INVESTIGATION OF HYDRATION PROCESSES OF NANOMODIFIED CALCIUM SULFATE HEMIHYDRATE

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1. INTRODUCTION

The article is concerned with development of new trend in the mineral binding substances nanomodification involving structure formation mechanisms and hence affecting various properties.

2. RATIONALE

Reports on successful nanosystems application in various areas encourage conduction of researches concerning impact the nanomodifiers have on mineral binding substance structure and properties. Effect is that additional phase boundary having the excess surface energy is formed in the "binder – gauging liquid" system [1]. This is one of factors influencing the hydration processes.

The literature review conducted by authors showed the null information on the reliable mechanisms of mineral binding substances hydration processes in the presence of nanomodifiers. The laboratory investigations show successful results in physical-and-mechanical properties changing, yet to a small extent. Problem complexity consists in unavailability of the adapted research technique, up-to-date equipment and materials.

3. RESEARCH OBJECTIVE

Study of impact factors and mechanism of calcium sulfate systems hydration process in presence of nanomodifiers.

4. RESEARCH TECHNIQUES AND MATERIALS

For the purpose of the present research, carbon nanotubes were used, which were made in the hydrocarbons catalytic pyrolysis plant of the Center of carbon nanomaterials of the Vladimir State University n.a. A.G. and N.G. Stoletov, Russia (Table 1).

Table 1. Properties of multilayer carbon nanotubes (CNT).

Material	**Number of layers**	**Length, μm**	**Diameter, nm**	**Specific surface area, m^2/g**	**Purity, %**
CNT	max 30	2-5	10-60	120	95

Gypsum binder with addition of surfactant in amount of 0.4% of binder mass (Table 2) is used as reference standard.

Table 2. Reference standard composition and properties.

Calcium sulfate, %	**Surfactant, %**	**W/G %**	**pH**	**Setting time, min**		**Strength, MPa**	
				start	**end**	**compression**	**bending**
100	0,4	59	7,2	6	8	4,6	2,2

Carbon nanotubes were added in form of suspension prepared as follows: powder of multilayer carbon nanotubes was preliminary added to water solution of plasticizer, then it was processed in sonicator, which ensured formation of steady dispersion of the nanoparticles suspended in water. Polycarboxylate P-11 by the Macromer Research and Development Enterprise (Vladimir, Russia) and Sika Retarder plasticizer (Switzerland) were used as plasticizers. The suspension preparation process was controlled for the following parameters: suspension density, colloidal system stability (electrokinetic potential determination [2]), CNT concentration, viscosity.

X-ray diffraction analysis methods and calorimetric tests were used for the investigation of mineralogical composition and kinetics of the processes occurring in the modified matrix. New formations structures, sizes and morphology were investigated with the use of scanning electron microscopes.

In order to improve efficiency of carbon nanotubes (CNT), CNTs surface was chemically modified with the functional groups, for example, hydroxyl or carboxylic groups [3]. Carboxylation of carbon nanotubes was carried out by their interaction with various oxidizing agents [4 - 6] (chromium and manganese salts in high oxidation states, hydrogen peroxid). For the CNTs oxidization by hydroxyl groups, mechanochemical method [7 - 8] was used, which consists in the CNT milling with alkali during 60 minutes.

5. RESEARCH RESULTS

Conducted researches on the determination of water-gypsum ratio, ultimate bending strength and compression strength of bending test beams at 2 hours show that the increase of nano-additive content causes monotonic increase in structural characteristics of composite material (fig. 1).

Maximum strength improvement (27 – 29%) is achieved at the use of carbon nanotubes with the hydroxyl groups. At the use of initial nanotubes, strength improvement makes 13-15% (fig. 2).

The increase in carbon nanotubes concentration results in the increase in colloidal solution pH from 7.2 to 8.1, which influences the calcium sulfate hydration processes, and hence the structure formation processes and physical-and-mechanical properties of final material. In this case, increase in hydrogen exponent value results in the gypsum binder structural characteristics improvement.

In the course of calorimetric tests, calcium sulfate hemihydrate particles were tempered with water and were not agitated. Test conditions are such that regardless of dilution by water, initial binder particles are separated by small spaces, and ions passing into solution hardly ever move over large distances due to difficulty of diffusion in the liquid phase.

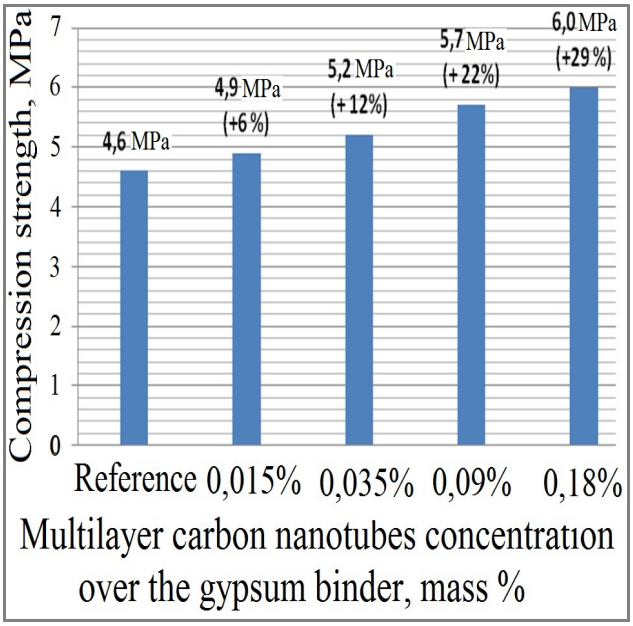


Figure 1. Histogram of the carbon nanotubes impact on gypsum binder strength.

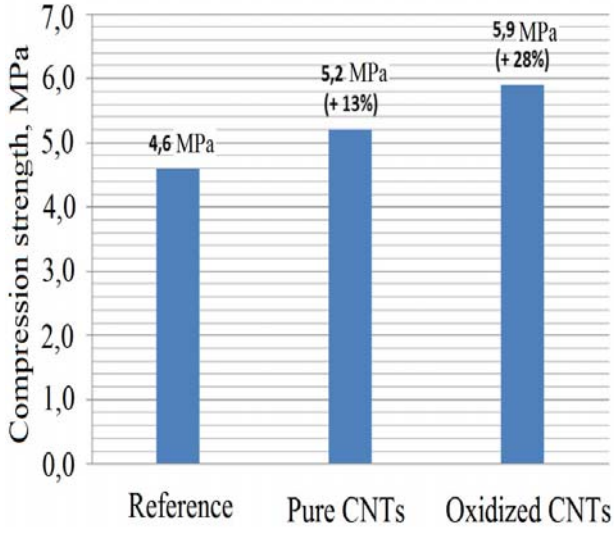


Figure 2. Histogram of calcium sulfate based composite compression strength vs. carbon nanotubes surface functionalization.

At the CNT addition, increase in the hydration reaction rate was observed. This owes to the active $CaSO_4 \cdot 2H_2O$ crystallization due to addition of

nanomodifier having the large specific surface area and high reactive capacity.

Results of measurement (fig. 3) of heat generation rate during calcium sulfate hemihydrate hydration show possibility of the technological control by means of technological processes in order to impart necessary properties to material.

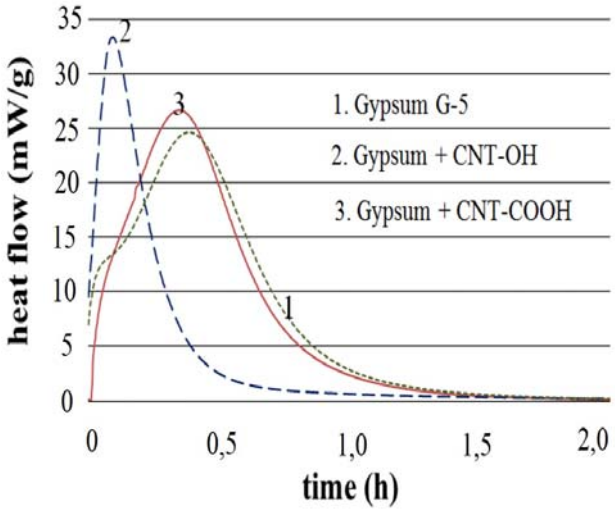


Figure 3. Heat generation rate during the calcium sulfate hemihydrate hydration process vs. nanomodifier type.

According to researches [10], Ca^{2+} sorption on the graphene-like CNT surface causes increase in near-surface solution oversaturation degree. This facilitates more complete and rapid calcium sulfate hemihydrate conversion into calcium sulfate dihydrate, and hence accelerates calcium sulfate dihydrate crystallization process. Thus, thermodynamical curves are representative of achievability of hardening processes in conjunction with achievement of the required technological characteristics – strength, setting time, etc.

During investigation with the use of X-ray diffractometer X`Pert PRO MPD 3040/60 Fa. PANalytical (Institute of ceramics, glass and build materials (IKGB TU Bergakademie Freiberg)), analysis was conducted of initial gypsum binder, building gypsum-based samples modified and non-modified with the carbon nanotubes (Table 3).

Following materials were used as structural models of mineral components for full-profile quantitative X-ray phase analysis: gypsum $CaSO_4 \cdot 2H_2O$ (PDF No. 01-074-1433); bassanite $CaSO_4 \cdot 0.5H_2O$ (PDF No. 01-081-1849); anhydrite $CaSO_4$ (PDF No. 01-086-2270), carbon C (PDF No. 01-075-2078).

Effect of nanomodifiers (CNT) on the hydration process is presented in the figs. 4, 5.

X-ray photograph of 1st cycle (fig. 4, curve 1) of gypsum sample shows a presence of large amount of calcium sulfate dihydrate (91 %), presence of calcium sulfate hemihydrate (up to 3%). Duration per cycle makes 5 minutes 16 sec. A hydration process is completed at 18th cycle (fig. 4, curve 2), i.e., upon expiration of 95 minutes, $CaSO_4 \cdot 2H_2O$ percentage makes 88%.

Table 3. Phase concentrations, % Wt.

	$CaSO_4 \cdot 0{,}5H_2O$	$CaSO4 \cdot 2H_2O$	$CaSO_4$	$CaCO_3$	C
Gypsum binder	91	3	4	2	-
Building gypsum	3	88	4	2	-
Building gypsum + CNT	1	93	3	2	1 (0,05)

Data from X-ray photograph of CNT-modified gypsum binder hardening are indicative of hydration processes intensification. Hydration process is also completed at 18th hardening cycle (upon expiration of 95 minutes), while calcium sulfate dihydrate formation rate is considerably higher, the $CaSO_4 \cdot 2H_2O$ percentage makes up to 93%.

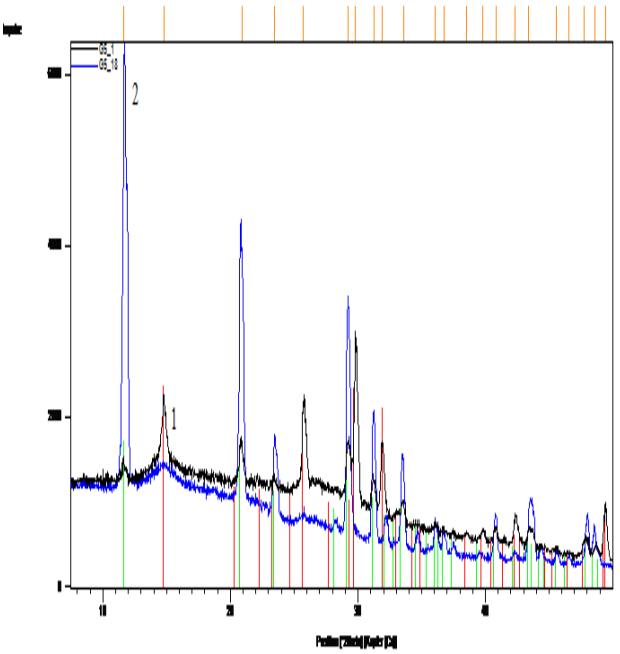


Figure 4. Rietveld diagram of gypsum hardening over time.

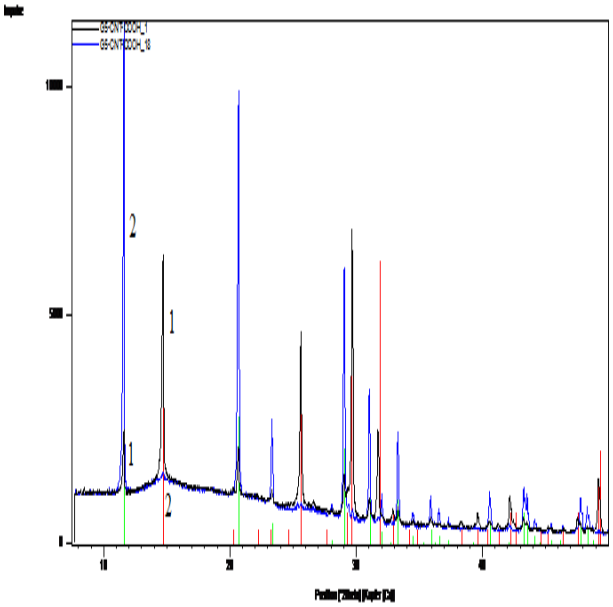


Figure 5. Rietveld diagram of CNT-modified gypsum hardening over time.

At hydration of the non-modified building gypsum during 18 cycles (95 minutes), process occurs with the $CaSO_4 \cdot 2H_2O$ formation up to 88%. At the same conditions, modified gypsum hydration makes up to 93%, and quantity of unreacted $CaSO_4$ some decreases (Table 3).

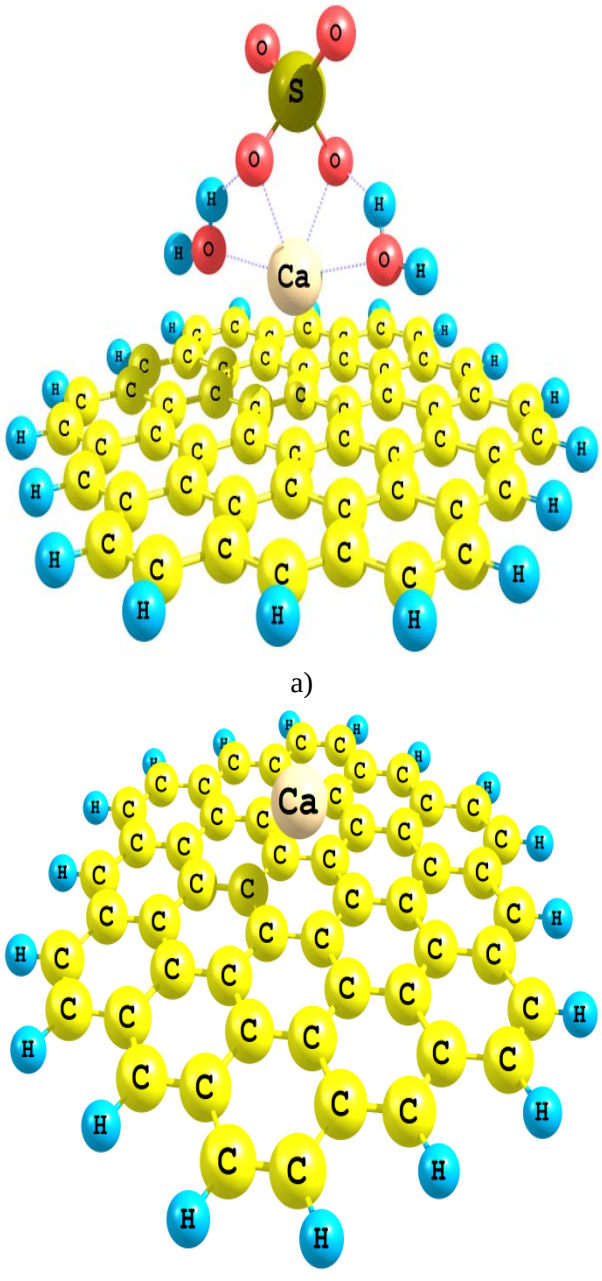
Based on data of quantitative X-ray photographs and X-ray photographs over time, it may be concluded that CNT introduction causes hydration process enhancement, more complete calcium sulfate hemihydrate conversion into dehydrate is observed, and calcium sulfate matrix physical-and-mechanical parameters improvement is provided.

The analysis of microstructure of gypsum composition samples showed that without the modifying additive, loose structure of gypsum samples is formed with significant amount of pores.

It may be assumed that nanodispersed CNT additives act as “crystallization nuclei”, on the surface of which calcium sulfate matrix structuring occurs with achievement of improvement of gypsum composition structural characteristics. This is due to that during growth, crystals partly penetrate into each other and form three-dimensional network permeating and incorporating entire gypsum stone into a body.

Study [11] presents carbon surface effect on the structure of calcium sulfate dihydrate molecule, and proposes hypothesis for mechanism of CNT impact on structure and mechanical properties of calcium sulfate composites. Calcium sulfate hydration model is based on the Le Chatelier’s theory positing that calcium sulfate hemihydrate interaction with water results in its dissolution with formation of the solution saturated with the Ca^{2+} and SO_4^{2-} ions.

Calculation of the calcium sulfate dihydrate molecule interaction with CNT surface showed that the molecule is prone to the chemical interaction with surface [12] through the calcium ion (fig. 6).



a)

b)

Figure 6. Model fragments of CNT surface interacting with:
a) –calcium sulfate molecule; b) Ca^{2+} ion.

CONCLUSIONS

Introduction of carbon nanostructures into the gypsum compositions results in the mechanical strength improvement due to formation of fine-cristalline needle-like structure of the increased density. Given the same nanomodifier content in the calcium sulfate matrix, maximum compression strength increment making 27-29% is achieved at the use of CNTs functionalized with hydroxyl groups. At the use of the non-modified carbon nanotubes, strength increment in the presence of additive only makes 13-15%.

Chemical functionalization of carbon nanotubes surface facilitates reduction of the sedimentation effect inherent to the nanoparticles. In addition, it enables more uniform nanostructure dispersion throughout the modified material volume and provides the chemical interaction between nanotubes and substance matrix.

Calcium sulfate dihydrate molecule interaction with the graphene-like surface is a chemical process, which is demonstrated by the quantum-chemical analysis methods. Improvement of CNT-containing gypsum composite strength is due to the accelerated process of calcium sulfate dihydrate crystallization at the graphene surface.

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