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Nano-Modification of Building Composite Structures

Evgeny Chernishov, Olga Artamonova and Galina Slavcheva

Abstract

The paper reviews the theoretical framework of nano-modification principles of building composites and experimental verification of these principles. The concepts of nano-modification of building composite structures are studied. The paper also suggests the conceptual model of the nano-modification from the point of view of the evolutionary model of a solid-phase formation depending on the kinetics of heterogeneous processes. The technological tools of nano-modification of building composites are substantiated. Cement-based materials are shown as an object of nano-modification. Their hydration kinetics, phase composition, microstructure, and strength characteristics are investigated. The results are analyzed based on the special performance criteria which confirm that the efficiency of cement-based materials technological cycle can be improved by nano-modification.

1. Introduction

The scientific substantiation of the principles of structure management at the nanoscale level is the key point in the development of high-performance and ultra-high-performance concrete [1, 2]. It is the class of materials, which includes the nanostructured elements as part of their structure. Moreover, to regulate their structure and properties, it seems logical to use nanoscale various types of particles. Nowadays, the problems of synthesis and construction of high-performance and ultra-high-performance concrete structures in building technologies more actively rely on nano-concepts and nano-approaches. It is relevant to identify the potential possibilities and limitations of the application of nanotechnological approaches in solving specific problems of the technology of building materials.

2. Theoretical framework

While applying the technologies of building materials and stages of transitions in the processes of forming the structures of their solid-phase state, it is necessary to keep in mind hydration (lime, gypsum, cement), hydrothermal-synthesis (silicate autoclave) hardening systems, and thermal-synthesis (ceramics, glass) composites (**Table 1**) [1].

The fixed assets of the "nano tool," implemented in construction material technologies, include the influence and effect of "**top-down**" and "**bottom-up**" nanotechnological approaches.

Type of HS	Hydration synthesis		Hydrothermal synthesis	Thermal synthesis
Form of HS	Monomineral	Polymineral	Polymineral	Monomineral
Synthesis technology	Sol gel	Sol gel	Hydrothermal synthesis	Thermal synthesis
Precursors for the synthesis of HS	Lime	Portland cement	Basic and acid oxide	Basic oxide
The composition of the hardening systems	Portlandite	Hydrosilicates and hydroaluminates of calcium, hydrogrenades, calcium hydrosulfoaluminates	Hydrosilicates and hydroaluminates of calcium, hydrogrenades, calcium hydrosulfoaluminates	Solid solutions based on individual oxides
The resulting building composite	Portland-calcium-calcium and portland-alum-silicate	Cement concrete	Dense and cellular silicate concrete	Constructional and functional nanoceramics

Table 1.
Hardening systems (HS) for design and synthesis structures of building composites.

The "nano" "top-down" approach is based on the use of the phenomenon of changes in the energy state of the structure and, accordingly, the physical and/or physicochemical activity of surface and internal volumes of particles of a solid as they are crushed by mechanical or physical methods.

The effectiveness of the principle is determined not only by the nano- and micro-size of particles but also by the measure of the amorphization of their surface volumes. Amorphization is expressed in the "saturation" of volumes with structural defects of the nano-size range. The principle is the basis of the mechanochemical activation of the components of raw mixtures in the technologies of building materials.

The "**nano**" "**bottom-up**" principle is based on the management of condensation phenomena in the evolutionary route of the formation of a solid-phase state of a substance in hydration, hydrothermal-synthesis, and thermal-synthesis hardening systems. The effectiveness of the principle is determined by the possibilities of influencing the development of stages, transitions, selections in the evolutionary route, and, in general, the kinetics of heterogeneous processes of hydration, colloidation, and crystallization in systems (mixtures) of basic and acid oxides upon receipt of building materials.

"Nano tool," based on "top-down" principles, includes mechanochemical activation of the substance during the dispersion of the initial components of the raw mixes, physical and chemical activations during the high-temperature processing of the mixture components, compulsory compaction of particles of components of a mixture, etc. "Nano tool," implemented in the principles of "bottom-up," includes the means of controlling the solubility of components and the degree of saturation of the system with cations and anions; methods of changing the rate of condensation and crystallization through thermal or other physical effects; methods of changing the spatial and geometric environment in the system by introducing additives of nano-modifiers, for example, nanoparticles with both related and non-related crystal-chemical structure of the synthesized compounds; and techniques for changing the state of the surface of solid particles when using additives of surface-active substances, etc.

The "top-down" and "bottom-up" principles act in a systemic unity, and their presence in nanotechnology of building materials is an objective fact. The principles operate within the framework of their own laws. However, it happens within the single process of structure formation and the formation of a solid state of materials. The effects of the above principles in nanotechnology are articulated and super-imposed based on the principle of "top-down," which is expressed in the role and influence of the phenomenon of mechanochemical metamorphism of the structure of the initial components (according to Avvakumov, Hodakov, etc.) and from the "bottom-up" principle (the phenomenon of stereochemical and topochemical memory according to Bokiy, Belov, Mamedov, Oleinikov, etc.). The principle of "top-down" has a precursor (preparatory) role, ensuring the activation of the initial components of raw mixes in nanotechnology. The evolutionary route of the formation of the nanostructure of the solid phase on the principle of "bottom-up" is developed in the framework of the action of this role.

In the compositional structure of conglomerate building materials, two types of structures are distinguished according to their origin ("genesis"). The first, related to macro-, meso- and microstructure, is the result of the addition of ready-made granular particles. The second one, related to the micro-, submicro-, and nano-structure, is the result of the synthesis of particles in the evolutionary route of their formation. Both types of structures in their genesis are integrated in the composite. The genesis (formation) of the first type of the structure is carried out according to the concept and bases of the mechanics of granular media; at the same time, the nanotechnological top-down principle with the corresponding nano-modifying effects can be realized at the same time. The genesis of the second type of structure is carried out according to the concepts and bases of the condensation mechanisms, which is implemented in the framework of the action of the nanotechnological principle "bottom-up," which predetermines the effects of nano-modification in the evolutionary route of the formation of a solid state. Thus, the development of the technology of nano-modification of the hardening system structures and construction composites should proceed from the systemic unity of the "top-down" and "bottom-up" principles.

2.1 Evolutionary route of solid formation

Heterogeneity is the main feature of all hardening systems; therefore, when analyzing an evolutionary model, one should consider a heterogeneous composition consisting of different dispersion of solid particles placed in a liquid or gaseous medium (internal medium of the system) and in contact with the external environment space from which matter, thermal, mechanical energy, etc. can be introduced into the hardening system. When considering the processes of evolution of a solid substance in a heterogeneous system, a microvolume can be distinguished at a certain homogeneity. In this conditionally homogeneous system, the nucleation of a solid phase occurs.

In the chemical technology of homogeneous system substances, three determining methods for the synthesis and nucleation of solid particles (including nanoparticles) are distinguished: the ones leading to the formation of a new phase; the method based on the high-temperature reactions of interaction of two or more substances, leading to the formation of an insoluble product; and the method of condensation from the gas phase, when, as a result of redox reactions or hydrolysis reactions occurring in the gas phase, the solid phase is released.

In disclosing and analyzing a general evolutionary model of the formation of a solid, one can follow the interpretations of Melikhova [3]. In accordance with modern concepts applicable to systems of any composition, the following main stages

in the evolution of a substance can be distinguished in the formation of a solid: the nucleation of a solid phase, particle growth, agglomeration, and spontaneous transformation in time (**Figure 1**). In this case, it is necessary to speak of three evolutionary transitions between the stages and, accordingly, the phenomena of molecular, topological, and morphological selection. In the evolution of solids, two branches of the process development could be implemented: the left, corresponding to small (pre-foreign) supersaturations, and the right, corresponding to large (super-foreign) supersaturations of the phase-forming macrocomponent.

It is important to emphasize that each stage corresponds to a certain range of sizes of solid particles based on them. The size scale shown in **Figure 1** illustrates dimensional and geometric boundaries and limits. It is clear that we can use the "arsenal of nano" most significantly at the stages of nucleation of the phase and growth of particles; at other stages, other physicochemical methods of technological impact, affecting the micro- and macroscale of the evolutionary process, become priorities. This should be taken into account when developing methods of influence on each of the considered stages and transitions of the evolutionary route. Based on this, a detailed discussion of the determining stages of the evolutionary route and transitions between them should be carried out, bearing in mind the rationale and formation of "nanotools" but not only "nano" in the technology of building materials, if we take into account the problem of modifying the structure on all its scale levels.
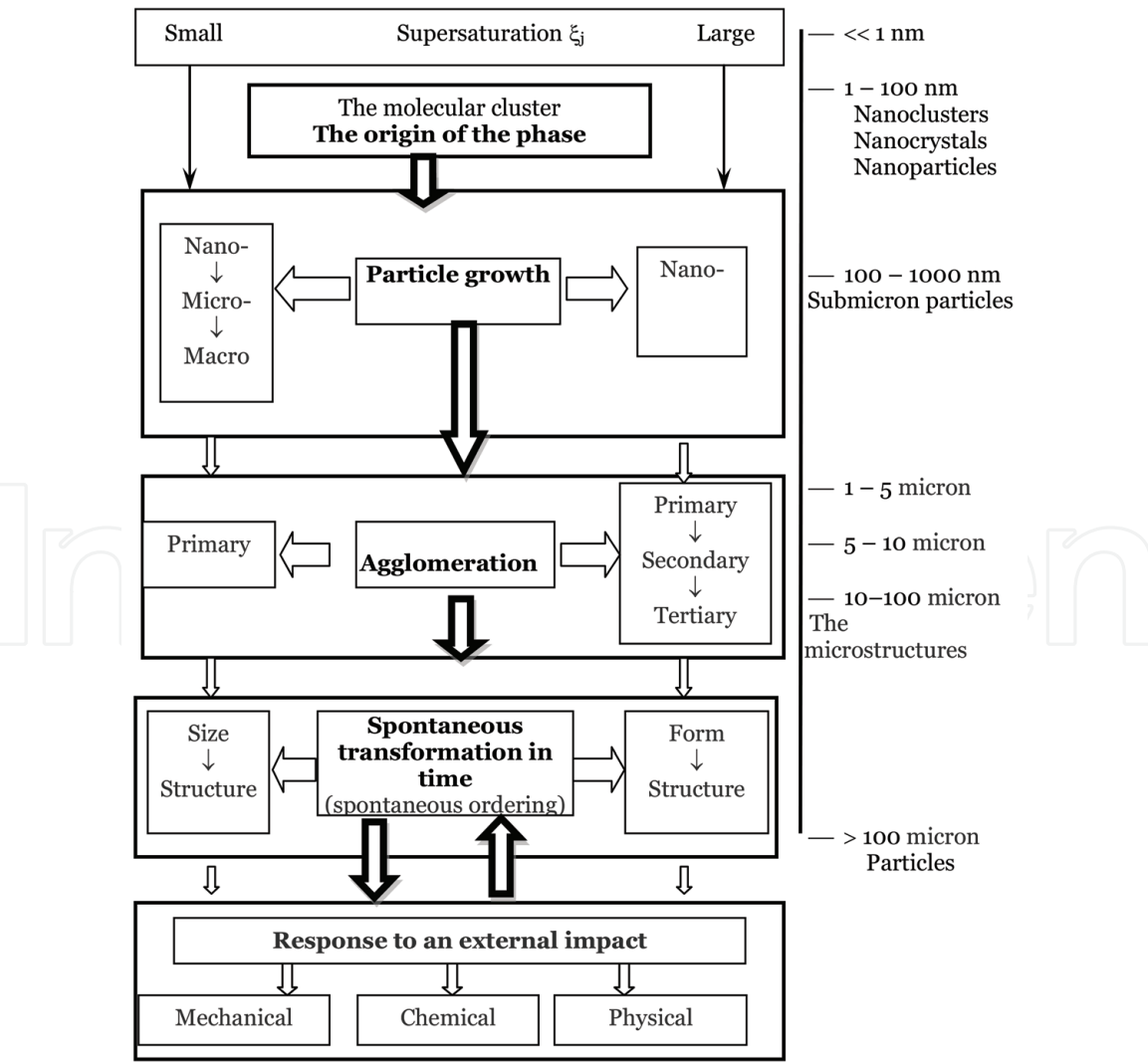

Figure 1.
The evolutionary path of formation of solid substances and "dimensional scale" of their structural components.

2.2 The "nucleation of the solid-phase" stage

According to the Gibbs-Volmer thermodynamic theory, the formation of a new phase is possible with a certain critical degree of supersaturation, which depends both on the nature of the starting materials and on the presence of condensation nuclei that can be introduced into the system from the outside. The formation of nuclei becomes possible when a certain (critical) degree of supersaturation of a solution is reached by the substance whose molecules are involved in the formation of a new phase.

Thus, bearing in mind the possibilities of nanotechnological influence on the stage of particle nucleation, first of all, one should speak about such control factors as the creation of supersaturation and the introduction of condensation nuclei (nuclei) from outside. The supersaturation can be created in two ways: by increasing the concentration of the substance molecules in the medium and (or) by decreasing its solubility.

2.3 "Growth of particles of phase-forming substance" stage

Each nucleated particle, being in supersaturated media, attaches to itself the molecules of the medium more often than their separation from the particles. In order to join a particle, the molecule moves from the volume of the medium to the surface of the particle, is adsorbed on it, and then, migrating along the surface, takes the place where its connection with the particle becomes energetically favorable and in this sense strong enough to fix on its place. The probability of fixing a molecule depends on its size, shape, and electronic structure. In fact, controlled molecular selection occurs on the surface of the growing particle.

Considering the decrease in the free energy of the system, a phenomenon of *molecular selection*, which develops in it, results in the following process: nuclei become clusters of molecules containing only slightly different in structure and size of the molecule.

From a nanotechnological point of view, it is possible to keep in mind the tasks of changing the concentration conditions of crystallization as well as the use of nano-additives with a crystal-chemical structure similar to the germ of the phase and providing targeted acceleration of the particles' growth processes of the phase-forming substance [4–6] and their morphological structure—finification. In connection with the three global transitions indicated by us during the evolution of a solid substance, it is expedient to refine the classification of additives, dividing them according to the size attribute into nanoscale, ultrafine, and microdisperse (**Table 2**). In the general case, the structure-forming participation and the modifying influence of nanoscale modifiers can be the result of interrelated mechanisms.

2.4 "Agglomeration" stage

After the accumulation of a sufficient number of particles in the system, when the probability of particles meeting and growing together becomes co-measurable with the probability of their molecular growth, the process of agglomeration begins.

There comes a second evolutionary transition "particle growth agglomeration." In this case, the main phenomenon is the topological selection of ordered aggregates, which consists in the fact that the medium destroys and eliminates disordered aggregates and contributes to the formation of ordered forms consisting of particles with similar morphological parameters.

№	Type systems	The name and the chemical composition	Particle size and morphology	The mechanism of action
1	The nano-sized	Nano-sized silica SiO_2 nH_2O	$\varnothing$ = 5–10 nm, spherical particles	(1) Direct chemical involvement of nanoparticles (NP) in heterogeneous processes of phase formation of hydrated compounds; (2) the catalytic role NP as nucleation (growth of a new phase)
2		Sol.$Fe(OH)_3$	$\varnothing$ = 5–10 nm, spherical particles	
3		Sol.$Al(OH)_3$	$\varnothing$ = 30–50 nm, spherical particles	
4		Montmorillonite, a synthetic $(Na, Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \bullet nH_2O$	~5–10 nm, hexagonal plates	
5		Chrysotile nanotubes $[Mg_3Si_2O_5(OH)_4]$	$\varnothing$ = 25–50 nm, l = 100–700 nm, a tubular structure	
6		Carbon nanotubes fulleroid-type carbon content ~99%	$\varnothing$ = 2 nm; l = 200 nm, tubes of graphite cloth	Increased packing density of particulate addition, changing the porosity of the material structure
7		The zeolite sol-type zeolite NaX, ratio Si/Al = 1.3...1.5	$\varnothing$ = 0.8–1.2 nm reticular structure	
8	Ultradispersed	"Astralen—S" water-soluble fullerene analogue carbon content ~99%	The average cluster size, 300 nm, a tubular structure	(1) Increasing the packing density of the addition of dispersed particles; (2) zoning structure
9		Micro silica SiO_2 nH_2O	~100–300 nm	
10	Microdispersed	Montmorillonite—natural $(Na, Ca)_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \bullet nH_2O$	<1 μm layered, leaf structure	Zoning structure hardening
11		Shungite—C 60–70%; ash 30–40%; SiO_2–35–50%; Al_2O_3–10–25%	0.1–10 μm, graphite-like globules	
12		Bergmeal—SiO_2–70–85%; Al_2O_3–5–13%; Fe_2O_3–2–5% и др	0.01–0.001 mm, spherical rounded opaline globules of silica	

Table 2.
Modifiers of nano-, ultra-, and micro-sized levels of dispersion and their mechanism of action.

In real technologies of materials, the stage of agglomeration can be regulated by the addition of additives of surface-active substances (surfactants), widely used plasticizers, and superplasticizers (SP) [7–10].

2.5 "Spontaneous structure formation" stage

The evolutionary changes of the hardening system are objectively related to the third evolutionary transition "agglomeration → spontaneous structure formation." At the end of the growth stage and the agglomeration stage, the state of the system is far from the equilibrium state, therefore at a certain period inside. Systems of substance and energy redistribution develop simultaneously, which leads to spontaneous ordering of the system. The phenomenon of morphological selection is observed, and a "change in the geometry of the system" takes place; ordered aggregates of a certain shape and size are formed instead of less ordered shapes.

Technologically, the management of the spontaneous structure formation stage can be based on different temperature processing, on the use of various types of forced compaction by pressing, on the introduction of additives of microparticles, etc. (**Table 3**).

Stage of the process	Transition phenomenon	Driving force	Management factors	Management techniques	Modifying mechanism	Modification result
Origin of the phase Particle growth	Molecular selection	Reducing the chemical potential of the system	(1) The radius of the nucleus phase; (2) the degree of supersaturation of the solution (concentration and solubility of the phase-forming substance)	(1) Methods of synthesis, depending on the type of the nascent phase; (2) the introduction of nano-sized additives	(1) Direct physicochemical interaction; (2) the catalytic role of nanoscale particles	(1) The formation of a molecular cluster; (2) a decrease in the activation energy of the process; (3) crystallization centers of the hardening structure
Agglomeration	Topological selection	Reducing the surface energy of the system	(1) The type of physical and chemical adsorption; (2) the degree of dispersion; (3) formation of a fractal grid of solvent	(1) The introduction of plasticizers and SP; (2) the introduction of nano- and ultrafine carbon particles	(1) Electrostatic interaction and dispersion of the system; (2) changes in the reaction surface and system morphology	(1) Change in thermodynamics and kinetics of the hardening process; (2) changes in the composition, structure, and properties of solids
	Morphological selection	Reducing the total energy of the system	(1) The change in the intergranular surface of the system; (2) the formation of additional boundaries	Heat treatment, pressing, the introduction of additives of microparticles	(1) Zoning structure of hardening; (2) implementation of topochemical memory additives	(1) An increase in the area of intergranular contacts; (2) dispersed reinforcement of the structure; (3) formation of ordered hardening structures with dense packing of crystals

Table 3.
Systematics of structural modification mechanisms on the main transitions of the evolutionary route solid substance formation.

The stage of spontaneous structure formation is completed by the formation of coagulation (thixotropically reversible) and condensation-crystallization (irreversible-decaying) structures that are capable of further evolutionary transformation when interacting with the external environment, which is associated with an evolutionary transition "spontaneous structure → response to external influence. In this case, the principle of equalization and equal distribution of substances and energies in the volume of each phase is implemented.

Summarizing the analysis of the evolutionary route of the solid state and the related analysis of engineering and technological methods and means of nano-modifying the structure, it is possibly reasonable to present a systematics of the main phenomena and driving forces of structural transitions between the stages of the route, factors controlling these transitions, and their mechanism effects on the hardening system (**Table 3**).

Using the method of introducing nanoscale particles, effects of structure formation control are being implemented. Those associated with the nano-size particles are playing the role of (a) structure-forming nuclei, (b) substrates for crystallization, (c) centers of new formation zoning in the matrix substance of the material, and (d) nano-reinforcing matrix element. In all of these cases, the essential point is the lowering of the energy threshold for activating the processes of synthesizing hardening systems and accelerating hardening. Another important point is the spatial geometric modification of the structure, which, as was noted, is its zoning and the corresponding effect on the characteristics of homogeneity-inhomogeneity and, as a result, on the mechanical properties of the material [11, 12]. Finally, we should also keep in mind the effects of disperse reinforcement [13, 14].

The effects of structure formation control could be observed when the method of introducing nanoscale particles is applied. These are associated with the nano-size particles playing the role of (a) structure-forming nuclei, (b) substrates for crystallization, (c) centers of new formation zoning in the matrix substance of the material, and (d) nano-reinforcing matrix element. In all these cases, the essential point is the lowering of the energy threshold for activating the processes of synthesizing hardening systems and accelerating hardening.

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3. Materials and methods

In the course of our experimental studies, we considered the possibility and efficiency of using 12 additives attributable [15, 16] to three groups on the basis of size: (1) the group of nano-sized ones are specially synthesized particles $SiO_2 \bullet nH_2O$, sols of aluminum hydroxide particles and iron hydroxide, montmorillonite, NaX type zeolite, chrysotile nanotubes, and fulleroid-type carbon nanotubes; (2) the group of ultrafine silica fume (waste of ferroalloy production), carbon pipes of the type "Astralen—C," and a departure from the combustion of high-energy fuel; and (3) the group of microdisperse natural montmorillonite, tripoli, and shungite.

These additives were monitored by the effect of their type, dosage, and methods of introduction into the cement-water suspension on the structure formation processes [16–20]. In experiments with changes in W/C, the introduction in some cases of superplasticizers (C-3 based on naphthalene lignosulfonate; GLENIUM® ACE 30 и Sika® ViscoCrete® 20HE based on polycarboxylate esters; Sikament FF

based on melamine sulfonate) fixed the degree of hydration in time and the kinetics of cement strength. The study of the hydration kinetics and strength of the modified cement stone was carried out based on the comparison of the reference cement system without additives.

When varying the dosage of nano-additives from 1 to 0.0001% of the mass of cement, it was shown that its optimal value corresponds to hundredths of a percent [16, 18]. Based on the monitoring, a different measure of the effect of the studied additives was revealed, and it was found that the most effective of them can be considered as a complex additive of SiO$_2$ nanoparticles in combination with Sika®ViscoCrete®20HE (additive CND) as well as individual addition of chrysotile or carbon nanotubes.

Below are experimental data on the use of this complex (additive CND) and the addition of carbon nanotubes of the fulleroid type of the brand "Nanocyl-7000," treated with ultrasound (additive CNT in the accepted designation) for the nano-modifying structure of the cement stone.

Portland cement CEM I 42.5 and these nano-additives with a dosage of 0.01% were used in the experiments for the production of cement paste with a W/C = 0.33. Studies of the parameters of the kinetics of the cement hydration process were carried out under thermostatic conditions at temperatures of 0, 20, 40, and 60°C (with, respectively, 273, 293, 313, 333 K), with the duration of the process implementation for 1, 3, 7, 12 hours and 1, 3, 7, 14, 28 days. The phase composition of the reference and nano-modified cement paste was monitored by an X-ray method (CuKα radiation, λ = 1.541788 Å, ARL X'TRA diffractometer). The processing of diffractometric data was carried out automatically using the PDWin 4.0 computer program. The hydration degree D$_h$ (C$_3$S) was calculated [21–23] by the formula:

$$D_h(C_3S) = \left(1 - \frac{I_m}{I_0}\right) \cdot 100\,\%, \tag{1}$$

where **I$_m$** is the diffraction intensity *of* 3CaO·SiO$_2$ (C$_3$S) (*d = 2.75 Å*) *phase for* hardening cement paste samples and **I$_0$** is the diffraction intensity *of* 3CaO·SiO$_2$ (C$_3$S) (*d = 2.75 Å*) for cement.

The hydration kinetics was formally described by the kinetic equation [24, 25]:

$$D_h(C_3S) = (k \cdot \tau)^n, \tag{2}$$

where $D_h(C_3S)$ is the *cement hydration degree* (g/g) to the point in time τ (hour), k is the *hydration rate constant*, and n is the *exponent of the kinetic equation*.

Taking into account Eq. (2), for all the above conditions, isotherms of the hydration degree were obtained and, on their basis, $n$cp was calculated considering this quantity based on the logarithmic equation

$$\mathbf{\ln(D_h) = \bar{n} \cdot \ln(\bar{k}) + \bar{n} \cdot \ln(\tau)} \tag{3}$$

We also determined $ln(\bar{k})$ for each of the temperatures and then considered the Arrhenius dependence $ln\bar{k} = f(1/T)$, by which the calculation found the effective activation energy (EEA) as an indicator characterizing the energetics of hydration process development in terms of the use of structure formation nano-modifiers. To draw a conclusion about the limiting kinetic or diffusion components of the cement hydration process, the temperature coefficients of its speed were determined. In this case, the calculation was carried out according to the van't Hoff rule using the kinetic dependences of the cement hydration degree on temperature obtained for different compositions.

The compressive strength of the hardened cement paste was determined after 1, 3, 7, 14, and 28 days in water-curing conditions; tests of samples with a size of "5 × 5 × 5 cm" were conducted on an INSTRON Sates 1500HDS test system; to ensure the statistical reliability of the results of physical and mechanical tests, the number of samples in the series ranged from 9 to 12. It was determined that the intra-serial coefficient of variability of the results of the strength assessment did not exceed 7–10%.

4. Results and discussions

The main problem of ensuring the conditions for the effective development of the process of cement hydration according to the criteria E and τ. in the case of nano-modification in the determining measure consists in the optimal combination of the kinetic and diffusion components of structure formation [26]. The kinetic component controls the evolutionary route of the formation of the solid phase during the hydration of cement as far as possible the realization of all the phenomena (stages, transitions, etc.) of the nucleation of particles of the new phase and their development; the diffusion component acting as opposed to the kinetic one controls the dynamics of the evolutionary route phenomena. With the optimal combination of these types of control, it is possible to ensure minimization of the energy intensity of the formation of the cementing bond and the duration of the hardening process.

The following conclusions about the energy efficiency of nano-modification are based on the results we obtained on speed change, temperature coefficient of speed, effective activation energy of cement hydration process under the influence of factors of introducing nano-additives, and changes in temperature conditions presented in **Tables 4** and **5** and in **Figure 2**.

The generalization of the experimental data shows that in systems with nano-modifying additives, the cement hydration process is substantially (**Table 4**) accelerated: to the daily duration of hardening at 20°C (293 K), the degree of hydration reaches at least 70–75%.

Such a result for the control "additive-free" system is recorded only by 28 days. And thus, in this example, hydration is accelerated by criterion τ. almost 30 times.

The effect of the accelerating action of additives is valid for all variants of the composition and temperature conditions of hydration, differing, however, in the magnitude and timing of the achievement of the limiting values of the hydration degree. For the options of low temperatures (0°C, 273 K), the hydration degree of 70–75% is reached by 7 days, if the additive of pressure coefficient is used, and by 14 days, if the additive of CNT is used. At the same time, in the "additive-free" system, such a hydration degree is not achieved at all. By the 28th day, it makes only 50% of the possible maximum value.

For elevated temperatures (40–60°C, 303–333 K), in systems with the considered nano-additives CND, the degree of hydration already reaches 80–85% by the hardening for 1 h; by 7 h it is 90%, and by the first day up to 95%. Based on this data, it can be concluded that, firstly, in the presence of nano-additives, the main part of the evolutionary route of cement hydration takes place almost within the first hour and, secondly, that the hydration of cement can be completed within the first day.

The effects of such acceleration of hydration are explained by the achieved decrease in the effective activation energy of the process under the conditions of nano-modification: the effective activation energy required for the process "start" decreases 2.3–2.8 times as compared with the control "additive-free" system.

Specimen ID	The cement hydration degree (mass%) for the process duration								
	Hour					Day			
	1	3	7	12	24	3	7	14	28
Curing temperature 273 K									
C + W	11	12	15	18	20	40	45	48	51
C + W + CND	37	42	54	57	62	67	72	75	78
C + W + CNT	28	33	37	42	49	55	64	69	73
Curing temperature 293 K									
C + W	39	41	49	53	55	61	65	68	75
C + W + CND	60	63	69	71	75	81	92	93	93
C + W + CNT	55	60	65	68	70	78	87	88	89
Curing temperature 313 K									
C + W	42	48	51	59	68	75	81	83	89
C + W + CND	81	85	88	91	93	95	96	96	97
C + W + CNT	78	79	83	88	91	94	95	96	96
Curing temperature 333 K									
C + W	71	75	79	85	91	92	93	95	95
C + W + CND	84	88	91	93	96	96	97	97	98
C + W + CNT	85	87	92	93	95	96	97	97	97

Table 4.
The hydration degree of cement depending on temperature for cement paste modified by nano-additives (0.01% mass cement).

Specimen ID	Hydration rate constant $\bar{k}$ in curing temperature				$\bar{n}$	EEA, kJ/mol
	273 K	293 K	313 K	333 K		
C + W	17.53	25.40	27.72	31.68	0.13	173.4
C + W + CND	46.53	54.19	56.71	57.19	0.08	61.7
C + W + CNT	42.84	53.55	56.00	57.29	0.08	76.2

Table 5.
Kinetic parameters of hydration process of cement paste modified by nano-additives (0.01% mass cement).

It is worth emphasizing that the experimentally obtained lowest EEA value (61.7 kJ/mol) corresponds to the use of a complex modifying additive based on nano-sized SiO_2 particles in combination with a superplasticizer. This is explained by the fact that, unlike carbon nanotubes, SiO_2 nanoparticles are related to the mineral phases of hardening cement neoplasms with a crystal-chemical structure that facilitates the formation of molecular clusters and nuclei on SiO_2 nanoparticles as active crystallization centers. We draw attention here to the fact that the accelerating role of the additive takes place, despite the fact that the surfactant present in the complex additive slows down the hydration processes.

Analyzing the results of kinetic studies, it is necessary to address the question of the feasibility of combining the factor of introducing additives of nano-modifiers with the temperature factor accelerating the process of cement hydration. And in this regard, we will review the data obtained on the values of the temperature coefficient of the reaction rate ($\alpha(T)$) (see **Figure 2**).
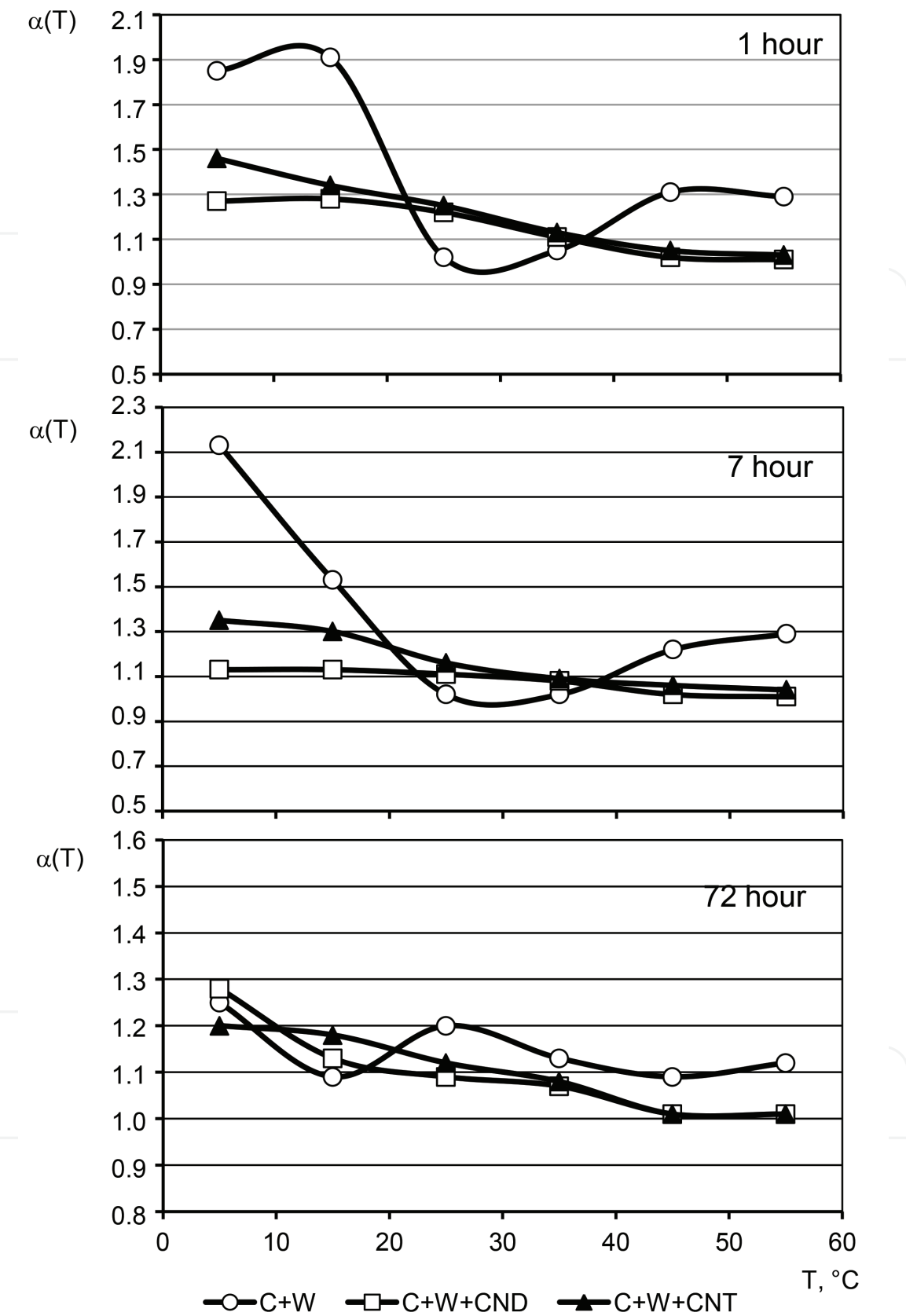
Figure 2.
The temperature coefficient of the reaction rate.

First of all, we note that only for the control "additive-free" system at lower temperatures of the hydration process, the situation of its kinetic control is realized. Indeed, the temperature coefficient of the reaction rate, up to the duration of hydration of 1 day, has a value close to 2 m (α(T) = 1.85–2.25). However, already after the 3 days, the coefficient α(T) decreases to values of 1.25 and subsequently (for durations

of 7, 14, and 28 days) remains at the indicated level. This indicates the transition of the process to the area of the diffusion control, which explains the relatively low (in the limit of about 50%) values of the degree of hydration, which are fixed for the standard system (see **Table 4**).

The use of nano-modifying additives fundamentally changes the kinetic picture of the process. It accelerates so much that even at low temperatures, in the first hour, it goes (see **Figure 2**) to the mixed (for the CNT $\alpha(T) = 1.46$) and diffusion (for the CND $\alpha(T) = 1.27$) control. The transition of the process kinetics from the kinetic control region to the diffusion region in systems with nano-additives is observed at a much earlier time than in the reference system.

In the cumulative effect of the introduction of nano-additives and temperature conditions, the manifestation of the first factor is much stronger. Therefore, the use of technologies that provide for raising the temperature of cement hardening above 30°C is not relevant but more unacceptable. Indeed, for all systems with additives, an increase in temperature leads to a decrease in the $\alpha(T)$ coefficient to values of 1.0–1.1, that is, to the transition of the hydration process to the region of strict diffusion control.

In contrast, for the reference "additive-free" system, the temperature increase is a positive factor for the kinetics of the process. In this case, we can speak about the phenomenon of the so-called "temperature breakdown," when the diffusion of anions and cations in the "inter-grain" volume through the "subsurface" volume is accelerated, with a layer of shielding surface of the cement grains. For this reason, at lower temperatures, the development of the process from the diffusion control region can pass into the mixed control region (the coefficient $\alpha(T)$ increases from 1.0–1.05 to 1.3).

Thus, it is clear that the use of nano-additives is accompanied by the change in the parameters of the development of the cement hydration process in terms of its kinetics and energy. The result of a possible reduction in the hydration time t is a consequence of the acceleration of the reactions due to a significant decrease in their effective activation energy. On the contrary, in the field of lower and possibly negative temperatures, the use of nano-additives seems to be very effective, providing a high temperature coefficient of the reaction rate, characteristic of the development of the hydration process in the kinetic region.

When modifying the structure of cement paste with nano-additives, the change in the parameters and indicators of the strength kinetics is decisive in terms of raising efficiency. These include the speed of curing, the duration of reaching the "tempering," and the achievable limit values of the strength of the hardened cement paste. Due to this fact, it was important to analyze the strength kinetics in relation to the type and dosage of nano-additives.

In the course of experiments, when *assessing the effect* of nano-modification of the structure on the strength, the above two additives in dosages of 0.01–1% by weight of cement were studied.

Figures 3 and **4** reflect the effect of these additives on the strength kinetics; a conclusion is drawn about the acceleration of the curing of the hardened cement paste using the minimum and maximum doses of additives. In the case of the use of the complex additive of nanoparticles SiO_2 in combination with a superplasticizer (CND), close to the limiting strength, values are achieved for compositions with different dosages by the third day of hardening. The use of CND allows you to provide 70% of the strength of the values achieved by 28 days, for 1 day. For the option of dosing an additive of 0.01%, an increase in the limiting values of strength up to 90 MPa against 50 MPa in the control "additive-free" system is noted. Such a difference is explained by the modifying effect of the additive on the dispersed and morphological composition of the cement stone neoplasms, which acquire a nano-dispersed and cryptocrystalline state. This is precisely in accordance with the
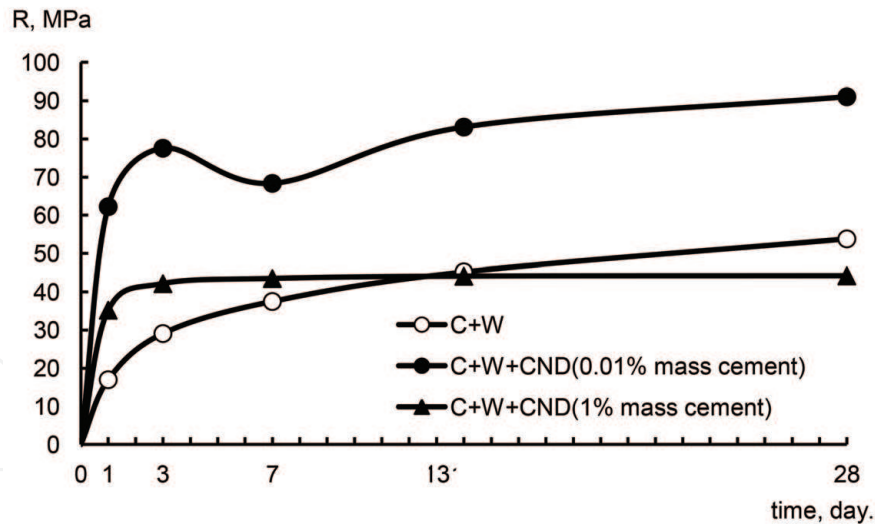
Figure 3.
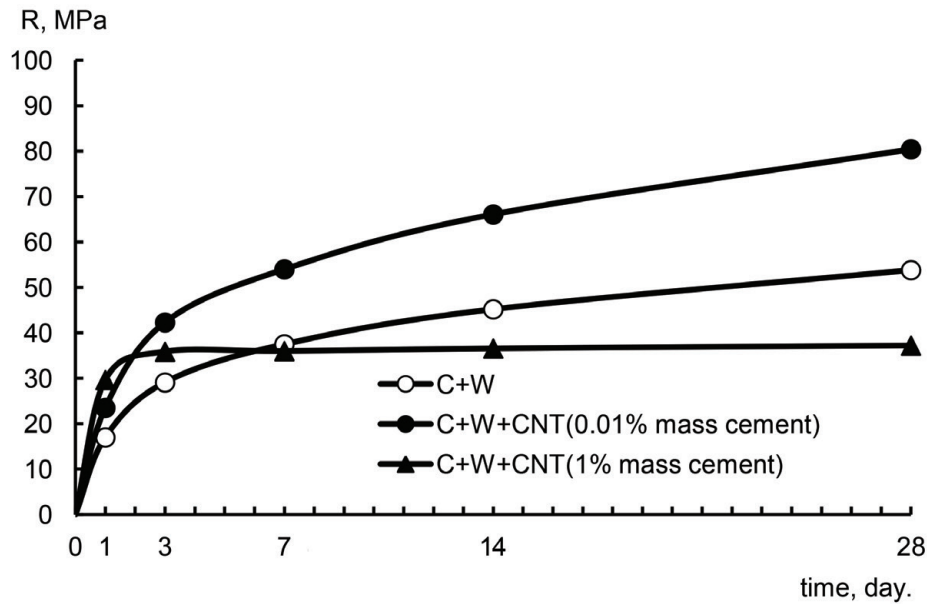*Strength kinetics curves of cement pastes modifying by CND.*

Figure 4.
Strength kinetics curves of cement pastes modifying by CNT.

well-known theory of "fine grain" of Rebinder P.A. and the pattern of Hall–Petch and determines the higher resistance of the modified structure to destruction.

A similar situation occurs when the carbon nanotube additives at a dosage of 0.01% are applied. However, the strength kinetics in this type of nano-modification is noticeably different in that in the early periods of hardening, strength is slower: achieving 70% strength from its values at 28 days old is provided in this variant for 7 days, and for 1 day cement stone gains only 20%. Another difference concerns the maximum achievable strength value, which is 80 MPa.

Based on this data, it can be observed that the introduction of an additive to carbon nanotubes is less effective in comparison with the addition of nanoscale particles of SiO_2 and above all in terms of the kinetic parameters of hardening strength.

Based on the results of the experiments, we should specifically dwell on the question of the strength kinetics for the variants with the dosage of additives of 1% by weight of cement. With this dosage, an accelerated increase in strength in the initial (1–3 days) hardening periods is also noted; however, no increase in strength is noted in the subsequent periods, and it remains at 35–40 MPa, which is lower than the

values for the control "additive-free" composition. It can be assumed that, at an elevated dosage, the so-called poisoning of the system occurs, when excessively accelerated hydration of cement and crystallization of new growths lead to the development of self-destructive crystallization pressure. This is true: in our experiments, which involved the introduction of a 5% dose of the additive of nano-particles SiO_2, self-destruction of cement paste samples was observed after the first day of hardening in normal temperature and humidity conditions. These experimental facts confirm the urgency of the problem of optimizing the dosages of additives recommended in the technology of nano-modification of the structure of cement stone.

Thus, it has been shown that the effect of nano-modification of cement paste in relation to R is that it hardens faster in the early stages of structure formation and becomes more durable when the curing process is completed. And this is the basis for a reduction in overall terms of hardening and refusal of heat treatment of hardening cement paste.

The criterion assessment of nano-modification effectiveness was made using comparative indicators, which allowed showing the measure of its action on the kinetic parameters of the hydration and hardening processes of cement paste (**Table 6**).

It has been established that the introduction of nano-modifying additives into the "cement + water" system changes the kinetic parameters of the evolutionary route development and accelerates cement hydration by 10–30 times, which is explained by a decrease in the activation energy of the process by 2–3 times.

Modification of the hardened cement paste structure according to the dispersion and morphology of the neoplasms is accompanied by an increase in the strength value at 28 days old by 45–65%, depending on the type of additive (at their dosage 0.01% by weight of cement).

The use of additives based on SiO_2 nanoparticles, which are related in their crystal-chemical structure to the minerals of the cement stone neoplasms, ensures the completion of the hardening process almost on the first day. The efficiency coefficient of nano-modification to increase the specific strength of hardened cement paste (that is, in terms of the effectiveness of the realization of the potential of the activity of cement in the synthesis of strength under the conditions of nano-additives) in the first days of hardening is 2.5 times higher for additive CND compared to adding CNT.

Criteria and efficiency ratios	Specimen ID		
	C + W	C + W + CND	C + W + CNT
EEA, kJ/mol	173.4	61.7	76.2
Required time to reach 75% cement hydration degree, day	28	1	3
Speedup cement hydration degree ratio	—	28–30	9–10
Relative strength hardened cement paste, $R(\tau)/D_h(\tau)$, MPa			
in 1 day	31	83	71
in 7 day	58	74	62
in 28 days	72	98	90
Strength hardened cement paste, $R(\tau = 28\ day)$, MPa	55	90	80
Increase strength ratio, $R(\tau = 28\ day)$	—	1.64	1.45
Required time to reach 75% of strength hardened cement paste, day	7	1	7

Table 6.
Criteria and efficiency ratios of cement paste nano-modification by the additives CND and CNT.

By reaching the "mature" 28-day-old age, the magnitude of the efficiency coefficient of nano-modifying increases the specific strength of hardened cement paste which is 1.36 for the additive of CND and 1.25 for the addition of CNT, and this shows that the effect of nano-modifying with the introduction of additives is not just in the first periods, when their accelerating effect is manifested on the parameters of hydration kinetics and, accordingly, on quantitative accumulations of the neoplasm phase but also in regulatory terms (28 days), when the quality begins to manifest itself of the cement hydration products.

5. Conclusions

Based on the theoretical analysis of the basic models of the kinetics of heterogeneous processes of structure formation of cement-based materials, we proved that they are the subject and purpose of nanotechnological control. The possibilities of regulating the evolutionary route of formation of a solid substance for cement-based materials at the stages of phase nucleation, particle growth, their agglomeration, and spontaneous and self-organized structure formation are revealed. It is shown that in the evolution of the structure of cement-based materials at the nanoscale level, its nano-modification is determined by a set of controls. In this complex, one of the effective means is the use of nanoscale additives, which determine the direct nano-modification of structural elements at the level of individual crystals and crystalline intergrowth, in the zoning and clusterization of the microstructure.

It was experimentally shown that the use of nano-modifiers based on nanoscale SiO_2 particles and carbon nanotubes determines the acceleration of hydration, hardening by 3–10 times, increasing the maximum values of the strength of cement-based materials by 1.5–2 times.

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