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Factors and mechanisms of nanomodification cement systems in the technological life cycle

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Abstract. The paper presents an analysis of the kinetics of heterogeneous processes and patterns of solid formation to substantiate factors and technological methods for nanomodifying the structure and properties of cement-based composites. According to the general evolutionary model of solid formation and evolution of hydration hardening systems model, the main factors and criteria of cement systems nanomodification have been identified for all stages of the technological life cycle. In accordance with the factors of nanomodification of cement systems, the technological methods of nanomodification are identified. As a result of nanomodification, the effects in the structure formation of cement systems are predicted and confirmed by experimental data. Theoretical analysis and experimental results showed that the factors and methods of nanomodification meet the terms of controlling the fracture strength of the cement-based composites. Together, the effects of nanomodification of the structure and factors of increasing the fracture resistance will determine the effectiveness of solutions for engineering practice in terms of reducing the time and the energy costs for processes in the life cycle of cement-based composites, enhancing their quality.

1. Introduction

Dozens of solid-state kinetic models developed over the 20th century are used in kinetic studies. Detailed analysis and systematization of commonly employed models presented in [1] allow us to classify them as nucleation, geometrical contraction, diffusion, and reaction order.

Kinetic models used for cement systems are a special interpretation of the basic solid-state kinetic models. The earliest of the general approaches to the description and modeling of structure formation processes and the resulting structure of cement systems are presented in [2].

The proposed models mainly relate to the description of the kinetics and features of cement hydration processes, the formation of the hydration products' structure under the influence of various factors, hardening kinetics, and strength development.

For example, Poppe et al. [3] and Ye et al. [4] proposed a model of the hydration process and microstructure development of limestone concrete. Kishi and Saruul [5] and Maekawa et al. proposed a model for evaluating the heat release rate of hardening concrete. Lothenbach et al. [7] proposed thermodynamic modeling of concrete hardening. The nucleation effect and effect of the formation of monocarboaluminate phase were modeled in [8–9]. In [10–15], the authors proposed effective functions for taking into account the effects of limestone, silica fume, slag, and fly ash on cement hydration, heat production rate, microstructure and strength development of concrete. Concerning the problems of nanomodification, [16–18] also proposed several special models, which allow one to take into account the effects of nanosilica introduction for hydration processes. All of these models allow one to rather accurately

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quantitatively takes into account the influence of individual components in cement-based composites on the kinetics of hydration processes, structure, and properties.

However, these models relate to individual private processes in the total set of problems of modifying (including nanomodifying) the structure and properties of cement-based composites in their technological life cycle.

We consider nanomodification of the structure as an action for organizing the processes of hydration and hardening of cement systems. Therefore, when substantiating the means of nanomodification, it is necessary to influence their kinetics and energy. The result of nanomodification should be to increase the speed and reduce the time of hydration and hardening processes, reduce the energy costs of these processes, and increase the strength of cement-based composites. Therefore, to advance nanomodification principles of cement-based composite structures, it is necessary to identify factors and technological methods of nanomodification. This will allow us to determine the options for technological solutions for engineering practice.

Therefore, it seems necessary to isolate and systematize existing conceptual models for the main phenomena and processes of nanomodification of a structure that reveal the relationships in the system "nanomodification factor – nanomodification technology – the result of nanomodification of a structure".

In this article, concerning the cement system, we present a theoretical analysis:

- 1) of the kinetics of heterogeneous processes of solid formation;
- 2) of the patterns governing the destruction processes.

The purpose of the analysis of these processes and patterns is to substantiate factors and technological methods for nanomodifying the structure and properties of cement-based composites.

2. Methods

The presented study used theoretical analysis. The previous studies, which are discussed to confirm the result of the theoretical analysis, used the following methods.

The amount and size of the colloidal nanoparticles SiO_2 synthesized by the sol–gel process were determined using dynamic light scattering (Photocor Complex spectrometer), and transmission electron microscopy (TEM) (Transmission Electron Microscope H-9500, $v_{acs} = 75$ kV).

The phase composition of the hydration products was controlled by the XRD-method (ARL X'TRA diffractometer, $\text{CuK}\alpha$ radiation ($\lambda = 1.541788$ Å)). X-ray decoding and phase identification were carried out using PDWin 4.0.

The morphology of the cement paste structure was examined on a JEOL JSM-7001F scanning electron microscope.

The hardening kinetics were evaluated by testing samples, cubes $5 \times 5 \times 5$ cm in size, after 1, 3, 7, 14, 28 days of curing under normal temperature and humidity conditions ($t = 20$ °C, $RH = 95 \pm 5$ %). The strength testing was carried out on a universal 4-column floor hydraulic test system INSTRON Sates 1500 HDS.

3. Results¹

3.1. Analysis of the kinetics patterns of heterogeneous processes of solid phase formation in cement systems

The evolution of solids in a real heterogeneous system is a collection of parallel and sequential phenomena and processes of solid phase formation. Moreover, the evolutionary hardening route of cement systems is a variation of the general form of the evolutionary route [19]. It is characterized by the stages and processes:

- generation of hydration products' particles,
- growth and accumulation of hydration products' particles,

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- agglomeration of individual primary particles of hydration products, by compacting them into aggregates,
- spontaneous structure formation (Ostwald ripening and recrystallization of hydration products' particles).

The nanomodification technology should be aimed at these stages and processes to obtain optimal crystal structures, their agglomerates and crystallites, hydration products in general.

Table 1 presents systemically the factors and technological control methods during nanomodification and the expected effect of nanomodification for each of the indicated stages and processes. The systematization is based on the thermodynamic Gibbs-Volmer theory of the formation of a new phase in the overseasable solutions (equations 1–4) that has been analyzed in [21]. Equations 5–8 are obtained in the J.D. Tretyakov's works, devoted to nonlinear dynamics and thermodynamics of irreversible processes in chemistry and technology and in the of E.A. Goodilin's works, devoted to the crystallization processes in chemical materials science. Let us consider them sequentially.

Table 1. To conceptual nanomodification models for the main stages of the evolutionary hardening route of cement systems.

ER stage		The origin of the phase		Conceptual kinetics models of heterogeneous processes of structure formation	Control factors for nano-modification	Control methods for nanomodification	Expected effect of nanomodification
Scale	Transition phenomenon	Particle growth	Structure level				
1 – 100 nm	Molecular selection	1) the ratio of cations and anions in the source system; 2) the critical radius of the crystal nucleus (r_{cr}); 3) the shape factor of the crystal nucleus; 4) the number of point defects per unit of volume of the crystal nucleus.	Single crystal	<p>Energy and size of a critical nucleus:</p> $\Delta G_{cr} = \frac{16\pi\sigma^3 V_m^2}{3R^2 T^2 (\ln \gamma_{cr})^2}; \quad (1)$ $r_{cr} = \frac{2\sigma V_m C_1}{T(C - C_1)}. \quad (2)$ <p>The total number of crystallization centers</p> $I_{cr} = a \cdot \exp \left[-\frac{1}{RT} \left(\frac{16\pi\sigma^3 V_m^2}{3(\Delta\mu)^2} + E_{act} \right) \right] + I_{sec} \quad (3)$ <p>The total increment of the volume of a new phase</p> $dV = \frac{4\pi J}{3} [V_0 - V(\tau)] g^3 (t - \tau)^3 d\tau \quad (4)$	<p>1) the degree of supersaturation of the initial solution; 2) the creation of additional crystallization centers</p>	<p>1) a change in the thermodynamic conditions of synthesis; 2) the introduction of nanoscale additives; 3) the introduction of surfactants.</p>	<p>1) acceleration of the formation of a molecular cluster; 2) lowering the activation energy of the process.</p>

ER stage					Conceptual kinetics models of heterogeneous processes of structure formation	Control factors for nano-modification	Control methods for nanomodification	Expected effect of nanomodification
Scale								
Transition phenomenon								
Structure level								
Structural parameters to be nanomodified								
Agglomeration	100 – 1000 nm	Topological selection	Crystalline intergrowth	<p>1) the size and shape of the intergrowth estimated by the specific surface area (S_{ag}); 2) the number of crystals in the intergrowth (N_c); 3) the number of crystal contacts in the intergrowth (N_{cc}); 4) the contact strength depending on its type (R_c); 5) the number of linear and planar defects in the intergrowth.</p>	<p>Aggregate specific surface area</p> $S_{ag} = \frac{1}{2} \cdot \pi \cdot d_0^2 \cdot N_0' = 2\pi\eta_f (D_0 - d_0)^2 \quad (5)$ <p>The number of particles in the aggregate</p> $N_q = n_f \cdot \left(\frac{D_0}{d_0}\right)^3 \quad (6)$ <p>Change in the area of the phase boundary:</p> $\Delta S = n_f \cdot \left(\frac{D_0}{d_0}\right)^3 \cdot \pi \cdot d_0^2 - 2 \cdot \pi \cdot n_f \cdot (D_0 - d_0)^2 = \quad (7)$ $= \pi \cdot n_f \cdot d_0^2 \left[\left(\frac{D_0}{d_0}\right)^3 - 2 \cdot \left(\frac{D_0}{d_0} - 1\right) \right]$ <p>System energy change</p> $E_{aggl} = E_k + E_s - E_r. \quad (8)$	<p>1) the formation of a fractal network of the solvent; 2) a change in the type of physicochemical adsorption at the phase boundary.</p>	<p>1) the introduction of nanoscale and ultrafine carbon particles; 2) the introduction of surfactants plasticizing</p>	<p>1) a change in the thermodynamics and kinetics of the hardening process; 2) a change in the structure and properties of the crystalline intergrowth</p>

ER stage		Transition phenomenon	Structure level	Structural parameters to be nanomodified	Conceptual kinetics models of heterogeneous processes of structure formation	Control factors for nano-modification	Control methods for nanomodification	Expected effect of nanomodification
Scale								
Spontaneous structure formation		1 – 100 μm	Morphological selection	Cementitious substance	<p>1) the volume ratio of crystalline and amorphous phases;</p> <p>2) the volumetric ratio of morphological differences: cryptocrystalline; fiber-needle; lamellar-prismatic;</p> <p>3) the specific volume of crystalline and gel pores.</p>	<p>Jander's equation:</p> $\frac{dx}{dt} = \frac{k_2}{x}, \quad (9)$ <p>or $x = k_3 \cdot \sqrt{t}, x^2 = k_4 \cdot t.$</p> <p>The magnitude of the change in the morphological parameter in the initial period of crystallization :</p> $\frac{\Delta l}{l} = \frac{1}{3} \cdot \frac{\Delta V}{V} \approx \frac{9 \cdot \sigma \cdot l}{4 \cdot \eta \cdot r} \cdot t, \quad (10)$ <p>Arrhenius equation</p> $K = A \cdot e^{-\frac{E_a}{RT}} \quad (11)$	<p>1) a change in the intergranular surface of the system; 2) the formation of additional interfaces; 3) the formation of ordered hardening structures with close packing; 4) the optimization of the ratio of amorphous and crystalline phases and their morphology; 5) the regulation of the structure of porosity.</p> <p>1) heat treatment; 2) pressing (compaction);</p> <p>3) the introduction of additives of microparticles (microfillers);</p> <p>4) dispersed structure reinforcement.</p>	<p>1) a change in the thermodynamics and kinetics of the hardening process;</p> <p>2) a change in the structure and properties of the cementitious substance.</p>

3.2. The particle generation process of hydration products

The use of nanotechnological control actions is motivated by the desire to accelerate the accumulation of hydration products, to reduce the energy costs of the process. At the same time, it is necessary to structurally divide the volume of accumulated hydration products in the system, bearing in mind the possibility of the formation of primary particles with controlled crystal-chemical and geometric characteristics.

To justify the factors controlling the development of the stage, let us turn to the analysis of conceptual models of the kinetics of the process (see Table). The process should be considered in the framework of the kinetic theory of the formation of a new phase. Therefore, in terms of control factors, it must be correlated with:

- the crystallization temperature (T);
- the specific surface free energy of crystals (σ);

- the molar volume of the new phase (V_m); the degree of supersaturation (γ), which is included in the ratio $\Delta\mu = RT\ln(\gamma + 1)$;
- the activation energy of the transition of ions, molecules from the medium to crystallization centers (E_{act});
- the intensity of secondary nucleation in the volume of the initial phase (I_{sec}), which is associated with external crystallization centers, for example, nanoscale particles.

In accordance with the Gibbs–Volmer theory [20], the formation of a critical-size nucleus (r_{cr}) is modeled by the equation for the total crystallization energy ΔG_{cr} (see Table). The appearance of nuclei becomes possible when a certain (critical) degree of supersaturation of the solution is reached with that substance whose molecules are involved in the formation of a new phase. The simplest ratio characterizing supersaturation has the form

$$\gamma = (C_m / L_{mj}) - 1, \quad (12)$$

where γ is the degree of supersaturation; C_m is the number of molecules or clusters from which the particles are built, per unit of volume of the medium; L_{mj} is the boundary value of C_m for the given particle.

The total number of the crystallization centers (I_{cr}) arising in a unit of volume of a solution, or the total intensity of their primary and secondary formation, depends on the kinetic coefficient of this process (α). The main means of control at this stage is the degree of supersaturation of the initial solution, which affects the rate of appearance and structure parameters of the crystal nucleus. With this in mind, in nanotechnology, one can turn to the methods of controlling the state of supersaturation, for example, introducing nanoparticles with a cognate crystal-chemical structure (to change C_m) and/or regulating solubility through thermal or other effects on the system (to change L_{mj}).

Regarding the first one, we can note that the chemical affinity (mineralogical and dimensional) of the introduced nanoparticles as possible centers of nucleation of particles of the solid phase is crucial for molecular selection in the system, that is, for the intensification of the first transition in the evolution path of a solid substance, “phase nucleation” – “growth particles”. Against a decrease in the internal energy of the system, the phenomenon of molecular (ion) selection [21] acts, as a result of which clusters of molecules (ions) become nuclei, containing, first of all, molecules (ions) similar in structure and size.

Thus, the mechanism of the nanomodifying effect of additives at the level of formation of a single crystal is associated with the possibility of direct chemical participation of nanoparticles in heterogeneous processes of phase formation of hydration products, which accelerates the development of the molecular cluster of the particle nucleus. And this possibility is determined by the chemical and mineralogical composition of the introduced nanoparticles and the activity of their surface. Based on these features, one can characterize and select additives for nanomodification technology [23].

3.3. The growth and accumulation stage of the particles of hydration products

The development of crystals after their nucleation is realized as a heterogeneous process that occurs when the interface is formed between the initial phase and hydration products. At this stage, the morphology of the system is constantly changing, due to the logical development of the phenomenon of topological selection. During selection, the medium destroys and eliminates disordered forms and promotes the formation of ordered forms consisting of particles with close geometric parameters.

At this stage, as a result of nanomodification, structural parameters such as the shape coefficient of the crystal, the number of probable point defects per unit of volume of the crystal can be changed (see Table).

The consideration of the main conceptual models for this stage (in a quantitative formulation of the question) is based on the assumption that after the appearance of the crystallization center in the volume V_0 at the time $t = 0$, the growth of the new phase occurs isotropically with a constant linear rate ν [20]. Then, at time $t = \tau$, the volume that the new phase will occupy will be equal to

$$V(t) = \frac{4\pi}{3} \nu^3 \tau^3. \quad (13)$$

The number of crystallization centers that appear in the system over a period of time from τ to $\tau + d\tau$ with a constant rate of nucleation of centers per unit of volume is $J[V_0 - V(\tau)]d\tau$. By the time $t > \tau$, the

total increment of the volume of the new phase only due to the centers arising in the time interval from τ to $\tau + d\tau$ will amount to dV (see Table). Moreover, the conceptual model of the particle growth process has the form

$$\frac{V(t)}{V_0} = 1 - \exp\left[-\frac{\pi}{3} J g t^4\right]. \quad (14).$$

The substance is supplied to the growing supercritical nucleus due to diffusion (D) from the surrounding solution. The growth rate of the nucleus (ν) will be equal to the rate of increase of its radius due to the molecules deposited on the spherical surface of the nucleus.

The structure-forming role and the modifying effect of the addition of nanomodifiers at the stage of particle growth and accumulation are associated with the catalytic role of nanoparticles as crystallization centers with the corresponding effect of lowering the energy threshold of this process and its acceleration. It should be assumed that the main control factor at this stage is the creation of additional crystallization centers. This is ensured by the introduction of a reasonable dose of nanoadditives of optimal size and a suitable crystal-chemical structure.

In addition, it should be noted that to form the necessary dimensional habit of crystals it is advisable to introduce certain surface-active substances (surfactants), which can selectively block the growth of their faces. As a result, the geometry of the crystals changes, for example, the formation of long crystals, which determine the effect of self-reinforcing and hardening of the structure of hydration products.

In the evolutionary route, the second transition “particle growth” – “agglomeration” objectively occurs, as a result of which the cement system is structured at the level of crystalline intergrowth.

3.4. Agglomeration stages of the particle of hydration products

At this stage, a spatial grouping of hydration products' particles takes place through adhesion. As a result, larger secondary particles are formed. Agglomeration occurs by binding of primary particles due to weak (leading to the formation of aggregates) or stronger (leading to the formation of agglomerates) interactions. Meanwhile, the primary particles in the agglomerate and aggregate to a large extent retain their primary shape and size.

Thus, in controlled agglomeration, the object of nanomodification is a polycrystalline intergrowth with the required characteristics and parameters.

Let us consider the basic conceptual models for this stage. The driving force of the agglomeration process is the desire of the system to reduce the area of the phase boundaries. The external surface area of the secondary particle is

$$S'_{ag} = \pi \cdot \eta_f \cdot (D_0 - d_0)^2. \quad (15)$$

On this surface of the aggregate, there are primary particles in the amount of

$$N'_0 = \frac{S'_{ag}}{\bar{s}_0} = 4 \cdot \eta_f \cdot \left(\frac{D_0}{d_0} - 1\right)^2, \quad (16)$$

where $\bar{s}_0 = \pi \cdot d_0^2 / 4$ is the projection of one particle onto the surface.

From here, we can proceed to the ratio for the specific surface area of the aggregate (S_{ag}) in contact with the liquid phase (see table). The ratio takes into account the dependence of S_{ag} on the linear size of the aggregate (D_0), the diameter of the nanoparticle (d_0), and the packing density of particles in the aggregate (η_f). Based on this, it is possible to determine the number of particles entering the aggregate (N_q) and the change in the total area of the phase boundary (ΔS). With a decrease in the size of the initial particles of the nucleus during nanomodification, the number of released energy increases, which contributes to the intensification of agglomeration and the reduction in the duration of the process. The agglomeration process takes place in the liquid phase (in water), in which primary particles are present in a certain amount. In this case, the water fractal network can specify a certain structure during the formation of secondary particles, aggregates, agglomerates. This will be directly related to the energy effects of

agglomeration. The energy released during agglomeration (E_{aggl}) can be composed of the energy E_k necessary to overcome the adhesion forces between the agglomerates, the energy costs to wet the formed surface of the agglomerate E_s and overcoming the resistance forces of the medium E_r when moving the agglomerate (see Table).

Thus, the special formation of the fractal structural network of the solvent (water) should be attributed to the main factor of nanomodification at this stage, since this causes a change in the mechanism of physicochemical adsorption at the phase boundary [24]. The formation of a fractal network of water can be achieved, for example, by introducing nanosized and ultrafine carbon-containing particles, which initially physically and chemically interact with a liquid medium (for example, mixing water), form its ordered “frame” structure due to hydrogen bonds and Van der Waals interactions. It is the resulting structural network that sets the necessary geometry of the crystalline structure (the number and packing density of aggregates and crystallites), that is, ensures its change, which ultimately affects the properties of the crystalline intergrowth.

The formation of a structured liquid phase can also be based on the method of introducing plasticizers and superplasticizers as a means of nanomodification. Their use allows us to control the process of agglomeration of crystals by changing the type of physicochemical adsorption at the phase boundary. The structure-forming participation of plasticizing additives is associated with mechanisms providing a change in the thermodynamics and kinetics of the process, making it possible to control the size and shape of the agglomerate, intergrowth, the number of crystals in them, and their contacts.

It is important to emphasize that the agglomeration process transfers the structure from the nanometer to micrometer size range. In this case, a structure is formed from individual crystals, which are represented by phases of typical mineralogy and morphology, filling the intergranular volume in the composite. The result is a continuous spatial framework of hydration products as a matrix of cement-based composites.

At the stage of growth and agglomeration, the arising formations are characterized by the disequilibrium of the thermodynamic state. Therefore, in the evolutionary route between the stages of “agglomeration” – “spontaneous structure formation”, the phenomenon of morphological selection develops, stimulated by the approximation of the size, shape, state of particles of their agglomerates, crystallites to equilibrium.

3.5. The stage of spontaneous structure formation of hydration products

In spontaneous structure formation, the size and shape of particle agglomerates change so that the minimum internal surface energy of the system is ensured. The morphological selection also determines the evolutionary transition of the structure to a new level – the level of hydration products.

The kinetics of processes at the stage of spontaneous structure formation is determined by:

- heat and mass transfer with a growth-supporting (internal and external) environment,
- molecular kinetic phenomena at the boundary “surface of the solid phase – medium”.

There are many conceptual models for describing this mechanism. Of these, Jander's equation [26] in our considerations can be applied under the assumption that the limiting stage of the process is the diffusion of reagents through the interaction product layer (dx/dt), and its diffusion layers on the grain surface of the initial components are flat. The rate of formation of a single three-dimensional crystalline structure is determined by:

- crystallization product layer thickness (x);
- constants depending on the properties of the reactants and the process conditions (coefficients k_2, k_3, k_4 , characterizing the nature of the reacting substances) and process time (t) (see Table).

With this in mind, the regulation of the heat treatment modes may be the technological method of changing the thermodynamics and kinetics of the process at this stage.

The emerging morphology of the cementing substance is determined by a change in the morphological parameter ($\Delta l/l$) in the initial period of crystallization of an integrated three-dimensional crystalline structure. It depends on several factors:

- the initial length (l) and volume (V) of the solid phase,
- their changes (Δl) and (ΔV) over time t ;
- the particle radius of the solid phase (r);

- the surface tension at the liquid – solid boundary (σ);
- the viscosity of the liquid phase (η).

As a result of the modifying effect, we can:

1. achieve a change in the state of the intergranular surface of the system;
2. promote the formation of additional types of interface;
3. form ordered hardening structures with close packing of crystals with a corresponding change in the structure of porosity of the crystalline intergrowth.

At the stage of spontaneous and self-organizing structure formation, the consequences of nanomodification undertaken in the previous stages will be manifested indirectly. For example, this may refer to the zoning phenomenon of the hydration products' structure.

3.6. The nanomodification of the structure of the cement system from the point of view of the fracture mechanics

According to the fundamentals of the manifestation of the structural properties of materials, let us indicate that the resistance of cement-based composites to destruction is based on three determining propositions [6]:

- the first propositions reflect the role and importance of physicochemical bonds that provide the level of possible resistance of the structure to mechanical stress;
- the second propositions take into account the conditions for the formation of the stress state of the material through the dependence of the measure of uniformity (heterogeneity) of the stress field arising in it on the uniformity of the composition and structure of the composite;
- the third propositions take into account the essence of the mechanism of destruction of the material in a direct relationship between the development of plastic deformation, the formation, and propagation of cracks in the material, and its composition and structure.

In problems of increasing the potential of the structure's resistance to fracture, it is advisable to single out the levels of its nanomodification:

- the level of a single crystal;
- the level of their agglomerates and crystalline intergrowth (crystallite);
- the level of hydration products.

When considering the factors of structural modification at the level of individual crystals, the well-known Hall-Petch equation can be used [27],

$$\sigma = m \cdot \sigma_0 + m \cdot k \cdot d^{-\frac{1}{2}}, \quad (17)$$

where σ is the ultimate strength; m is the coefficient associated with the characteristics (crystal chemistry and morphology) of the structural unit; σ_0 is the stress required to cause the beginning of the fracture of the structural unit in the absence of resistance from the boundaries in the crystallite; d is the structural unit size; k is the stress concentration at the top of the initial crack, depending on the number and nature of defects in the structural unit.

This equation reflects the relationship of the ultimate strength σ of a structural unit with its size d , crystal-chemical and morphological characteristics and the degree of imperfection, that is, with those structural parameters that are subjected to change through nanomodification at the stage of nucleation of solid particles.

At the level of agglomerate and intergrowth of crystals (crystallite), the influence of individual crystals on strength is realized through the spatial-geometric design of their compacted structure. The strength of the contacts in the intergrowth is a probabilistic distribution function of values in the range from the maximum possible value for regular (for example, epitaxial) to the minimum for non-regular contacts of coalescence or contiguity. In general, the fracture resistance is determined by the features of the packing of crystals into enlarged crystalline agglomerates (aggregates) and intergrowth.

Shchurov A.F. proposed a relationship between the strength and the average size of agglomerates, crystallites in the form of a modified Griffiths-Orowan equation [27], which includes the value of the modulus of elasticity of the substance associated with the composition and crystal-chemical structure of the crystal included in the crystalline intergrowth:

$$\sigma_{pm} = \left(\frac{E_{pm} \cdot \gamma^*}{r} \right)^{1/2} \cdot (1 - V_n)^n = C_v \cdot r^{-\frac{1}{2}} \cdot (1 - V_n)^n, \quad (18)$$

where σ_{pm} is the uniaxial compression stress; E_{pm} is the elastic modulus; $\gamma^* = \gamma + \Delta\gamma$ is the effective surface energy of fraction, here γ is the surface energy, and $\Delta\gamma$ is the additional work spent on producing local plastic deformation and the formation of stepped cleavage surfaces; r is the average crystallite size; C_v is the fracture toughness coefficient; V_n is the porosity; n is the empirical coefficient, which varies in the range from 2.6 to 4.3.

The strength of the agglomerate, the crystalline intergrowth R_{sc} in connection with the features of its formation into a continuous three-dimensional skeleton is determined by the following factors:

- the number of contacts per unit of geometric volume of the agglomerate, (crystalline intergrowth);
- the size distribution of crystals and submicron crystals
- the geometric packaging of elements in the agglomerate, intergrowth;
- the strength of individual contacts, determined by their type and type of bond in the contact (ionic, covalent, Van der Waals, etc.)
- the degree of defectiveness and the degree of the stress state of the contact.

In the transition to the technological tasks of nanomodification of the structure, these factors are the basis for considering controlling the stages of the evolutionary route of a solid-state formation. The control action through nanomodification for the structural levels of individual crystals and crystal intergrowth is carried out by regulation of

- the sizes, crystal-chemical and morphological characteristics, the measure of defectiveness of individual crystals;
- the geometry of the packing of crystals and submicron crystals in agglomerates (aggregates), crystalline intergrowth, the number and strength of contacts in them. It is precisely in connection with this that the problem of zoning the volume of the accumulating and changing submicrocrystalline and crystalline phases become obvious.

At the level of hydration products (as a matrix of cement-based composites), the resistance of the structure to fraction depends, first of all, on the spatial-geometric distribution and volumetric ratio of kinds of hydration products:

- cryptocrystalline, increasing the fracture toughness of the cementitious substance, providing an increase in energy expenditures for the production of plastic deformations of the solid phase until crack formation;
- fiber-needle, which increases the energy of fraction due to a large number of randomly placed contacts and interfaces;
- lamellar-prismatic, increasing elastic properties and additionally providing a self-reinforcing effect and an increase in the fracture toughness of a cementitious substance [28].

Very significant strength characteristics at this structural level are also determined by the specific volume of nano- and micropores, which are independent stress concentrators.

Summarized for the considered structural levels, we distinguished three groups of structural factors for controlling the resistance of cement-based composites to a fraction.

The first group of structural factors relates to controlling:

- a) the type of physical and physicochemical internal bonds of crystals (submicron crystals) of the resulting solid phase of a substance by controlling their crystallochemical characteristics and chemical-mineralogical composition;

b) the number of bonds per unit volume of agglomerates and crystallites by controlling the dispersion and morphology of its constituent particles;

c) the volumetric content of neoplasms (crystals, agglomerates, crystallites) of the cementitious substance, filler grains in the matrix of cementitious substance;

d) the condition, quality of the bonds in the contact zone of the filler grains with the cementitious substance.

The second group of structural factors corresponds to controlling:

a) the volumetric ratio of structural elements in the geometric volume of the material as a whole and within the considered scale levels;

b) the size distribution function of the structural elements of the constituent material (cementitious particles, pores, grains of filling components, etc.);

c) a measure of the homogeneity of the spatial distribution of the structural components of the material in its volume.

The third group of factors takes into account the possibilities of controlling the force and energy conditions of plastic deformation, formation, inhibition of the development and propagation of cracks due to the structure's capabilities (including, for example, self-reinforcing). It is also possible to inhibit the development and propagation of cracks by introducing additional structural elements into the material that can change the conditions of plastic deformation.

We can note that the directional regulation of the selected structure parameters in science and technological practice of obtaining cement-based composites has been studied and used to a certain extent. The achieved effects of nanomodification of the structure at the level of individual crystals, their agglomerates, and crystalline intergrowth (crystallite) certainly manifest themselves at the level of structure of hydration products as a consequence of these effects. This is the result of nanomodification technology since it is the structure of hydration products that determines the properties of the resulting cement systems and cement-based composites.

4. Discussion

The efficiency of the provided theoretical approach has been affirmed by some of our experimental results. The results show efficiency of nanomodifying of cement systems with three kind of complex nanoadditives:

- 1) CND based on SiO₂-nanoparticles,
- 2) CNT based on Nanocyl-7000 fulleroid,
- 3) ChN based on chrysotile nanotubes.

Methods of the synthesis of nanoadditives and the nanomodification of cement systems have been published earlier [22, 24, 25, 27].

The intensification of the first transition in the evolution path of a solid substance ("phase nucleation" – "particles growth") is achieved by the introduced nanoparticles as possible centers of particle nucleation. In [22], we showed that the introduced nanoparticles that have a mineralogical and dimensional affinity with hydration products can be effective crystallization centers. The significant change in the process of structure formation at the stage of "phase nucleation" can be obtained in case the critical particle size of nanoadditives has to be no more than 10 nm.

The second transition "particle growth" – "agglomeration" objectively occurs, as a result of which the cement system is structured at the level of crystalline intergrowth. In order to form the necessary dimensional habit of crystals, it is advisable to introduce certain surface-active substances (surfactants), which can selectively block the growth of their faces. As a result, the geometry of the crystals changes, for example, the formation of long crystals, which determine the effect of self-reinforcing and hardening of the structure of hydration products. The work [24] well affirms these statements. The use of all complex nanoadditives accelerates the speed of hydration processes by 20 – 25 times (Table 2.). The use of complex nanoadditives based on SiO₂-nanoparticles (CND) that have an affinity crystal-chemical structure with cement systems accelerates the speed of hydration processes during curation in low temperatures (Table 3.). According to X-ray analysis data volume of hydration products significantly was increased too. This is due to the catalytic effect of nanoparticles that decrease the activation energy of the hydration process by 2.5 – 2.8 times and participate in heterogeneous phase-formation processes (Table 4). As a result of the catalytic effect, the hydration process in cement systems with nanoadditives is substantially

accelerated: by the daily duration of hardening at 20 °C (293 K), the degree of hydration reaches at least 70 – 75%.

At the stage of spontaneous and self-organizing structure formation, the size and shape of particle agglomerates change so that the minimum internal surface energy of the system is ensured. The morphological selection also determines the evolutionary transition of the structure to a new level – the level of hydration products. At this stage, the consequences of nanomodification undertaken in the previous stages will be manifested indirectly. For example, these indirect effects have been significantly shown when we used chrysotile nanotubes (ChN) as a modifier of cement systems [25]. It was obtained that using the chrysotile nanotubes with related crystal-chemical structure accelerated the speed of hydration processes by 30 times and increase the strength of hardened cement paste by 3 times (Table 5, Fig.1,2,3).

Table 2. The hydration degree of cement modified by different nanoadditives (0.01% mass cement).

Specimen ID	The cement hydration degree (mass%) – over line, volume of hydration products, m ³ /m ³ – under line				
	1 day	3 day	7 day	14 day	28 day
C+W	<u>21</u> 0.15	<u>35</u> 0.25	<u>58</u> 0.41	<u>65</u> 0.46	<u>75</u> 0.53
C+W+CND	<u>76</u> 0.52	<u>90</u> 0.61	<u>92</u> 0.62	<u>93</u> 0.63	<u>94</u> 0.64
C+W+CNT	<u>67</u> 0.41	<u>78</u> 0.50	<u>87</u> 0.55	<u>88</u> 0.57	<u>89</u> 0.59
C+W+ChN	<u>83</u> 0.59	<u>90</u> 0.62	<u>92</u> 0.64	<u>93</u> 0.66	<u>94</u> 0.68

Table 3. The hydration degree of cement depending on temperature for cement paste modified by nanoadditives (0.01% mass cement).

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

Table 4. Kinetic parameters of the hydration process of cement paste modified by nanoadditives (0.01% mass cement).

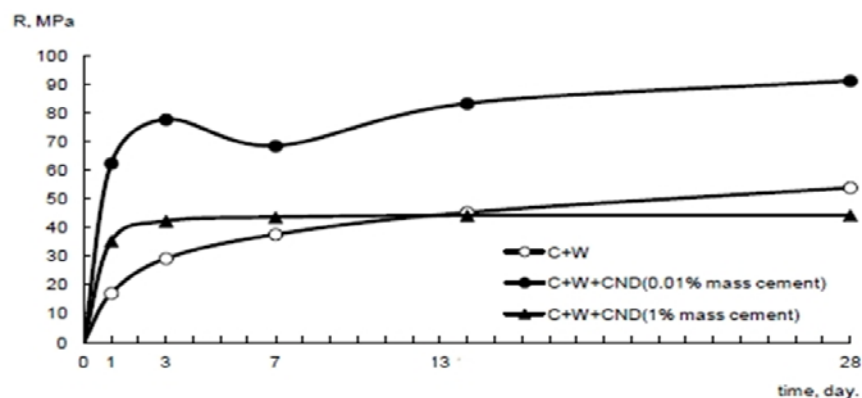
Specimen ID	Hydration rate constant \bar{k} in curing temperature				\bar{n}	EEA, kJ/mol
	273 K	293 K	313 K	333 K		
C+W	17.53	25.40	27.72	31.68	0.13	173.4
C+W+CND	46.53	54.19	56.71	57.19	0.08	61.7
C+W+CNT	42.84	53.55	56.00	57.29	0.08	76.2
C+W+ChN	49.63	55.89	58.62	59.91	0.07	57.7

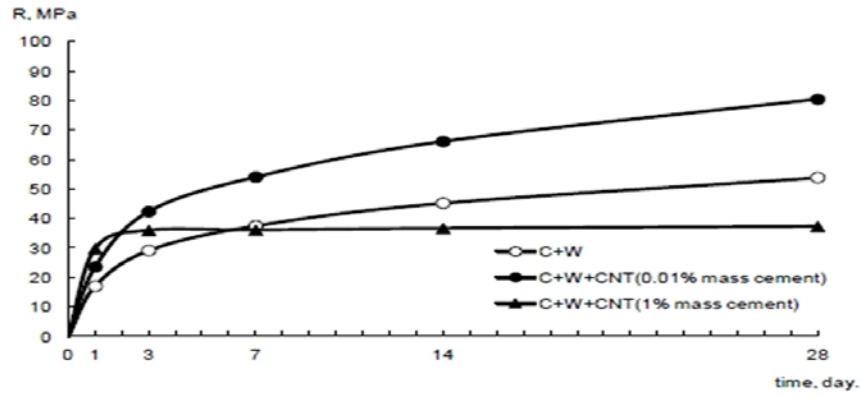
Table 5. Criteria and efficiency ratios of cement paste nanomodification by the nanoadditives.

Criteria and efficiency ratios	Specimen ID			
	C+W	C+W+CND	C+W+CNT	C+W+ChN
EEA, kJ/mol	173.4	61.7	76.2	57.7
Required time to reach 75% cement hydration degree, day	28	1	3	3
Speed-up cement hydration degree ratio	-	28 – 30	9 10	25 – 28
Relative strength hardened cement paste				
$R(\tau) / D_h(\tau)$, MPa:				
in 1 day,	31	83	71	58
in 7 day,	58	74	62	78
in 28 day.	72	98	90	98
Strength hardened cement paste	55	90	80	140
$R(\tau = 28 \text{ day})$, MPa				
Increase strength ratio $R(\tau = 28 \text{ day})$,	-	1.64	1.45	2.54
Required time to reach 75% of strength hardened cement paste, day	7	1	7	3

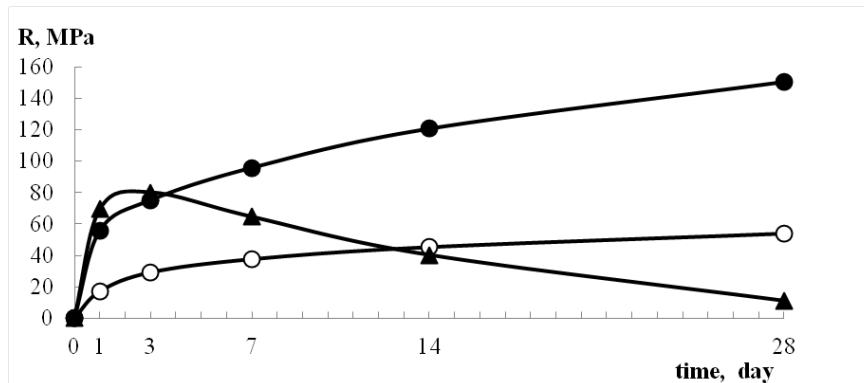
This is due to a change in the phase composition and microstructure of cement hydration products modified by nanoadditives, namely: an increase in the volume, density of hydration products; the predominance of high-strength phases of hydration products such as $x\text{CaO} \cdot \text{SiO}_2 \cdot z\text{H}_2\text{O}$ and $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ and absence low-strength phases $\text{Ca}(\text{OH})_2$ (Fig. 4–7). At the agglomeration stages of the particle of hydration products, a spatial grouping of hydration products' particles takes place through adhesion. Thus, the special formation of the fractal structural network of the solvent (water) should be attributed to the main factor of nanomodification. The formation of a fractal network of water can be achieved by introducing nanosized and ultrafine carbon-containing particles, which initially physically and chemically interact with water. It is the resulting structural network that sets the necessary geometry of the crystalline structure (the number and packing density of aggregates and crystallites). In [25], it was shown that the introduced the carbon-nanoparticles in cement systems obtained zoning of the crystallization structure of cement hydration products. At the same time, the carbon-nanoparticles are nano-reinforcing elements in the structure of the cement hydration product. However, the kinetics of strength in this variant of nanomodification is noticeably different in that in the early stages of hardening, the curing is slower: achieving 70% of the strength of its values at the age of 28 days is provided in this variant for 7 days, and for 1-day cement paste gains only 20%. Based on this data, it can be observed that the introduction of a carbon nanotubes additive 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.

Therefore, we experimentally confirmed that the nanomodification effects associated with the catalytic role of nanoparticles in cement hydration processes, with a change in the morphology of hydration products, with zoning and clustering of the hardened cement paste microstructure. As a result, the introduction of various types of nanoadditives into cement systems contributes to the decrease of effective activation energy required for the process "start" by 2.3 – 2.8 times, the acceleration of cement hydration processes by 20 – 30 times, and the increase in strength by 1.5 – 3 times (See Table 5).

**Figures 1. Strength kinetics curves of cement paste modifying by CND [24].**



Figures 2. Strength kinetics curves of cement paste modifying by CNT [24].



Figures 3. Strength kinetics curves of cement paste modifying by ChN [24].

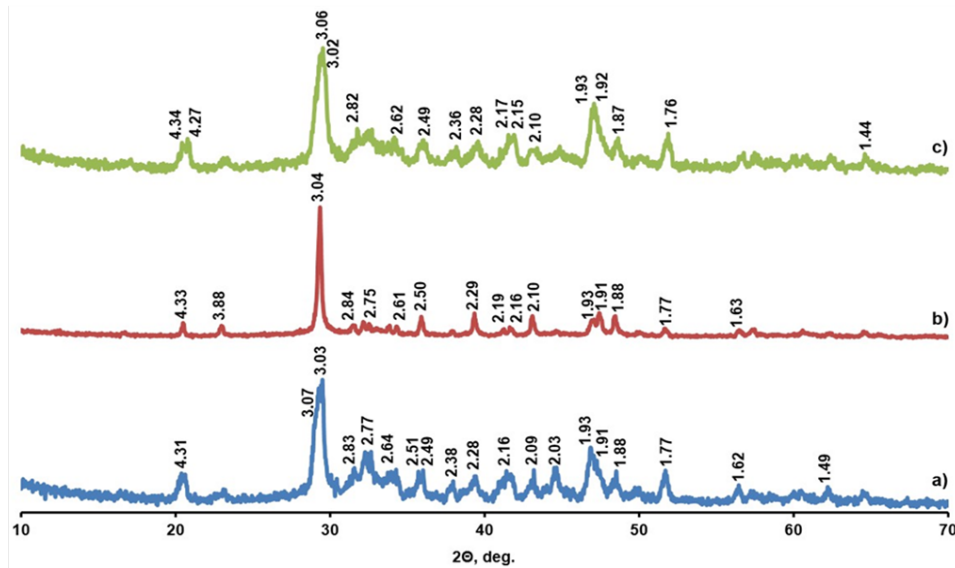


Figure 4. X-ray diffraction patterns for a nanomodified cement system modified by CND: a) without additives of 28-day curing; b) 1-day curing; c) 28-day curing.

$3\text{CaO}\cdot\text{SiO}_2$ (d = 3.02; 2.75; 2.61; 2.18; 1.76; 1.48); $2\text{CaO}\cdot\text{SiO}_2$ (d = 3.80; 3.01; 2.74; 1.80; 1.63); $\text{Ca}(\text{OH})_2$ (d = 4.93; 3.11; 2.63; 1.93; 1.79; 1.69); $2\text{CaO}\cdot\text{SiO}_2\cdot\text{H}_2\text{O}$ (d = 4.77; 3.01; 2.92; 2.37; 2.25; 1.96); $x\text{CaO}\cdot\text{SiO}_2\cdot z\text{H}_2\text{O}$ (d = 3.06; 2.97; 2.80; 1.83; 1.67); $2\text{CaO}\cdot\text{SiO}_2\cdot 0.5\text{H}_2\text{O}$ (d = 2.99; 2.77; 2.67; 2.58; 1.80)

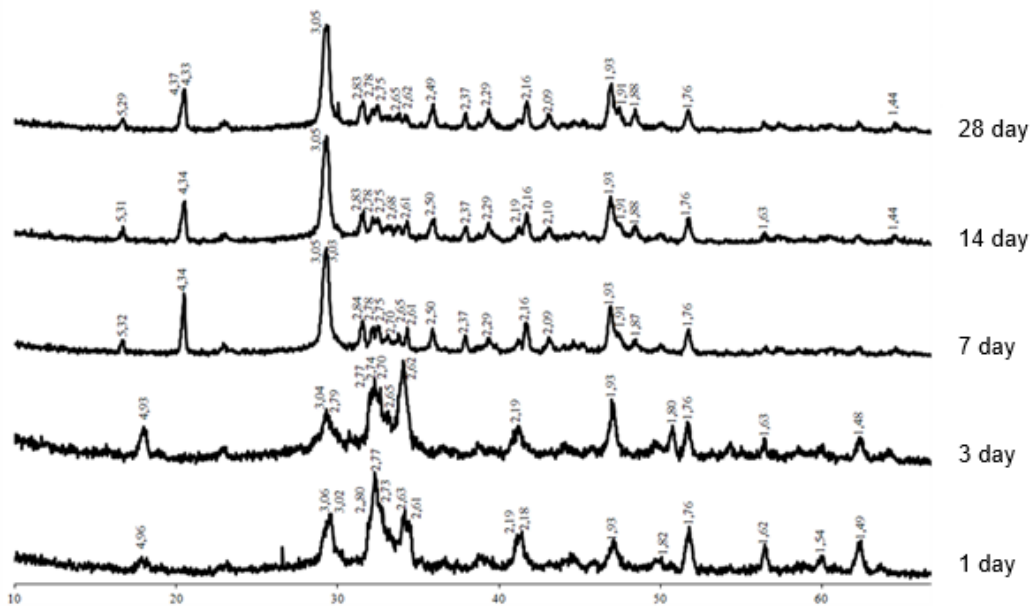


Figure 5. X-ray diffraction patterns for a nanommodified cement system modified by CNT.
 $3\text{CaO} \cdot \text{SiO}_2$ ($d = 3.02; 2.75; 2.61; 2.18; 1.76; 1.48$); $\text{CaO} \cdot \text{SiO}_2 \cdot z\text{H}_2\text{O}$ ($d = 5.6; 3.07; 2.97; 2.80; 2.28$);
 $x\text{CaO} \cdot \text{SiO}_2 \cdot z\text{H}_2\text{O}$ ($d = 3.07; 2.97; 2.80; 2.28; 2; 1.83$); $2\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ($d = 3.04; 2.7; 1.9; 1.84;$
 1.49); $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ($d = 3.03; 2.47; 1.77; 1.63; 1.51$); $3(2\text{CaO} \cdot \text{SiO}_2) \cdot 2\text{H}_2\text{O}$ ($d = 3.07; 2.82; 2.72;$
 $2.28; 2.17$).

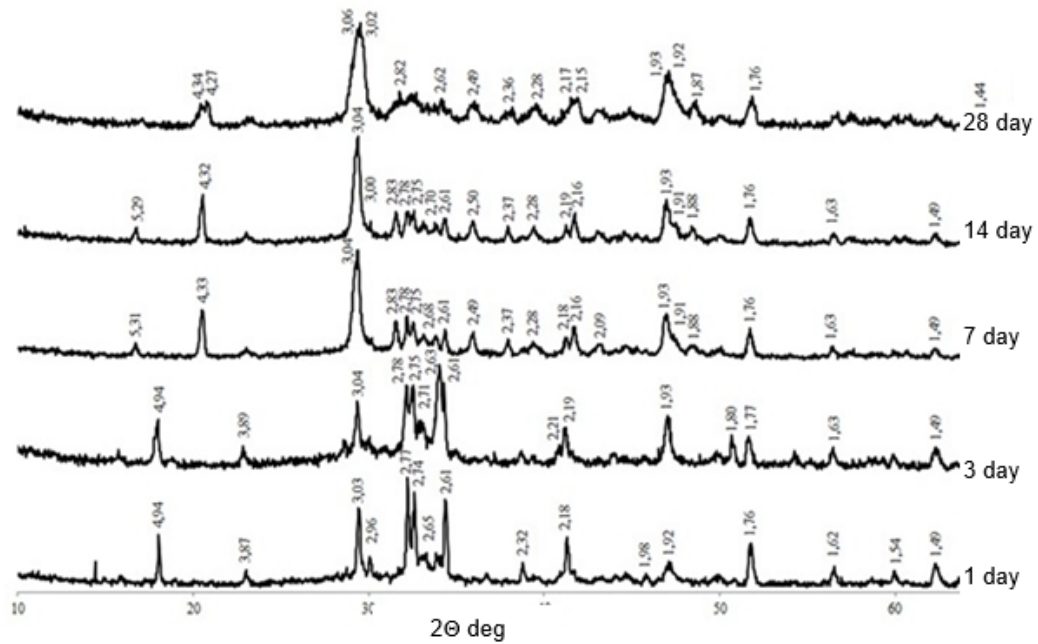


Figure 6. X-ray diffraction patterns for a nanommodified cement system modified by ChN.
 $3\text{CaO} \cdot \text{SiO}_2$ ($d = 3.02; 2.75; 2.61; 2.18; 1.76; 1.48$); $x\text{CaO} \cdot \text{SiO}_2 \cdot z\text{H}_2\text{O}$ ($d = 3.07; 2.97; 2.80; 2.28; 2;$
 1.83); $\text{CaO} \cdot \text{SiO}_2 \cdot \text{H}_2\text{O}$ ($d = 3.07; 2.8; 1.83; 1.67; 1.53$); $3\text{CaO} \cdot \text{SiO}_2 \cdot 2\text{H}_2\text{O}$ ($d = 3.03; 2.47;$
 $1.77; 1.63; 1.51$); $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ ($d = 2.86; 2.46; 2.31; 2.1; 1.93; 1.86$).

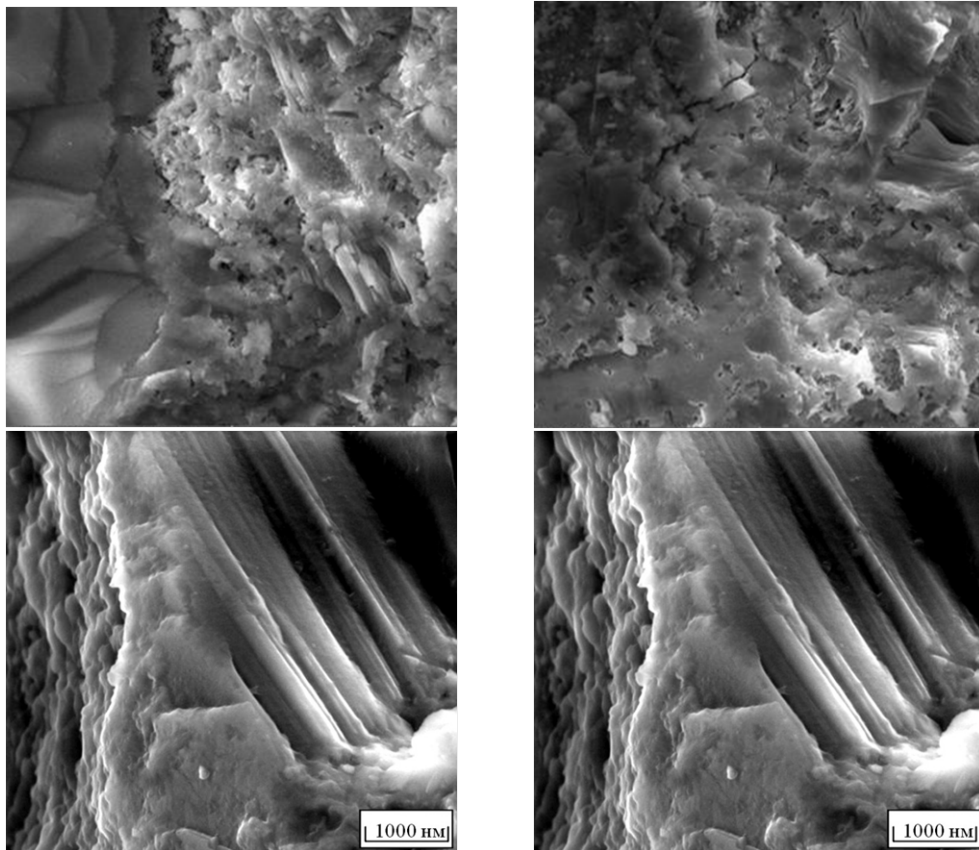


Figure 7. Hardened cement paste micrographs (hardening time 28 days, SEM)
a – without additives; b – modified by CND; c – modified by CNT; d – modified by ChN.

5. Conclusions

1. The analysis of regularities of the kinetics of heterogeneous processes of the evolutionary route of hardening cement systems resulted in the systematization of the conceptual model of structure formation. Consequently, we proposed factors of nanomodification of cement systems. The factors of the nanomodification are represented by the degree of supersaturation of the initial solution, the creation of additional centers of crystallization, the change in the intercrystalline surface of the system, the formation of additional boundaries, the formation of ordered structures of hardening with a dense package, optimization of the ratio of amorphous and crystalline phases and their morphology, alteration of the intergranular system surface, the regulation of the porosity structure.

2. In accordance with the factors of nanomodification of cement systems, the technological methods of nanomodification are identified: heat treatment, pressing (compaction), dispersed structure reinforcing, the introduction of nanosized and ultrafine particles of different nature, the introduction of surface-active additives, changes in the thermodynamic conditions of the synthesis.

3. As a result of nanomodification the following effects in the structure formation of cement systems can be achieved: acceleration of the formation of a molecular cluster, lowering of the activation energy of the process, modifying the thermodynamics and kinetics of the hardening process, changes in the structure and properties of crystalline intergrowth, changes in the thermodynamics and kinetics of the hardening process, changes in the structure and properties of a cementitious substance. The factors and methods of nanomodification meet the terms of controlling the fracture strength of the cement-based composites.

4. Together, the effects of nanomodification of the structure and factors of increasing the fracture resistance will determine the effectiveness of solutions for engineering practice in terms of reducing the time and the energy costs for processes in the life cycle of cement-based composites, enhancing their quality. The research will further focus on effective nanotechnological solutions for engineering practice.

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