

# Nanomodified energy-efficient gypsum materials: structure and properties

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**Abstract.** Currently, many building materials for interior finishing are based on gypsum as a binder. Usage of gypsum allows to significantly simplify both the production of building materials and to increase the operational properties related to energy efficiency. This makes important the studies directed to the improvement of gypsum-based binders. In the present work the influence of nanoscale modifiers based on zinc hydrosilicates to the structure and properties of gypsum was examined. The dependence between compressive strength of gypsum and content of the modifier was approximated by a rational function. It was found that the reason for the increase of strength is a change in the structure of the newly forming gypsum; such a change consists, in particular, in the formation of split crystals. At the same time, chemical composition of the nanomodified gypsum remains unchanged. It is shown that the formation of split gypsum crystals is observed when using nanomodifiers that significantly shorten the setting time.

## 1. Introduction

In current construction industry it is common to use the gypsum mixtures for production of building materials that are intended for interior finishing works. Usage of gypsum allows to significantly simplify both the production of materials and to increase the operational properties related to energy efficiency. At the same time, the known deficiencies of gypsum are insufficient strength, recrystallization in a humid environment, insufficient resistance to the microbiological objects and high intercrystalline porosity. For this reason, the problem of managing the gypsum quality is still requires an effective solution. Quality can be managed by changing the structure of gypsum by means of various modifiers, including nanomodifiers [1-3]. According to [4] and [5], silica-based nanoscale modifiers demonstrate quite high efficiency.

The colloidal solution of zinc hydrosilicates is one of the silica-based nanomodifiers. Such colloidal solution is of high aggregative and sedimentation stability [6]. Distinctive features of this nanomodifier are availability, ease of manufacturing technology, safety of use and homogeneity of nanoparticle distribution in the volume of building materials. The chemical composition of such nanomodifier can be controlled by varying the concentration of the iron (III) hydroxide sol and silicic acid during the synthesis of zinc hydrosilicates (in our earlier works, e.g. [7], this concentration, that is strongly depends on the amount of silicic acid, was denoted as  $\alpha$ ).



## 2. Materials and methods

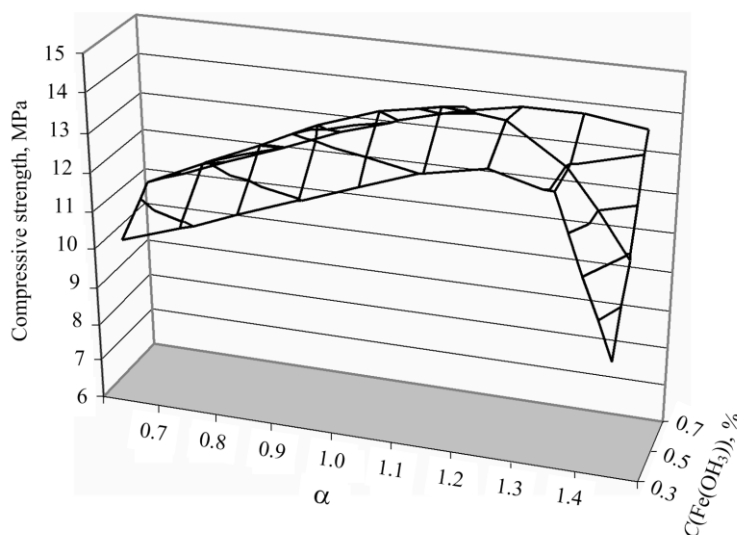
The ordinary gypsum G-6 by RU GOST 125-79 was used during experiments. The primary properties of G-6 gypsum are: initial setting time is 510 s, final setting time is 780 s, standard thickness is 62% and compressive strength of hydration products is 10.5 MPa.

Several compositions of nanoscale modifiers were used. These nanomodifiers are based on nanosized zinc hydrosilicates that were synthesized by low-temperature technology [6] and differ both by  $\alpha$  parameter and concentration of iron (III) hydroxide sol.

A study of the effect of nanomodifiers on chemical composition, structure and properties of gypsum was carried out by means of IR spectroscopy and scanning electron microscopy. IR spectra were obtained using the Cary 630 FT-IR spectrometer (Agilent Technologies, Santa Clara, CA, USA). Analysis of the gypsum structure was carried out using a Quanta 200 microscope (FEI, Hillsboro, Oregon, USA).

## 3. Results and discussion

Admixture of nanoscale modifier that is based on zinc hydrosilicates makes it possible to increase the strength of gypsum samples (figure 1).



**Figure 1.** Dependence between chemical composition of nanomodifier and compressive strength of gypsum samples

Analysis of the data presented on figure 1 shows that the dependence between compressive strength of gypsum and  $\alpha$  parameter can be approximated by function

$$R = \frac{a + b\alpha}{1 + c\alpha + d\alpha^2},$$

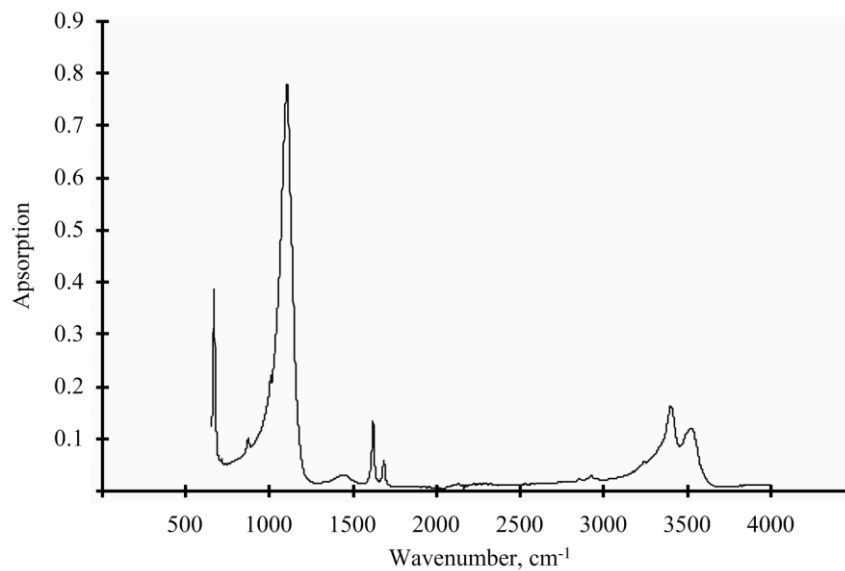
where  $a$ ,  $b$ ,  $c$  and  $d$  – empirical parameters.

Both the reasons for such dependence of strength and mechanism of the influence of the nanomodifier based on zinc hydrosilicates on the strength of gypsum have not been established yet. Identification of the chemical composition and structure of nanomodified gypsum will allow to establish the peculiarities of structure formation in case of nanoscale modifiers that are based on zinc hydrosilicates.

Concentration of zinc hydrosilicates in the solutions ranges from 0.052% to 0.160% (table 1). There is no essential influence of nanomodifier to the chemical composition of gypsum hydration products (namely, influence to the formation of calcium hydrosilicates). This is evidenced by the identity of the IR spectra of the control and nanomodified gypsum (figure 2).

**Table 1.** Concentration of zinc hydrosilicates in colloidal solution, %

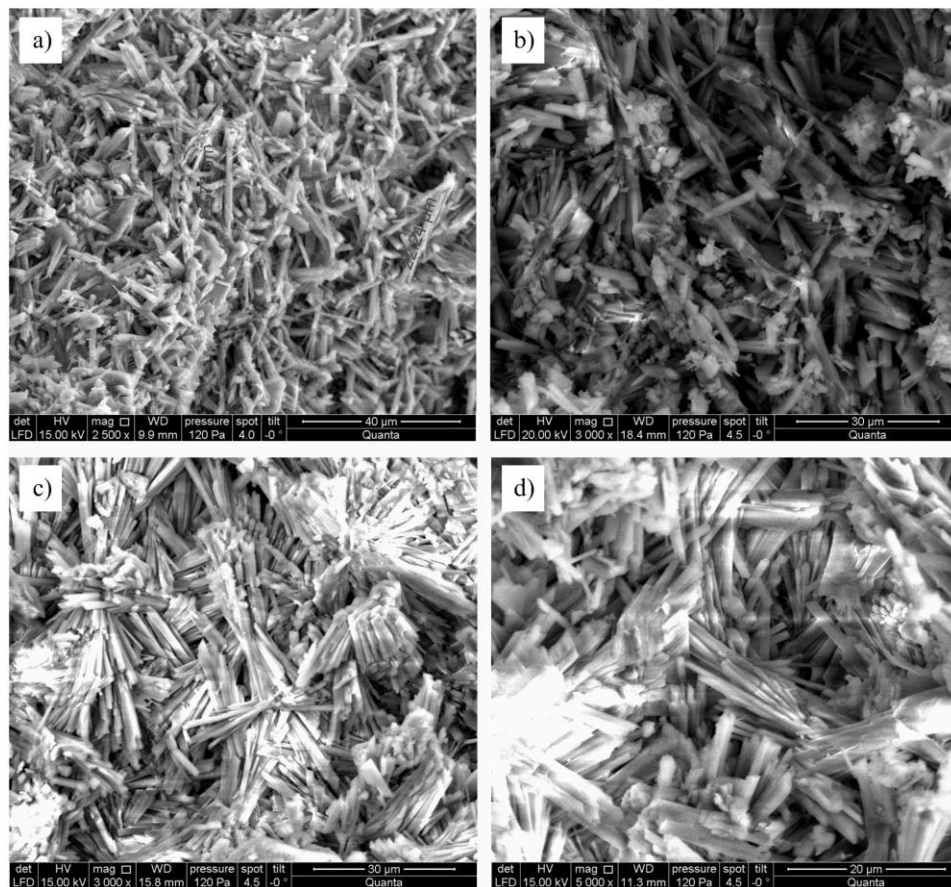
$\alpha$	$C(\text{Fe}(\text{OH})_3)$ , %		
	0.3	0.5	0.7
0.7	0.052	0.070	0.088
0.8	0.056	0.076	0.097
0.9	0.060	0.083	0.106
1.0	0.064	0.089	0.115
1.1	0.067	0.096	0.124
1.2	0.071	0.102	0.133
1.3	0.075	0.108	0.141
1.4	0.079	0.115	0.151
1.5	0.083	0.121	0.160

**Figure 2.** IR spectrum of both control sample and nanomodified samples of gypsum

The reasons that lead to change of strength of nanomodified gypsum can be identified if the characteristic features of its structure are examined (figure 3).

Analysis of figure 3 shows that the bulk of the control sample of gypsum is composed of polydisperse needle-like crystals with sparse inclusions of prismatic ones. Gypsum crystals of lamellar morphology are formed under steady growth conditions with small supersaturations of the crystal-forming medium. The prismatic crystals are not observed in the structure of gypsum that is nanomodified by zinc hydrosilicates. Structure of all nanomodified gypsum has a more dense packing of hydration products, and the crystals of such products are quite uniform.

It is known that formation of needle crystals occurs at high supersaturations (of crystallizable component) of the crystal-forming medium. Therefore, it is obvious that needle crystals initially appeared, and then, when the supersaturation of the crystal-forming medium decreased, plate-like morphological varieties of gypsum began to appear. Thus, in case of using a colloidal solution of zinc hydrosilicates, the concentration of the crystal-forming medium (gypsum sulfate dihydrate) increases.



**Figure 3.** Gypsum crystals: a) control sample; b) nanomodified sample,  $C(\text{Fe}(\text{OH})_3) = 0.3\%$  and  $\alpha = 1.3$ ; c) nanomodified sample,  $C(\text{Fe}(\text{OH})_3) = 0.5\%$  and  $\alpha = 0.7$ ; d) nanomodified sample,  $C(\text{Fe}(\text{OH})_3) = 0.7\%$  and  $\alpha = 1.1$ .

There are practically no plate crystals in the structure of gypsum that is nanomodified by zinc hydrosilicates. The structure is almost completely formed by relatively large radial-radiant mineral aggregates. According to [8] and [9], similar structures are usually formed in case of high concentration of crystallizable substance. Such structure formation is possible in case of the following crystal growth mechanism: zinc hydrosilicates were firstly adsorbed on the surface of gypsum crystallizing nuclei and thus caused local growth blocking, leading to the formation of split crystals. In this case a more dense structure of gypsum can be formed. Obviously, in this case, the area of contacts between crystals will be larger, and the formation time of such crystals will be shorter. It is also necessary to take into account additional influence of electrolyte solutions on the shift of setting time (table 2).

Analysis of table 2 also shows that iron hydroxide, silicic acid in iron hydroxide and silicic acid obtained from sodium hydrosilicates, accelerate the setting time. In this case, the silicic acid sol, synthesized in iron hydroxide medium, most intensively accelerates the setting time. It should be noted that the joint presence of both iron hydroxide sol and silicic acid leads to an additional acceleration of setting time. Zinc acetate is also an active accelerator of the formation of gypsum. In the presence of sodium acetate, as well as chlorides in an amount that corresponds to one in the colloidal solution of zinc hydrosilicates colloidal solution, initial setting time is equal to one for control sample, while the final setting time is less if compared with one for control sample and slows down if compared to the one for gypsum nanomodified by zinc hydrosilicates. This is an indirect evidence of the sorption of zinc ions from the solution and the formation of zinc hydrosilicates.

**Table 2.** Setting times of nanomodified gypsum

Type of modifier	Initial setting time, s	Final setting time, s
Control sample	510	780
$C(\text{Fe}(\text{OH})_3) = 0.3 \%$ , $\alpha = 1.3$	480	540
$C(\text{Fe}(\text{OH})_3) = 0.5 \%$ , $\alpha = 0.7$	360	510
Sodium acetate	510	630
Sodium acetate and chlorides	510	630
Zinc acetate	210	300
Sodium hydrosilicates that corresponds to $\alpha = 1.3$ and $C(\text{Fe}(\text{OH})_3) = 0.3 \%$	510	630
Silicic acid sol in iron hydroxide medium that corresponds to $\alpha = 1.3$ and $C(\text{Fe}(\text{OH})_3) = 0.3 \%$	330	450
$C(\text{Fe}(\text{OH})_3) = 0.3 \%$ sol	420	540
$C(\text{Fe}(\text{OH})_3) = 0.5 \%$ , $\alpha = 1.0$ after one year of storage	390	510

As the concentration of the iron (III) hydroxide sol increases, the gypsum setting speed also speeds up. This, apparently, is the primary reason for growing the compressive strength of gypsum together with the increase of iron (III) hydroxide sol concentration that is used for the synthesis of zinc hydrosilicate sols.

An analysis of the shift of setting time of gypsum modified with zinc hydrosilicate sols, both prepared just before the test and stored for one year, shows that storage has no significant effect on the structure formation and properties of material.

#### 4. Conclusions

As a result of the experimental studies carried out, it has been established that the increase of the compressive strength of gypsum that was nanomodified by zinc hydrosilicates is mostly due to change of structure, but not chemical composition. The admixture of nanomodifier leads to the formation of a structure with relatively large radial-radiant mineral aggregates. In this case, a denser gypsum structure is formed, which is accompanied by both an increase in total area of contacts between the crystals and the acceleration of the setting time.

#### Acknowledgments

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