% and water resistance by 32%. Studying the structure of modified GCPB by means of physico-chemical analysis (scanning electron microscopy, infrared-spectral analysis and differential scanning calorimetry) has proved the improvement of physical and mechanical properties due to changes in mineralogical composition of new formations in hardening composition and morphology of the forming crystal hydrates in the structure of modified gypsum cement pozzolanic matrix. At the same time, it is noted that gypsum crystalline hydrates are coated with calcium silicate hydrates compacting the structure of the composition and increasing the total contact surface of the new formations. At the same time calcium silicate hydrates prevent water from the surface of crystals of calcium sulfate dihydrate, thereby increasing the water resistance of the composition.

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1. Introduction

Berenfeld [1] indicate that one of the current priorities of the gypsum industry is improving product quality and producing materials with the predetermined properties. According to Volgenskiy et al. [2] producing gypsum-cement pozzolanic binder (GCPB) due to the simplicity of its production, environmental friendliness, rapid hardening and better water resistance in comparison with gypsum binder has improved the strength characteristics of materials and expanded the application range of products based on calcium sulfate. Ferronskaya [3] set that materials based on gypsum binder are attractive due to the resource-saving manufacturing technology because it does not require a lot of energy. At the same time, the effective use of such binders in the construction has not exhausted its possibilities. Mahmoud and Rashad [4] proved that applying fine pozzolanic additives including technogenic wastes in the form of silica fume for stabilizing new formations in order to exclude the formation of ettringite.

Korolev and Bazhenov [5] suppose that one of the priority areas of controlling the properties of GCPB is adding modifying ultra- and nanodispersed additives with high-surface area into its composition. Gaiducis et al. [6] and Izryadnova [7] indicate that GCPBs have significant potential, their physical and mechanical properties being enhanced due to the directed changing of the structure of binding matrix in the process of modifying with a polyfunctional additive which consists of silica fume (SF-85) and extended carbon nanosystems (CN). The relevance of the research in this area is confirmed with the insufficiency of the previous studies of the interaction mechanism of the structuring ultra and nano-disperse additives and the original binder matrix.

2. Materials and research methods

The binder used is gypsum G-4 of the average fineness grade meeting the requirements of GOST 125-79 and Portland cement CEM I 32.5B. The quantitative content of gypsum and Portland cement varies within 55-75% and 5-35%, correspondingly.

The pozzolanic additive used is silica fume SF-85 produced by Chelyabinsk electrometallurgical plant with the average particle size of 300 nm, with the content of more than 90% of amorphous silicon oxide with the specific surface of the particles 20 m²/g (Fig. 1c). According to TC 14-106-709-2004 [8] silica fume SF-85 is a man-made metallurgical product of ferrosilicon smelting. The chemical composition is shown in Table 1.

Table 1. The chemical composition of silica fume SF -85.

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	Na_2O	K_2O	C	S
90-92%	0.68%	0.69%	0.85%	1.01%	0.61%	1.23%	0.98%	0.26%

MWCNT dispersion C-100 produced by Arkema French corporation prepared in hydrodynamic cavitator is applied as a nano-dispersed component for producing a polyfunctional additive according to Korzhenko et al. [9] technology. The dispersion is a mixture of MWCNTs in the medium of Relamix superplasticizer containing 0.5 g of MWCNT per 1 l of suspension.

During the research bar samples with the edge size 4*4*16 cm were studied. Water-binder ratio was selected in accordance with the normal density of GCPB (150-210 mm) which meets GOST 31376-2008. The control and modified samples were tested at the age of 7 days.

3. Discussing the result

Volgenskiy et al. [10] proved that the effectiveness of the modifying additives is determined by the nature, size and shape of the particles. According to Yakovlev et al. [11] silica fume particles are characterized with aggregation during their storage due to their high activity, its dispersion is required before applying polyfunctional additive in the composition. Fig. 1 shows the comparative analysis of dispersibility of SF-85 which shows that the average size of aggregated particles is 20 μm (Fig. 1a), and after the dispersion - 300 nm (Fig. 1b). This predetermines high pozzolanic activity of silica fume in GCPB.

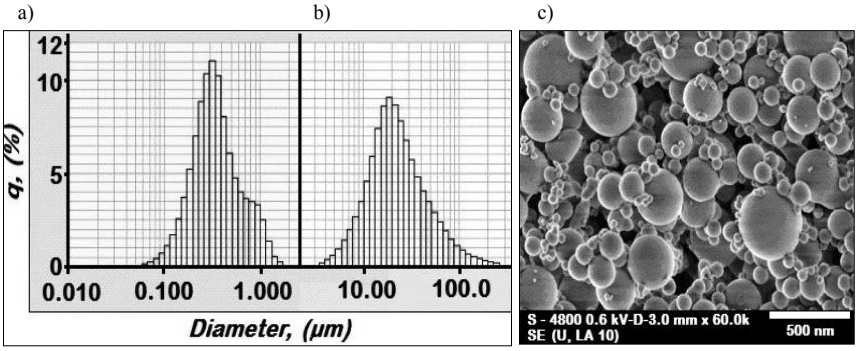

Fig. 1. Distribution of silica fume particles in aqueous dispersion: (a) - after ultrasonic treatment for 6 minutes, (b) - without preliminary ultrasonic treatment, (c) - microstructure of silica fume particles.

The results of the optimization of the composition are shown in Fig. 2a, which shows that the optimum strength values were obtained with the volume component ratio of 75:15:10 (G:PC:SF). This composition was taken as a control one. Singh and Karade [12] proved that the further decrease in strength, cement concentration increasing, is due to the formation of ettringite in the gypsum matrix structure. The content of silica fume increasing, mechanical properties decrease. Tokarev et al. [13] explained the fact that under the conditions of the excess of SF there is deficiency of calcium hydroxide forming during the cement hydration, due to which the excess of SF becomes an inert additive.

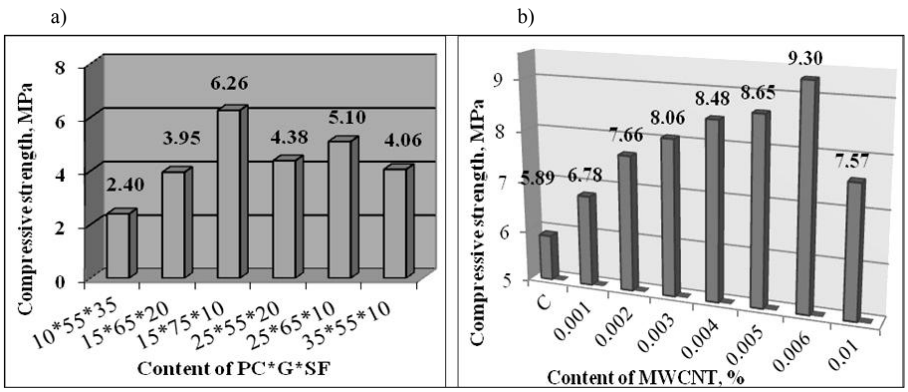

Fig. 2. The strength characteristics GCPB on the 7th day: (a) optimization of GCPB composition in combination with SF; (b) dependence of the strength values of GCPB on the content of MWCNT (% from the mass of the binder).

The interaction of silica fume and the hydration products of Portland cement leads to significant densification of gypsum matrix structure with calcium hydrosilicates. Brikov and Kamaliev [14] proved that it ultimately results in increasing not only strength but also water resistance of products based on gypsum cement pozzolanic binders.

Physical and mechanical tests of the samples modified with polyfunctional additive show that MWCNT dispersion at the amount of 0.006% from the mass of the composite binder (gypsum-cement-silica fume) increases the strength on the 7th day by 55% (Fig. 2b) and the softening coefficient (Cs) by 32% in comparison with the control composition.

Sobolkina et al. [15] set that the increase of the strength characteristics of products occurs due to the synergistic effect of the interaction of nanoparticles in a complex additive with high surface energy and acting as crystallization centers on the surface of which there is intensive formation of ordered crystals of calcium sulfate dehydrate. The decrease in strength, the concentration of nanotubes increasing, may be the evidence of the lack of a binder required for modifying the structure of GCPB.

According to Izryadnova and Yakovlev [16] the analysis of the images of the microstructure of the control (Fig. 3a) and modified GCPB samples (Fig. 3b) shows the densification of the structure in the latter sample due to the densification of calcium sulfate dehydrate crystals with low-basic calcium hydrosilicates.

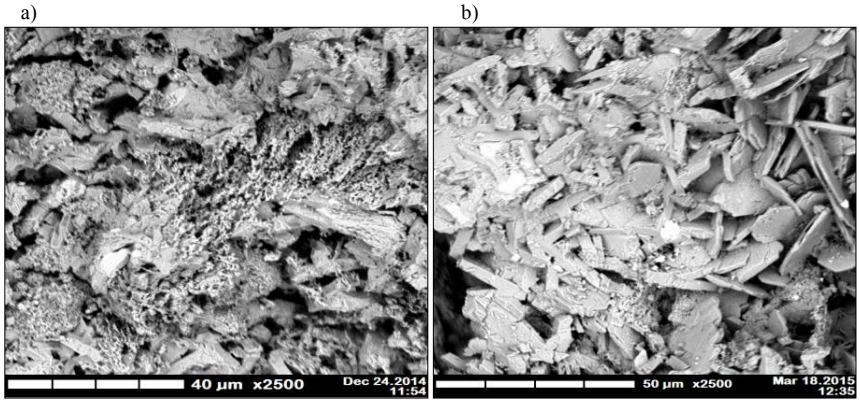

Fig. 3. Microstructure of GCPB: (a) without polyfunctional additive ×2500, (b) modified with carbon nanostructures of 0.006% and 10 % of SF-85 ×2500.

Zvironaite [17] researched that results can be explained by the fact that ultra-dispersed additives together with cement and silica fume intensify the process of structure formation. As a result of the interaction of calcium hydroxide and silica fume, calcium hydrosilicates are formed coating the crystals of calcium sulfate dehydrate, thus, increasing their contact area and at the same time protecting them from water influence.

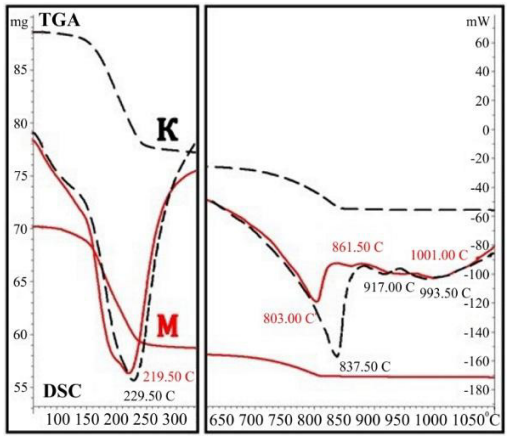

Fig. 4. DSK and TG curves of gypsum-cement matrix in the control sample “K” and the sample “M” modified with carbon nanostructures with 0.006% and 10% content of SF-85.

The analysis of gypsum cement matrices of the control and modified GCPB samples by means of differential scanning calorimetry (Fig. 4) shows the differences in the temperature range of 160 - 270°C. Thus, the control sample shows intensive water exhalation from calcium sulfate dehydrate at the temperature of 229.50°C. At the same time, the analysis of TGA lines shows a higher content of water in the tested samples (Fig. 4 “M”), which suggests better hydration of Portland cement with the formation of calcium hydroxide, which reacts with silica fume forming extra calcium hydrosilicate. The endothermic effects at the temperature above 800°C indicate that the formed hydrosilicates have different basicity as their dehydration occurs at different temperatures: 837.50°C (Fig. 4 “K”) for the control samples and 803.00°C for the modified ones.

Zinuk et al. and also Gorshkov and Timashev [18,19] set that the research of the control and modified compositions of GCPB by means of infrared spectral analysis (Fig. 5) shows that the intensity of absorption lines in the modified sample corresponding to OH-group in the frequency range of 3400 cm^{-1} and free water in the frequency range of 1690-1620 cm^{-1} increases which suggests an increase in the total content of calcium hydrosilicates in GCPB composition modified with polyfunctional additive.

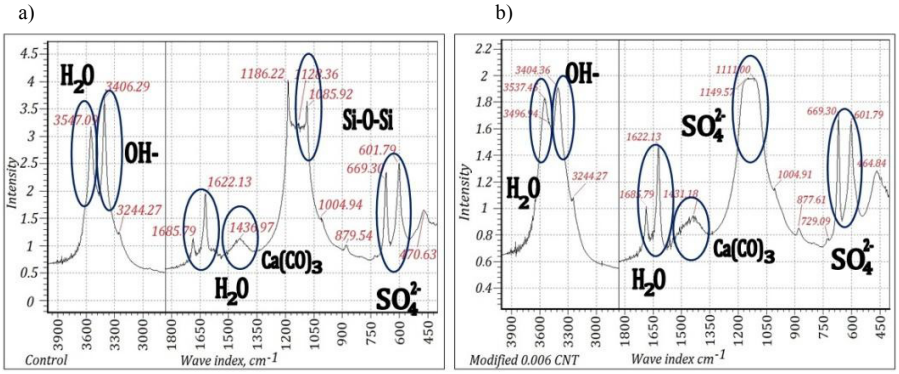

Fig. 5. IR-spectra of gypsum cement pozzolanic matrix: a) – without additive; b) – with MWCNT with 0,006% content from the mass of the binder.

The intensity of absorption lines in the frequency range of 1431.18 cm^{-1} and 1436.97 cm^{-1} inherent in calcium carbonate is 42.5% lower in the modified composition than in the control sample. According to Nakomoto data [20] in the spectra of the modified and control GCPB samples in the frequency range of 879.54 cm^{-1} and 877.61 cm^{-1} correspondingly a line is recorded, which is also typical for calcium carbonate. The decrease in the intensity of absorption lines inherent in carbonates is associated with the reduced amount of calcium hydroxide in the solution due to the formation of low-basic calcium hydrosilicates (CHS).

The analysis of the IR-spectrum of the control GCPB sample (Fig. 5a) shows the appearance of a strong line at the frequency of 1186.22 cm^{-1} typical for tobermorite gel 11.3 Å of $C_5S_6H_5$ composition. MWCNT being added to the GCPB composition, this line is not recorded in the indicated frequency range, which is due to the changing of the calcium hydrosilicates basicity (Fig. 5b).

According to study of Gharehbash [21] the typical lines for silica fume are 1100 cm^{-1} and 470 cm^{-1} (Fig. 6), which are well seen in the control sample, but in the modified one the absorption line 1100 cm^{-1} is practically absent, and the absorption line 470 cm^{-1} in the modified sample is shifted to 464.84 cm^{-1}. This indicates changes in the environment around the molecules of amorphous silicon oxide by their binding into additional calcium hydrosilicates.

Consequently, the data of IR spectral analysis and differential scanning calorimetry studies also confirm the

results of the study of microstructure of GCPB samples. The decrease in intensity of the main frequencies inherent in hydroxyl groups, sulfates, carbonates and silicates suggests the modifying effect of MWCNTs on the structure, water resistance and mechanical properties of GCPB.

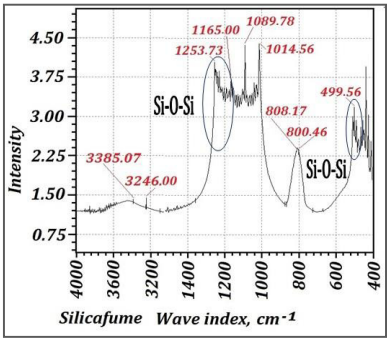

Fig. 6. IR-spectrum analysis of silica fume.

4. Conclusions

Thus, adding MWCNT dispersion to the traditional composition of GCPB can improve its mechanical properties and increase its water resistance due to densification of the composite structure. The increase in strength of the modified GCPB sample on the 7th day in comparison with the control one was 55%, while the water resistance increased by 32%.

High dispersity and pozzolanic activity silica fume provides significant densification the structure of gypsum stone with low-basic calcium hydrosilicates, increasing not only strength, but also water resistance of their products.

Carbon nanostructures act as crystallisation centers on the surface of which a dense pack of crystals is formed. At the same time, gypsum crystalline hydrates due to the polyfunctional additives in GCPB composition are covered with new formations which prevent water from affecting the binding matrix.

References

[1] Berenfeld VA. Binding materials in a building of XXI century. *GUPNIIMosbuild - Engineering Data Book* 2009;3:33–36.
[2] Volgenskiy AV, Stambulko VI, Ferronskaya AV. *Gypsum cement pozzolan binders, concretes and products*. Moscow: Stroiizdat; 1971.
[3] Ferronskaya, AV. *Longevity of gypsum materials, products and constructions.* Moscow: Stroiizdat; 1984.
[4] Mahmoud MMH, Rashad MM, Ibrahim IA, Abdel-Aal EA. Crystal modification of calcium sulfate dehydrate in the presence of some surface-active agents. *J. Coll. Int. Sci.* 2004; 270: 99-105.
[5] Korolev EV, Bazhenov YM, Beregovoy VA. The modifying of building materials with carbone nanotubes and fullerenes. *Construction materials – science* 2006; 8:2-6.
[6] Gaiducis S, Zvironaite Ja, Maciulaitis R, Jakovlev G. Resistance of Phosphogypsum Cement Pozzolanic Compositions against the Influence of Water. *Materials Science (Medziagotyra)* 2011;17:308-313.
[7] Izryadnova OV, Sychugov SV, Polyanskikh IS, Pervushin GN, Yakovlev GI. Polyfunctional admixture based on carbon nanotubes and nanosilica for enhancing physical and mechanical properties of gypsum cement pozzolanic binder. *Construction materials* 2015;3:63-67.
[8] TC 14-106-709-2004 "Condensed silica fume"
[9] Korzhenko, A., Havel, M., Gaillard, P., Yakovlev, G.I., Pervuchin, G.N., Oreshkin, D.V. Procede D'introduction de nanocharges carbonees dans un inorganique durcissable. Patent № 2 969 143. C 04 B 16/12 (2012.01), C 04 B 28/00. Bulletin 12/25 pub. 22.06.12.
[10] Volgenskiy AV, Rogovoy MI, Stambulko VI. *Gypsum-cement-puzzolan and gypsum-slag binders and products*. Moscow: Stroiizdat; 1960.
[11] Yakovlev GI, Pervushin GN, Maeva IS, Keriene J, Pudov IA, Shaybadullina AV, Buryanov AF, Korzhenko A, Senkov SA. Modification of Construction Materials with Multi-Walled Carbon Nanotubes. *In: Procedia Engineering 57, 11th International Conference on Modern Building Materials, Structures and Techniques, MBMST 2013;* 407–413.
[12] Singh LP, Karade SR, Bhattacharyya SK, Yousuf MM, Ahalawat S. Beneficial role of nanosilica in cement based materials. *A review Construction and Building Materials* 2013; 47:1069–1077.

[13] Tokarev YV, Yakovlev GI, Pervushin GN, Buryanov AF, Keriene Ja. The role of ultrafine additives in hydration processes of anhydrite binder. *Construction materials, equipment, technologies of XXI century* 2010; 5 (124):18-23.
[14] Brikov AS, Kamaliev RT, Mokeev MV. The Influence of ultrafine silica to hydration of Portland cement. *Journal of applied chemistry* 2010; 83(2):211-216.
[15 Sobolkina A, Mechtcherine V, Bellmann C, Khavrus V, Oswald S, Hampel S, Leonhardt A. Surface properties of CNTs and their interaction with silica. *Journal of Colloid and Interface Science* 2014; 413: 43-53.
[16] Izryadnova OV, Yakovlev GI, Polyanskikh IS, Fischer H-B, Senkov SA. Change of morphology of crystalline hydrates at introduction ultra- and nanodisperse modifiers of structure in gypsum cement pozzolanic binder. *Construction materials* 2014; 3: 63-67.
[17] Zvironaite Ja *et al*. The Peculiarities of Hardening of Composite Anhydrite Cement Pozzolanna Binding Materials with not Burned Natural Anhydrite. *Materials Science (Medziagotura)* 2010; 16(2):159–164.
[18] Zinuk RY, Balykov AG, Gavrilenko IB, Shevyakov AM. *Infrared Spectra of inorganic technology*. Moscow: Chem.; 1983.
[19] Gorshkov VS, Timashev ZV, Saveliev VG. *The physicochemical analyze methods of binding materials.* Moscow: High School; 1981.
[20] Nakomoto K. *Infrared and Roman Spectra of inorganic and coordination compounds.* 4th Ed. New York: Chichester; 1991.
[21] Gharehbash N, Shakeri A. Modification of the surface of silica nanoparticles; studying its structure and thermal properties in order to strengthen it in preparing Nanocomposites. *Journal of American Science* 2013; 9 (4):602-606.