Наносистеми, наноматеріали, нанотехнології
Nanosistemi, Nanomateriali, Nanotehnologii
2022, т. 20, № 1, сс. 127–144

© 2022 ІМФ (Інститут металофізики
ім. Г. В. Курдюмова НАН України)
Надруковано в Україні.

PACS numbers: 61.05.cp, 61.46.Np, 61.48.De, 62.23.Pq, 65.80.-g, 78.30.Na, 83.80.-k

Nanomodifying of Gypsum Binders with Carbon Nanotubes

V. N. Derevianko[1], N. V. Kondratieva[2], H. M. Hryshko[3],
and V. Y. Moroz[3]

[1]*SHEE 'Prydniprovs'ka State Academy of Civil Engineering and Architecture',*
24-a, Chernyshevs'ky Str.,
UA-49600 Dnipro, Ukraine
[2]*SHEE 'Ukrainian State University of Chemistry and Chemical Technology',*
8, Gagarin Prosp.,
UA-49005 Dnipro, Ukraine
[3]*Dnipro State Agrarian–Economic University,*
25, Serhii Efremov Str.,
UA-49600 Dnipro, Ukraine

One of the directions in development of nanotechnologies used for production of building materials, development of theoretical and practical methods applied for improving the properties of finished products and operational constructions in Ukraine consists in use of nanosystems for regulation of material structure and binder properties. The hydration mechanism of mineral binders in the presence of nanomodifiers is quite poorly described in the scientific literature, but the results of laboratory studies confirm their significant impact on the technological process and changes in physical and mechanical properties. Studies on both the influence caused by nanomodifiers and the mechanism of gypsum binder hydration in the presence of nanomodifiers are topical. The goal of this article is studying the mechanism of hydration process, structure and properties of gypsum binders in the presence of carbon nanomodifiers. As revealed, introduction of carbon nanostructures into gypsum compositions affects, first of all, the rate of chemical reactions (hydration of binders), morphology of crystals and composition structure. Use of a relatively small amount of modifier makes it possible to change the structure of mortar or concrete, to increase significantly the strength characteristics and to improve the physicochemical properties. Carbon nanotubes (CNTs) are one of modifiers. They are mainly neutral with respect to the components of the binder solution and affect the hydration process by increasing the surface energy, creating crystallization centres and nanoreinforcing the structure. For achieving a more efficient action of the nanomodifier, mechanical or chemical destruction of separate chemical bonds on the surface of nanotubes is applied (functionalization). Functionalization of CNTs' surface gives an opportunity to disperse them more evenly throughout the bulk of the modified material; it also contributes to reduction of sedimentation effect and provides chemical interaction between nanotubes and matrix of the substance. Modification of gypsum with nanomaterials increases its compression strength and bending strength as well as water tightness. It is experimentally established that the optimal concentration of CNTs with the greatest increase in strength observed is of 0.005–0.05% of the binder dry mass. Providing the same content of nanomodifiers in the gypsum matrix (0.035%), the maximum increase of compression strength (28–30%) is achieved by means of using CNTs functionalized with hydroxyl groups.

Одним із напрямів розвитку нанотехнологій виробництва будівельних матеріялів, розробки теоретичних і практичних метод поліпшення властивостей готових виробів та експлуатаційних споруд в Україні є використання наносистем для реґулювання структури матеріалів і властивостей в'яжучих речовин. Інформації щодо механізму процесів гідратації мінеральних в'яжучих речовин у присутності наномодифікаторів в науковій літературі достатньо мало, але результати проведених лабораторних досліджень підтверджують значний вплив їх на технологічний процес і зміни фізико-механічних властивостей. Дослідження впливу та механізму процесу гідратації гіпсових в'яжучих у присутності наномодифікаторів є актуальними. Мета статті — дослідження механізму процесу гідратації, структури та властивостей гіпсових в'яжучих у присутності вуглецевих наномодифікаторів. Зроблено висновок: введення в гіпсові композиції вуглецевих наноструктур впливає в першу чергу на швидкість хемічних реакцій гідратації в'яжучих речовин, морфологію кристалів і структуру композиції. Використання достатньо незначної кількости модифікатора дає можливість змінити структуру розчину або бетону та значно підвищити міцнісні характеристики, поліпшити фізико-хемічні властивості. Одним із наномодифікаторів є вуглецеві нанотрубки (ВНТ), які в основному нейтральні по відношенню до складових розчину в'яжучої речовини та впливають на процес гідратації за рахунок збільшення поверхневої енергії, створення центрів кристалізації та наноармування структури. Для більш ефективної дії наномодифікатора проводиться руйнування механічним або хемічним способом (функціоналізація) окремих хемічних зв'язків на поверхні нанотрубок. Функціоналізація поверхні ВНТ уможливлює більш рівномірно дисперґувати їх по всьому об'єму модифікованого матеріялу, сприяє пониженню седиментаційного ефекту та забезпечує хемічну взаємодію між нанотрубками та матрицею речовини. Модифікація гіпсу наносистемами збільшує його міцність на стиск і вигин, а також водонепроникність. Експериментально встановлено, що оптимальна концентрація ВНТ становить 0,005–0,05% від сухої маси в'яжучого, за якого спостерігалося найбільше збільшення міцности. За однакового вмісту наномодифікаторів у гіпсовій матриці (0,035%) максимальний приріст міцности за стиснення досягається з використанням ВНТ, функціоналізованих гідроксильними групами, і становить 28–30%.

Key words: nanomodifying, gypsum binders, carbon nanotubes, hydration, nanosystem, solidified (hardened) structure.

Ключові слова: наномодифікування, гіпсові в'яжучі, вуглецеві нанотрубки, гідратація, наносистема, затверділа структура.

(Received 9 March, 2021; in revised form, 18 March, 2021)

1. PROBLEM STATEMENT

The concept of developing building materials science is aimed at development of modern materials with their properties being superior to existing ones. A variant of solving the problem may consist of the use of nanotechnology, which is in its infancy, as there are no theoretical provisions for creating bulk materials. There are several lines of research on development of nanotechnologies for production of building materials, development of theoretical and practical methods to improve the properties of products and service facilities [1–3].

One of these lines in Ukraine is presented as use of nanosystems to regulate the structure of materials and in accordance with the properties of binders. The hydration mechanism of mineral binders in the presence of nanomodifiers is quite poorly described in the scientific literature, but the results of laboratory studies confirm their significant impact on the technological process and changes in physical and mechanical properties.

The present article is concerned with solving problems of theoretical generalization and studying complex technological processes of hydration of solutions with nanomodifiers added, their influence on structure formation and physical and mechanical properties of binders, relationship with the composition of raw materials and technological process of receiving products.

2. THE AIM OF THE ARTICLE

The goal of this article is studying the mechanism of hydration process, structure and properties of gypsum binders in the presence of carbon nanomodifiers.

3. RESULTS AND DISCUSSION

Carbon nanotube-based modifications of composite materials located, according to the authors [4], on edges of separate crystals of hydrated calcium silicate contribute to filling microcavities and connecting them to each other. At the same time, carbon nanotubes (CNTs) of smaller length bind structural formations of short order, while long nanotubes bind crystallites that are more distant.

The most scientific hypotheses are based on the assumption that carbon nanoparticles (CNPs), carbon nanotubes (CNTs) are crystallization centres by means of increasing the phase interface surface and changing the surface energy of the system. Gypsum structure is mainly formed by means of changing the input parameters that is obviously insufficient as far as this process is prolonged, and it is determined by numerous parameters (volume, temperature, pressure, concentration of source components, diffusion rate, crystallization, *etc.*).

According to the experimental studies performed, general state of the system can be characterized using chemical potential or using changes in thermal energy [5]. The theoretical assumption is that adding nanoparticles with a large specific surface changes properties of the system, *i.e.*, the first stage of controlling of the process of hydration with nanoparticles can be represented as follows:

$$CaSO_4 \cdot 0.5H_2O + 1.5H_2O + \text{nanoparticles} \rightarrow CaSO_4 \cdot 2H_2O. \qquad (1)$$

The process of calcium sulphate hemihydrate transition to calcium sulphate dihydrate is studied in the article; change of conditions and hydration rate in the process of the hydration can change the structure of crystals as well as their spatial structure and filling of frame that is never less important. In research studies [6, 7], it was found that, by means of changing the morphology of gypsum crystals (through adsorption modification), we can change the strength of crystallization structures on the base of calcium sulphate dihydrate.

Formation of structure of gypsum binders can be regulated by means of changing the rate of calcium sulphate hydration [8, 9]. In turn, this depends on the hemihydrate solubility rate and is subject to the laws of diffusion [10]:

$$\frac{dc}{dt} = SD\frac{C_1 - c}{\delta}, \qquad (2)$$

where dc/dt is amount of substance dissolved per unit of time; D—diffusion coefficient; S—specific surface of the soluble substance; C_1—concentration of saturated solution; c—actual concentration at the given moment of time; δ—thickness of the diffusion layer.

Changing the rate of calcium sulphate dissolution may affect the structure of the material. In turn, the rate of crystal formation depends on the surface energy. If the surface energy at the interface between the crystal and the solution decreases, the stability of the system is improved. The amount of energy can be changed through adsorption of surface-active substances (surfactants). There is dependence (Gibbs equation) between the excess of material in the surface layer and its concentration in the solution [10, 11]:

$$G = -\frac{c}{RT}\left(\frac{\partial\sigma}{\partial c}\right), \tag{3}$$

where $\partial\sigma/\partial c$ is surface energy; c—concentration of the additive; G—adsorption of the additive; R—gas constant; T—absolute temperature.

Concentration of initial components, volume, temperature and pressure inside the system change during hydration of gypsum binders or other mineral compounds. Due to this, composition of the solution is changed. This system can be characterized by a chemical potential μ_1.

Chemical potential of additives can be presented as a coefficient of intensity (degree of stress) of substance chemical energy in the system (it can be viewed as the product of the intensity factor and the power factor, and, at the same time, capacity factor is the number of moles or the concentration of the substance):

$$\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2,n_3.....}, \tag{4}$$

where P, T, $\{n_i\}$ mean stability of pressure, temperature, numbers of moles of all areas except first one.

Increase of chemical energy can be presented as a chemical energy intensity factor of the given substance in the system. Thus, chemical potential is the measure of change of the specific function at constant parameters and masses (concentrations) of all materials, except mass (concentration) of the component being variable in the system. Then, chemical potential can be considered as a thermal effect:

$$\overline{(Q_V)} = -\Delta U \text{ or } \overline{(Q_P)} = -\Delta H, \tag{5}$$

where Q_V is isochronal thermal effect; Q_P—isobaric thermal effect; ΔU—change of internal energy; ΔH—thermodynamic function of enthalpy.

Use of modifying additives is an effective technological method of purposeful influence on these processes. Solving tasks of optimal modification requires determining the relationship between the type, composition, concentration and method of controlling and obtaining the functional characteristics of binders. This system includes a rather complicated, but very important process—it is a physical and chemical mechanism of interaction between components during transition of solution into artificial stone. Developing theoretical explanation of this mechanism will give an opportunity to organize a highly efficient control of the hydration process.

When considering the process of hydration and structure formation of gypsum binders, physical and mechanical tests were performed within the frames of this work in order to determine influence of nanosystems on these processes. Possibilities of developing theoretical supports for the purpose of practical application for regulation of hardening processes aimed at improved properties of solutions and concretes were considered too.

The following materials were used in the work: gypsum binder (Table 1), plasticizer (Sika Wiskogret) and distilled water. Multilayer carbon nanotubes (CNTs) were used as nanomaterials; their parameters are presented in Table 2.

The following substances were also used in our studies: carbon nanoparticles (CNPs), carbon nanotubes functionalized (CNTs–OH, CNTs–COOH). These are CNTs' surfaces chemically modified with functional groups, for example, hydroxyl one or carbonyl one [12–16]. For CNTs oxidation with hydroxyl groups used, a mechanochemical method is used [17, 18], which consists in a joint grinding of CNTs and alkali during 60 minutes (Fig. 1).

Carboxylation was carried out through the interaction of nanotubes with various mineral acids [19–21] (chromium salts and manganese salts in oxidation stages, hydrogen peroxide).

Figure 2 shows CNTs after ultrasound processing. Functionalised CNTs (unlike initial ones) do not form large agglomerates and are well separated.

A gypsum binder with the addition of a surfactant (which was predetermined in amount of 0.4% of the binder mass) was used as a reference sample (Table 3).

A uniform distribution of nanoparticles in matrix volume is an

TABLE 1. Characteristics of the gypsum binder.

Gypsum binder	W/G, %	Solidification periods, min		Strength, MPa	
		start	end	compression	bending
G-5	65	7	12	3.35	2.1

TABLE 2. Properties of multilayer carbon nanotubes.

Names of materials	Number of layers	Length	Diameter	Specific surface	Frequency
Multilayer CNTs	not more than 30	2–5 μm	10–60 nm	120 m^2/g	95

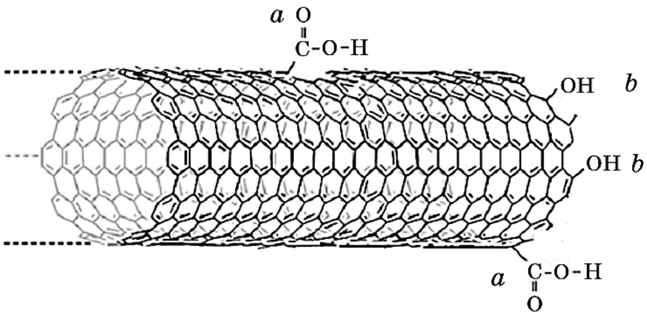
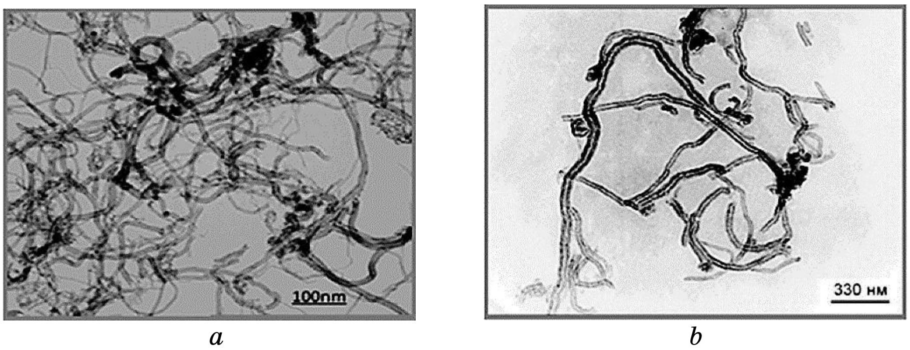


Fig. 1. Schemes of functionalised carbon nanotubes: *a*) with carboxyl groups; *b*) with hydroxyl groups.



a *b*

Fig. 2. Photomicrographs of multilayer carbon nanotubes: (*a*) pure CNTs; (*b*) modified CNTs.

TABLE 3. Composition and properties of the reference sample.

Gypsum, %	Surfactant, %	*W/G*, %	pH	Solidification periods, min		Strength, MPa	
				start	end	compression	bending
100	0.4	59	7.2	6	8	4.6	2.2

important factor of production technology for creating optimal crystallization conditions [13, 14]. This means that the modifying additive (despite its insignificant concentration) must be evenly distributed in the medium of the solidifying material.

In Johann Plank's works [15], it was noted that, during binder modification with multilayer carbon nanotubes including calcium ions and polycarboxylate superplasticizer, there is a moderate increase of concrete strength for 28 days not more than 30%, which is related with insufficient degree of CNTs' dispersion due to deposition of calcium ions to the surface of separate nanotubes.

The developed technology of producing samples includes dispersion (in an ultrasonic mixer) of nanoparticles (carbon nanotubes, activated nanotubes) in a concentrated solution of plasticizer (in our investigations, it is Sika plasticizer) and water according to the corresponding regime. Homogeneity is controlled based on optical density and zeta potential. Then, the dispersed solution is mixed in a turbine mixer with water in quantity corresponding to the water–gypsum ratio for the given batch of the binder.

Samples-beams are made according to the standard method according to DSTU B B.2.7-82 2010.

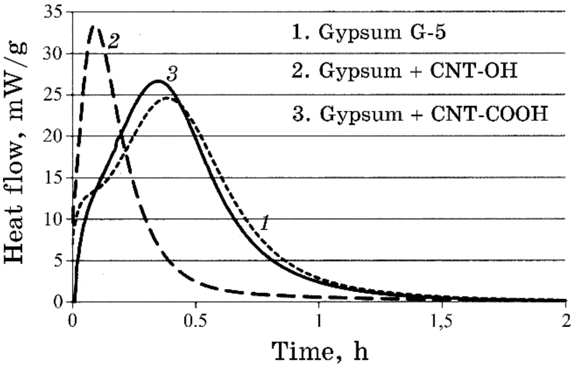


Fig. 3. Dependence curves of heat-release intensity during hydration of calcium sulphate hemihydrate: *1*—gypsum; *2*—gypsum + CNTs–OH; *3*—gypsum + CNTs–COOH.

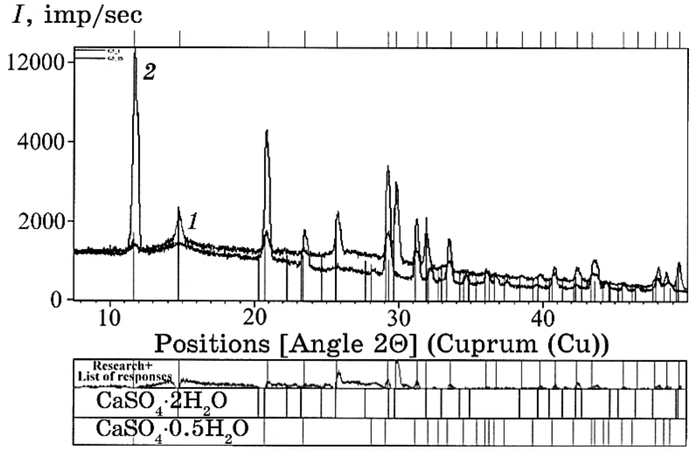


Fig. 4. Rietveld diagram of gypsum hardening over time for G-5: *1*—after the 1st cycle; *2*—after the 18th cycle.

Main testing methods are as follow: chemical tests for determination of changes in pH of the environment; physical tests—electron microscopy, infrared microscopy, x-ray phase analysis, calorimetric studies; mechanical tests for determination of strength properties.

In the process of performing studies, the following tasks were set: 1) to investigate dispersion of the modifier in the bulk of the binder; 2) to study the influence of hydration-process mechanism and properties of gypsum binders in the presence of CNTs.

Hydration is a physical and chemical transformation of a binder solution into a hardened stone (effectiveness of this process is determined by properties of this stone). Regulation of it by means of various factors gives an opportunity to change mineralogical composition and structure of the hardened solution and its properties. By means of nanoadditives introduced, fundamentally new materials can be obtained (with properties of the next higher order in comparison with properties of existing materials).

As mentioned above, this process can be represented with a chemical potential, *i.e.*, coefficient of intensity (degree of stress) of substance chemical energy in the system. Chemical potential can be viewed as a thermal effect giving an opportunity to regulate the rate of physical and chemical transformations and structures.

Thus, calorimetric studies of gypsum–water solutions and gypsum–water–nanoadditive compositions showed an increase in heat-release intensity during hydration of gypsum in the presence of nanoadditives (Fig. 3). This indicates the possibility of controlling the process of hydration and solidified (hardened) structure formation in order to provide required properties of mineral binders.

During studies with the use of x-ray diffractometer (X'Pert PRO MPD 3040/60 Fa. PANalytical, Institute of Ceramic, Glass and Building Materials—IKGB TU Bergakademie Freiberg), the hydration processes of the initial mineral binder (gypsum plaster) and this binder modified with carbon nanotubes were analysed in time (Figs. 4, 5; Table 4).

The x-ray photograph (Fig. 5, curve *1*) of the gypsum sample shows significant amounts of calcium sulphate hemihydrate (24%) and calcium sulphate dihydrate (up to 67%) after the 1st hardening cycle (5 min 16 sec). The hydration process is completed at the 18th cycle (Fig. 5, curve *2*), *i.e.*, after 95 minutes. Main-intensity impulses of the rejected lines of calcium sulphate dehydrate correspond to 6200, 4250 and 3300.

Data from the x-ray photograph of CNTs-modified gypsum binder hardening are indicative of the hydration process intensification. The hydration process is also completed at the 18th hardening cycle (upon expiration of 95 minutes); however, calcium sulphate dehydrate formation rate is considerably higher. The lines of main im-

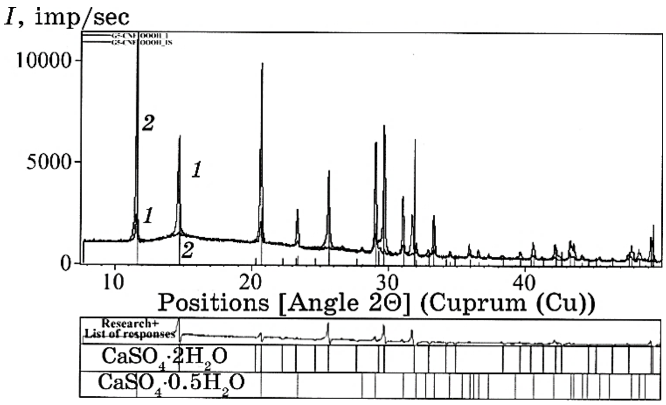


Fig. 5. Rietveld diagram of gypsum hardening over time for G-5 modified with CNTs: *1*—after the 1st hardening cycle; *2*—after the 18th hardening cycle.

TABLE 4. Changes in mineralogical composition of calcium sulphate hemihydrate in the time (by weight %).

Hardening cycles	$CaSO_4{\cdot}0.5H_2O$	$CaSO_4{\cdot}2H_2O$	$CaSO_4$	Impurities
Mineralogical composition of unmodified calcium sulphate hemihydrate after the 1st hardening cycle, Curve *1*, Fig. 4	24	67	4	5
Mineralogical composition of unmodified calcium sulphate hemihydrate after 18 hardening cycles, Curve *2*, Fig. 4	5	86	4	5
Mineralogical composition of modified calcium sulphate hemihydrate after the 1st hardening cycle, Curve *1*, Fig. 5	14	77	4	5
Mineralogical composition of modified calcium sulphate hemihydrate after 18 hardening cycles, Curve *2*, Fig. 5	1	93	1	5

pulses of calcium sulphate dehydrate correspond to 11300, 9900, 6000 (Fig. 6).

During hydration of unmodified gypsum plaster within the 18 cycles (95 minutes), the process is running with formation of $CaSO_4{\cdot}2H_2O$ in the amount of up to 86%. Under the same conditions, hydration of the modified gypsum reaches the level of 93% and amount of unreacted $CaSO_4$ is even slightly decreased (Table 4).

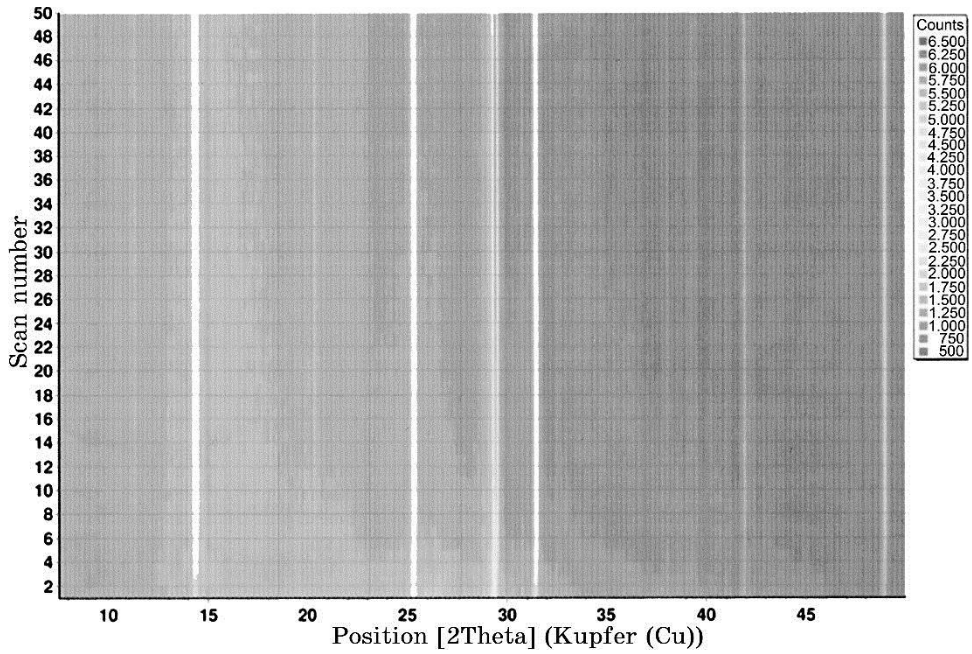


Fig. 6. Intensity of calcium sulphate hemihydrate hydration process.

Results of quantitative x-ray diffraction analysis using the Rietveld method are presented in Table 4.

The follow-up analysis of x-ray photographs shows that, when adding CNTs, the hydration process is intensified and the transition of calcium sulphate hemihydrate to dihydrate is more complete. It is also confirmed by comparison of x-ray photographs of hydration process intensity (Figs. 6, 7).

Analysis of performed studies shows that one of high-impact factors affecting the mechanism of physical and chemical interactions in a dispersed medium is surface energy that should be taken into account, when creating a model.

We see the process of hydration of mineral binders as a system, which changes over time and undergoes macro → micro → nano → → micro → macro stages.

At the macro–micro–nano stage, the structure is partially destroyed to nanoscale elements, since the destruction of main impurities (5 to 15% or more) in the binders does not occur [13].

The studies have determined the influence of carbon nanoadditives on the change of pH composition, which is also an important factor in the control during hydration of binders. According to the data presented in Fig. 8, it is evident that, at increased concentration of carbon nanotubes, there is an increase of the value of the

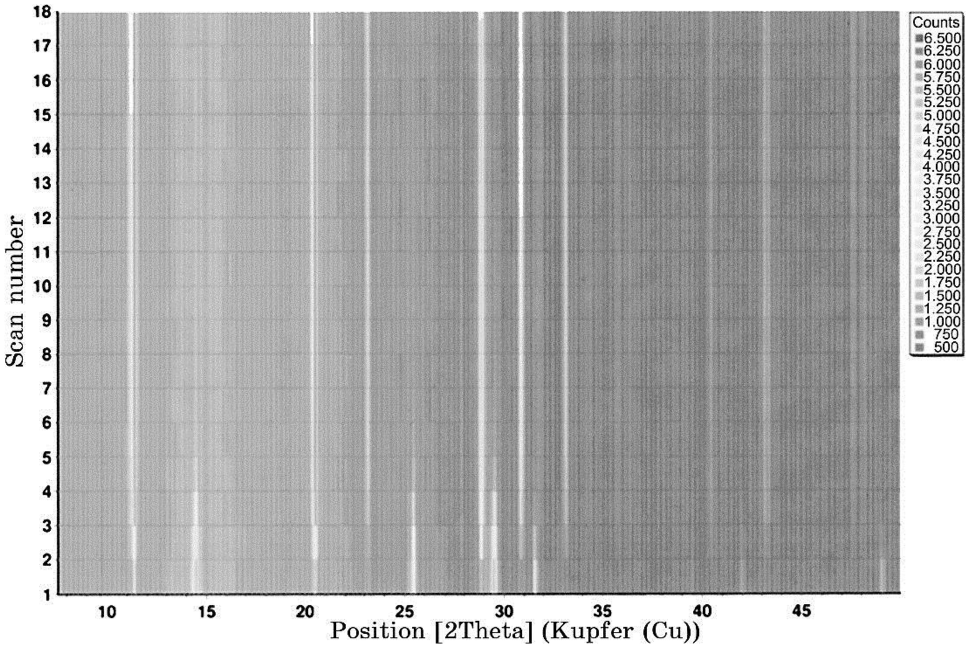


Fig. 7. Intensity of hydration process of calcium sulphate hemihydrate modified with CNTs.

colloidal solution pH from 7.2 to 8.1, which affects the processes of gypsum hydration and, consequently, the processes of structure formation and physical and mechanical properties of final material. It is established that, in this case, the increase of the hydrogen index (pH) leads to increase of the gypsum binder strength.

Based on the above, we can conclude that thermodynamic curves reflect the possibility of implementing hardening processes in conjunction with achieving necessary technological characteristics: times of setting, rheological properties, structure, *etc*.

In studies performed in the sphere of building materials science, the main task consists in developing the structure of materials with given properties, and an important factor of influence caused by nanoadditives is their quantitative content (Fig. 9).

Figure 10 presents data of compression tests of samples with the addition of pure CNTs and carbon nanotubes functionalized with hydroxyl groups. In this case, content of the nanoadditive was 0.035% of the binder mass. It has been found that oxidized CNTs contribute to a more intense increase in strength (up to 28%) compared to unmodified tubes.

Microstructure analysis of gypsum composition samples (Fig. 11) shows that, without a nanoadditive, the structure of gypsum crys-

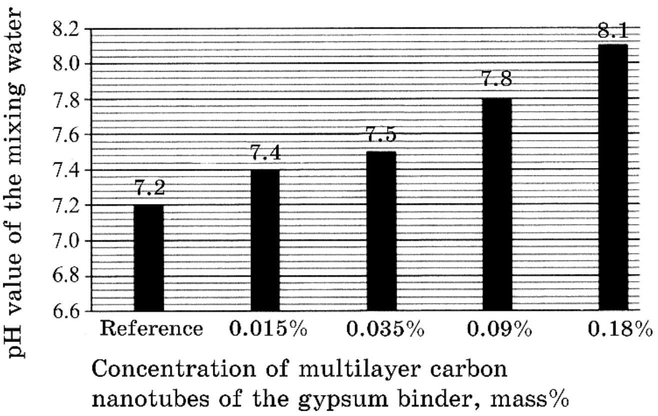


Fig. 8. Histogram of changes in hydrogen index value (pH) of the mixing water.

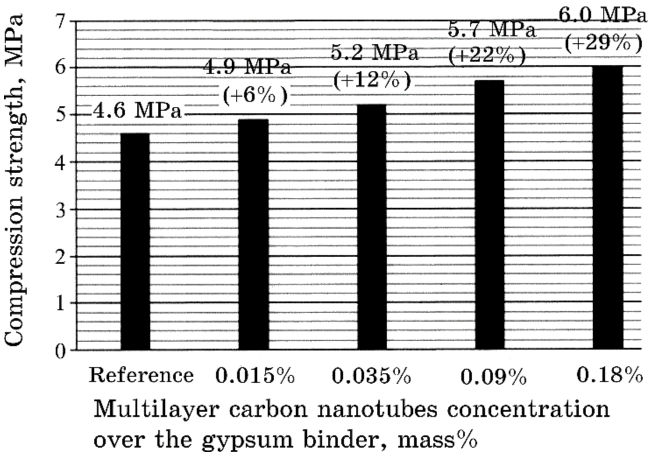


Fig. 9. Histogram of the effect caused by carbon nanotubes on the strength of gypsum binder.

tals formed is characterized by a significant number of pores (Fig 11, *a*). Modification by carbon nanotubes gives an opportunity to form structures with close packing of crystal hydrates with an increased area of contacts between crystals of new growths (Fig. 11, *b*, *c*).

This leads to a significant increase in the strength of gypsum material. It can be assumed that CNTs' additives play the role of 'crystallization centres' with gypsum matrix structuring occurring throughout their surface that gives an opportunity to achieve an increased strength of gypsum composition. This is because the

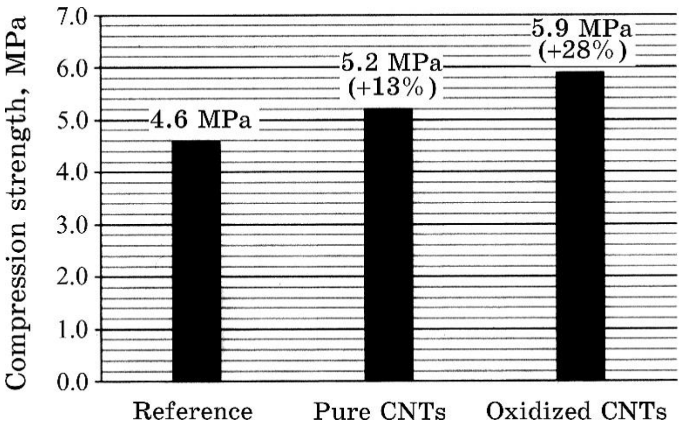


Fig. 10. Histogram of dependence of gypsum-based composite compressive strength on the surface functionalization of carbon nanotubes.

number of crystallization centres per unit volume increases and crystals partially penetrate in each other creating a spatial network connecting the entire gypsum stone into a comprehensive whole.

Considering chemical potential as a factor of the energy system intensity, we should take into account not only the characteristics of the input factors, but also changes in the hydration process. Control and regulation of input parameters is not a significant problem, but control and regulation of system changes require a theoretical representation of the hydration process over time, and only then, we should select factors capable controlling the structure formation. The effect of CNTs' nanomodifiers is as follows.

Sorption of Ca^{2+} on the nanotube surface promotes supersaturation of the solution near the surface and, consequently, accelerates crystallization of calcium sulphate dihydrate. Thus, it contributes to a more complete and fast transition of $CaSO_4{\cdot}0.5H_2O$ to $CaSO_4{\cdot}2H_2O$.

Probably nanotubes attract crystals and form dense structure (Fig. 11) due to their high surface energy, *i.e.*, nanotubes act as crystallization centres with a larger number of calcium sulphate dihydrate crystals formed on their surface that increases physical and mechanical properties.

It is also possible to explain the structure of forming solid particles in positions of the close and remote coagulation. With the help of fully hydrated gypsum binder, water forms a shell around solid phase particles that corresponds to fixation of calcium sulphate dihydrate particles in the position of remote coagulation.

If gypsum dispersion includes particles of a typical size of about 100 nm, distance between them decreases by an order or more that

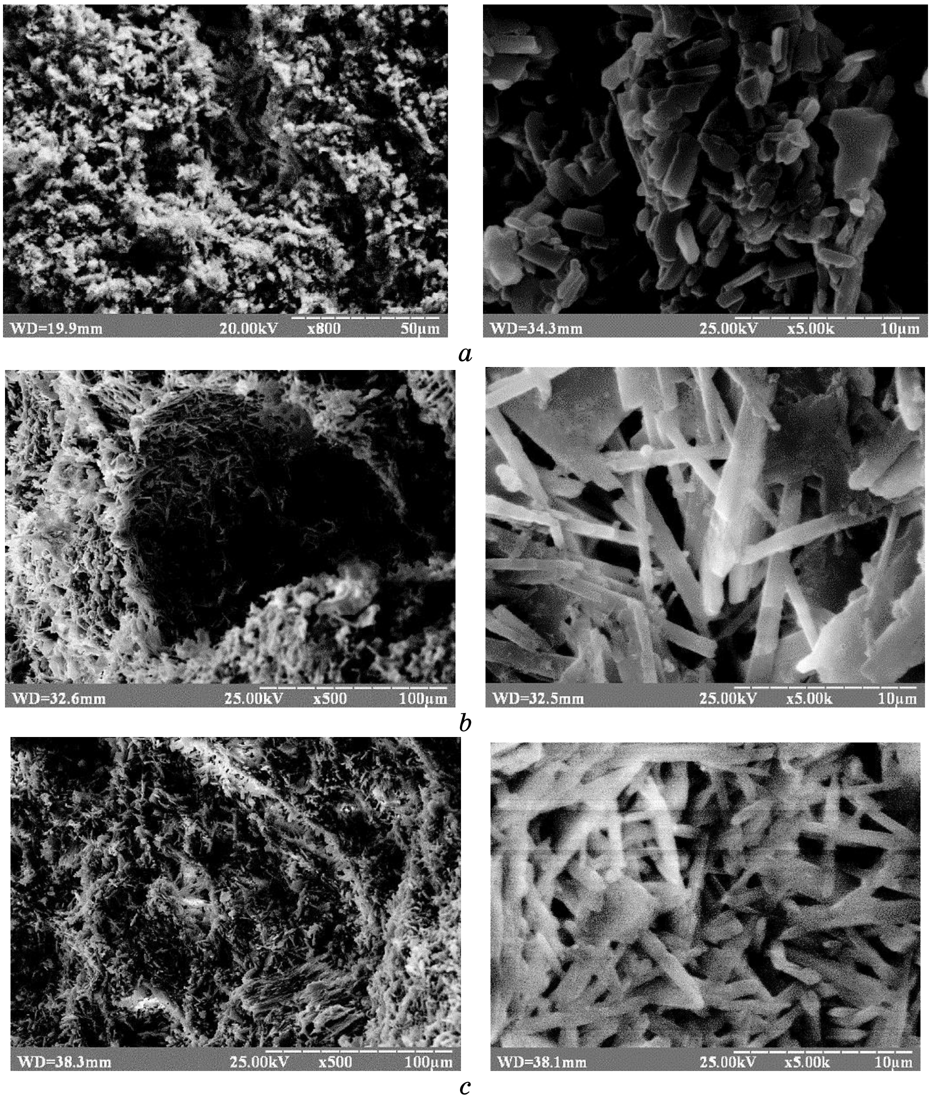


Fig. 11. Photomicrographs of the gypsum plaster structure: *a*) gypsum plaster; *b*) gypsum modified with pure CNTs; *c*) gypsum modified with hydroxyl groups.

corresponds to closing particles in the area near coagulation. This leads to an increase in cohesive forces between contacting particles, which is accompanied by an increase in their strength and, consequently, an increase in gypsum strength physical and mechanical properties.

Influence of CNTs on the intensity of heat release during gypsum

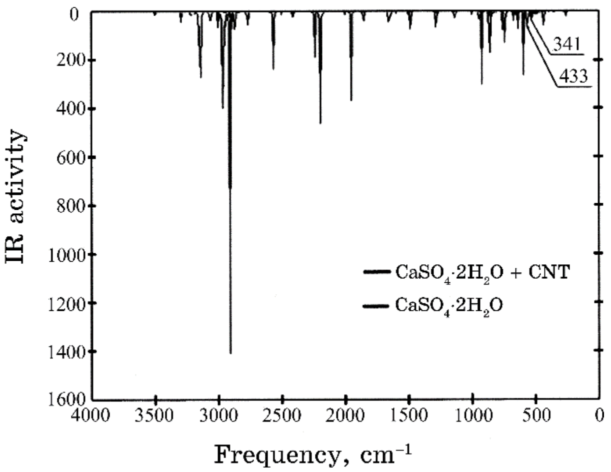


Fig. 12. IR spectroscopy of gypsum compositions.

hydration indicates the possibility to intensify hydration process for achieving required technological characteristics—strength, installation time, *etc*. An increased crystallization rate of modified gypsum samples is reached by means of introducing the nanomodifiers with a high surface area and a high reactive capacity.

IR spectroscopy studies (Fig. 12) have revealed reduced intensity of frequency oscillations for gypsum composition modified with CNTs providing a slight change in the frequency of valence oscillations. There are noticeable differences in the area of high frequencies (over 1000 cm^{-1}). These frequencies correspond to oscillations of hydrogen atoms in hydrogen bonds (lower frequencies of about 1000–2000 cm^{-1}) and covalent bonds (of about 3000 cm^{-1}). There are also frequencies of dry mixture oscillations (of about 800 and 1600 cm^{-1}). Shifts of hydrogen frequencies are not yet entirely clear. They may probably occur through the fragment boundaries, and, in the real system, they will not be observed. Shift of the peaks corresponding to the hydrogen bonds (1000–2000 cm^{-1}) in the area of lower frequencies may also be caused through the transfer of charge from the CNTs to the gypsum surface as well as through the weakening of hydrogen bonds O–H. Changes in frequency of calcium valence oscillations in the gypsum structure (433 cm^{-1} without CNTs and 341 cm^{-1} with CNTs) may indicate interaction of calcium sulphate with the CNTs [12].

4. CONCLUSIONS

Addition of carbon nanostructures to gypsum compositions creates conditions for the formation of a high-density structure with a fine-grained coating that indicates increased strength characteristics of the material. Carbon nanostructures play the role of reinforcing discrete structure of gypsum systems.

Chemical functionalization of carbon-nanotube surface gives an opportunity to disperse nanoparticles more evenly throughout the bulk of the modified material; it also contributes to reduction of sedimentation effect and provides chemical interaction between nanotubes and matrix of the substance.

Modification of gypsum with nanoparticles increases its compression strength and bending strength as well as water tightness. It was experimentally established that the optimal concentration of CNTs with the greatest increase in strength observed was of 0.005–0.05% of the binder dry mass.

Increased efficiency of modifying gypsum systems with functionalized nanotubes has been established, and this can be a line of studies aimed at development of modern building materials.

REFERENCES

1. V. V. Reshetnyak, V. E. Vaganov, S. Yu. Petrunin, A. G. Chumak, and M. Yu. Popov, *Stroitel'stvo, Materialovedenie, Mashinostroenie*, **67**, Iss. 67: 261 (2013) (in Russian).
2. M. A. Sanytsky, H.-B. Fischer, R. A. Soltysik, and S. W. Korolko, *Internationale Baustofftagung 'Ibausil', Tagungsband 1* (2003), p. 0211 (in German).
3. A. Ye. Kononiuk, *Obobshchyonnaya Teoriya Modelirovaniya: Nachala, Kniga 1* (Kyiv: Osvita Ukrayiny: 2012), Ch. 1 (in Ukrainian).
4. P. V. Kryvenko, K. K. Pushkariova, V. B. Baranovskyi, M. O. Kochevykh, Ye. G. Khasan, B. Ya. Konstantynivskyi, and V. O. Raksha, *Budivel'ne Materialoznavstvo: Pidruchnyk* (Ed. P. V. Kryvenko) (Kyiv: Lira-K: 2015) (in Ukrainian).
5. A. Yu. Zakgeym, *Obshchaya Khimicheskaya Tekhnologiya: Vvedenie v Modelirovanie Khimiko-Tekhnologicheskikh Protsessov: Uchebnoe Posobie* (Moscow: Logos: 2012) (in Russian).
6. A. A. Pashchenko, V. P. Serbin, and Ye. A. Starchevskaya, *Vyazhushchie Materialy* (Kiev: Vysshaya Shkola: 1985) (in Russian).
7. K. K. Pushkariova and M. O. Kochevykh, *Materialoznavstvo dlya Arkhitektoriv ta Dyzayneriv: Navchal'nyy Posibnyk* (Kyiv: Lira-K: 2018) (in Ukrainian).
8. A. V. Volzhenskiy, Yu. S. Burov, and V. S. Kolokolchikov, *Mineral'nyye Vyazhushchie Veshchestva (Tekhnologiya i Svoistva): Uchebnik dlya Studentov Vuzov* (Moscow: Stroyizdat: 1979) (in Russian).
9. P. F. Gordashevskiy and F. V. Dolgoryov, *Proizvodstvo Gipsovykh Vyazhushchikh Materialov iz Gipsosoderzhashchikh Otkhodov* (Moscow: Stroyizdat: 1987), p. 104 (in Russian).
10. O. P. Mchedlov-Petrosyan and V. I. Babushkin, *Kristallografiya*, **6**, No. 6: 933 (1961) (in Russian).
11. W. M. M. Heijnen and P. Hartman, *Journal of Crystal Growth*, **108**: 290 (1991).

12. S. Y. Petrunin, L. V. Zakrevska, and V. Ye. Vaganov, *XXII International Science and Technology Conference Proceedings 'Starodubov Readings. Construction, Materials Science, and Engineering' (April 19–21, 2012, Dnipro)*, vol. **64**, p. 74 (in Ukrainian).
13. V. Derevianko, N. Kondratieva, N. Sanitskiy, and H. Hryshko, *Journal of Engineering Science*, **XXV**, No. 3: 74 (2018); http://doi.org/10.5281/zenodo.2557324
14. V. Derevianko, N. Kondratieva, and H. Hryshko, *French–Ukrainian Journal of Chemistry*, **6**, No. 1: 92 (2018); https://doi.org/10.17721/fujcV6I1P92-100 (in Ukrainian).
15. L. Kondofesky-Mintova and J. Plank, *Superplasticizers and Other Chemical Admixtures in Concrete: Proceedings Tenth International Conference (October 2012, Prague)*, p. 423.
16. V. G. Zavodynskyi, *Komp'yuternoye Modelirovanie Nanochastits i Nanosistem: Spetskurs* (Moscow: Fizmatlit: 2013), p. 174 (in Russian).
17. Yu. V. Ustinova, S. P. Sivkov, and V. M. Aleksashin, *Bulletin of MSUCE*, No. 7: 130 (2012); https://cyberleninka.ru/article/v/izuchenie-kristallizatsii-dvuvodnogo-gipsa-v-prisutstvii-polimernyh-dobavok-1
18. V. V. Belov, A. F. Buryanov, G. I. Yakovlev, V. B. Petropavlovskaya, H.-B. Fisher, I. S. Mayeva, and T. B. Novichenkova, *Modifikatsiya Struktury i Svoistv Stroitel'nykh Kompozitov na Osnove Sul'fata Kal'tsiya* (Moscow: De Nova: 2012) (in Russian).
19. M. A. Sanytskyi and N. V. Kondratieva, *III All-Ukrainian Science and Technology Conference 'Modern Trends in the Development and Production of Silicate Materials' (September 5–8, 2016, Lviv)*, p. 93 (in Ukrainian).
20. A. F. Gordina, Yu. V. Tokarev, G. I. Yakovlev, Ya. Kerene, and E. Spudulis, *Building Materials,* **2**: 34 (2013) (in Russian).
21. *Fizika i Khimiya Poverkhnosti. Kniga I. Fizika Poverkhnosti* (Eds. M. T. Kartel and V. V. Lobanov) (Kyiv: O. O. Chuiko Institute of Surface Chemistry of the N.A.S. of Ukraine–Interservis LLC: 2015) (in Ukrainian).