Nanomodification of mineral binders

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\textbf{Abstract.} In the result of researches performed on the directed regulation of properties of gypsum binders, it was determined that the specific surface of various anisotropic surfaces regulates the shape of crystals as well as kinetics of their formation and growth. It has been established that the process of hydration and formation of gypsum binders can be regulated through the size of the specific surface, parameters of nanoadditives as well as through the change of concentration in solution. The influence of micro- and nanoadditives on the change of the system surface energy, as well as on introduction of plasticizer and change of time solution is in the supersaturated state (which increases the number of nuclear centers of crystallization) has been established experimentally and theoretically proved.

Nanotechnology is the science of direct influence on individual atoms and molecules and the main purpose of research is to create structures of materials with defined properties. The essence is in the fact that particles with nanomaterial dimensions have special properties, which sometimes are not subordinated to the existing laws of physics, chemistry. Analysis of scientific achievements shows that the world is on the threshold of the third scientific and technological revolution, which is going to determine the place of countries in the technological sphere of the XXI century. Up to date, more than 70 countries are implementing state programs for nanotechnology development. More than 29000 scientific centers and “nanocompanies” are organized and successfully functioning in the world. They carry out research and have certain developments in the field of nanotechnology and related disciplines.

There is no international information on financing nanotechnology in Ukraine. It is the more so in the construction industry. For the sake of justice, it should be noted that the research is being conducted. Example: Kharkiv Machine Building Plant (FED Plant), Malyshev Factory, “Motor Sich” in Zaporizhia, Kharkiv Institute of Railway Engineers’ Medical Center.
So a research laboratory and NANONAT-Eps workshop are functioning at the FED Plant. At PSACEA (2015), KNAHU (2018), KNUCA (2020) doctoral theses were defended. Their authors considered theoretical issues concerning application of nanostructures for modification of composite materials. Ukraine has signed a project to support the development of nanotechnologies in Europe (European Partnership countries (EPS), Institute for Problems of Material Sciences (IPMS). The pilot project Europe: Armenia-Germany, Belarus-Luxembourg and Ukraine-UK. NANONAT-EPS - November 2013 Kyiv (Ukraine).

The relevance of the research is characterized through the data of financial costs for the development and manufacture of products with the use of nanotechnology (Fig. 1): 2008 - USD 200 billion, 2015 - about USD 1,000 billion, 2020 – more than USD 2,000 billion [1].

The main trends of nanotechnological development in the field of construction are directed on designing new products, with improved quality and functional characteristics, as well as on increasing application efficiency of existing materials [2]. Materials have unique properties and their use can make a revolution in many spheres of construction materials production. [3].

With the help of nanoparticles you can change the color of coating, create self-cleaning functions, form a special antibacterial layer and perform ultraviolet protection. Structural composite materials based on nanotechnologies have a strength that many times exceeds that of traditional analogues.

Developments in the field of construction nanotechnologies of building products are distributed in the following way. The largest segment belongs to nanomodifications of cement binders (Fig. 2).
In this concern a promising area is the use of nanomaterials for the modification of gypsum binders. The most widespread hypotheses explaining the change in properties of binders during modifying by means of ultradisperse additives and nanoagents can be grouped as follows: Nanoparticles cause influence on the electrosurface properties (Fisher G B and Plugin A A); rheological characteristics are changed (Voitovich Y V); nanostructures play the role of crystallization centers (Yakovlev and Derevianko V M); the number of point contacts is increased (Gharkavi M S and Yakovlev); the effect of introduced nanoparticles is associated with an additional active specific surface area of the phase separation and excessive surface energy Buryanov A F, Tokarev Y V, Sanitskiy M A and Tolmachov S M).

It should be noted that the concept of phase is expressed less clearly in conditions of reduced particle size. It is difficult to determine borders between homogeneous phase and heterogeneous phase and between amorphous and crystalline states. The usual physical and chemical ideas, including notions of “composition-property”, “structure-function” are in this case supplemented with such terms as “size”, “self-organization” [3-4].

Introduction of binding nanoparticles into the mixture results in a change of structure formation and affects the properties of construction materials. The influence of dimensional effects (the upper limit is considered to be particle sizes up to 100 nm) causes a change in physical and mechanical properties in the specified size range of materials [3]. The Nanoparticles are classified: by size, energy and geometric characteristics, composition, shape, methods of formation [5]. The following types of nanostructures are most often distinguished by their shape: fullerenes, single-layer and multi-layer nanotubes, nanowires, hemispheres and nanoparticles, nanoclusters and nanocrystals.

In our studies, we used carbon nanoparticles (CNP), carbon nanotubes (CNT), functionalized carbon nanotubes (CNT-OH), and carboxylated carbon nanotubes CNT-COOH) Gypsum plaster was used as a binder Plasticizers: MasterAir 81 (fig.), Master X-Seed 100, Master X-Seed 100, Glenium ACE 430, Polyplast P1, Sika Retardatcur.

Application of carbon nanotubes (CNT) for modifying properties of gypsum binders is considered as an effective means of improving the physical and mechanical properties of composite materials.

Improved efficiency of carbon nanomodifier in composites can be achieved by means of chemical modification of the CNT surface by functional groups, for example hydroxyl group or carboxylic group [6] (Fig. 3).
Carboxylation of carbon nanotubes was carried out by interaction of the latter with various oxidizing agents [4, 7] (nitric acid in various media, salts of chromium and manganese in higher oxidation states, hydrogen peroxide). For CNT oxidation with hydroxyl groups a mechanochemical method is used, which consists in a joint grinding of CNTs and alkali during 60 minutes. Figure 4 shows CNTs after ultrasound processing. Functionalized carbon nanotubes (unlike initial ones) do not form large agglomerates and are well separated.

Modification of binders with nanosystems is complicated due to obtaining a heterogeneous structure (because of small number of nanocomponents). Technology of their introduction into the composition of dry binders is in the stage of development, and at present the process includes preparation of a dispersed solution “nanosystem-sealant”. In order to reduce sedimentation, increase the viability of the solution and form heterogeneity of the structure studies were conducted with various sealants [7] (Fig. 5). Dispersion was performed with the use of ultrasound in the following media: CNT - water; CNT – plasticizer - water; CNT-OH – plasticizer - water; CNT-COOH - plasticizer - water.
For studying the influence of nanoadditives on the processes of crystallization the method of counter diffusion of crystals growing [8, 9] has been improved. According to the stereochemical reaction:

\[ CaCl_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaCl, \]

prepared solutions \( Na_2SO_4 \) and \( CaCl_2 \) were added in different containers with distilled water (Fig. 6). Concentrations of solutions were calculated taking into account the maximum solubility of these substances at room temperature. Crystals are formed through diffusion in an aqueous medium at room temperature. In general, experimental studies of the effect caused by nanosystems on the structure and properties of gypsum binders were carried out according to the following scheme, determining the shape and other parameters of crystals grown based on \( CaCl_2, Na_2SO_4, 2H_2O \) : 1 - solutions - without additives; 2 - with addition of plasticizers; 3 - with addition of plasticizers and ultra- and nanosystems (nanoparticles, nanotubes). In parallel, samples based on gypsum plaster of similar compositions were used to test the basic physical and mechanical properties.

The choice of initial materials was based on the proposed scientific hypothesis consisting in the fact that mineral binders with special properties can be obtained by means of controlling processes of hydration and structural formation of crystal lattice with necessary characteristics while introducing nanomodifying additives.

The block of initial materials consisted of mineral binders (variety of gypsum plaster) and surface active substances (surfactants), nanoadditives (in the form of 1D-3D nanoparticles of CNT (fullerenes), CNT nanotubes, dispersive solutions of industrial waste and natural materials), plasticizers [10]. Calcium chloride and sulfates were used for the growth of calcium sulphate dehydrate crystals.
The purpose of the research is to study the effect of nanomodifiers on the mechanism of the hydration process and structure formation of gypsum binders. Processes of hydration of binders are directly related to the subsequent processes of crystal formation. Their structure forms and sizes determine the properties of hardened materials. Results of growing gypsum crystals from saturated solutions of CaCl$_2$ and Na$_2$SO$_4$ (using the method of counter diffusion without/with ultra- and nanoadditives are presented below. Theoretical and experimental substantiation of composite formation principles and peculiarities of hydration processes, structure formation of gypsum systems as well as analysis of their modification possibilities has been carried out.

Based on the technological chain (raw materials - thermal treatment - hydration processes - hardened structure) it is possible to emphasize that the process of hydration is the most manageable, although it is also more complicated from the theoretical point of view. All modifications of gypsum systems are based on calcium sulfate dehydrate (CaSO$_4$·2H$_2$O). It has a very perfect degradation in the plane (010), perfect degradation in the plane (111) and imperfect degradation in the plane (100). There are two different types of water: weakly retained (1.5 H$_2$O) molecules are attached directly to calcium and strongly retained ones (0.5H$_2$O) are bound to hydrogen sulfide ion) (Fig. 7). Modification is aimed at changing the structure [11].

![Fig. 7. The structure of relations in calcium sulphate dehydrate](image)

Energy calculations of modification strips have the following values: $I_k$ CaSO$_4$·2H$_2$O $q$ 2300 kJ/mol; $I_k$ CaSO$_4$·0.5H$_2$O $q$ 2505 kJ/mol; $I_k$ CaSO$_4$·2H$_2$O $q$ 2638 kJ/mol. Analysis of various structures of gypsum crystals shows that the key factor is the change of the system energy state [11].

The strength of the structure formed is largely determined by the size and saturation kinetics in the suspension liquid phase. Therefore, change in hydration process conditions can regulate formation of structure, framework and properties.

Given the model, the faces on the crystal surface have different structures at the atomic level, depending on their orientation. There are three types as functions of the number of parallel lines of connections; F (2 or more connections), S (1 connection) and K (no connections) [12, 13].

Control of the structure formation process is determined primarily by the degree of mineral hydration, the number and type of crystal intervals between them depending on the degree of liquid phase saturation relative to the maximum dissolution of hydrates crystallized from it.

Adsorption of modifiers is possible: – on the edges of crystals, which have the largest surface energy. For example, polymers adsorb mainly on the edges of {111} and {011}, and thus they change the rate of crystal nucleation [14].

The article presents the results of studies of the effect of ultra-plasticizers and nanoadditives on hydration and structural processes. They represent a complex that combines chemical interaction and formation of hydrate modifications, and accompanies physical, physical and chemical and colloidal processes. The technology of modification of binders with nanoadditives, according to the results of previous tests, is not yet possible without the use of PAW. In this regard, the study was initially conducted concerning their impact on hydration processes and the structure of gypsum systems.
Adding a PAW to the calcium sulphate hemihydrate solution changes the rate of physical and chemical processes: electrical conductivity, thermodynamics, rate of hydration processes (Table 1), and morphology of crystals (Table 2) and structure of solutions.

In the case of growing crystals in a medium without a plasticizer, we can say that the decisive factor is the degree of solution re-saturation and the time of the system. Introduction of a plasticizer into the crystal-forming solution (in addition to changed degree of re-saturation and time in the pre-saturated state) passes through the stage of plasticizer selective adsorption on the crystal faces. The surface energy is changed in the result.

**Table 1. Change in the duration of calcium sulfate hemihydrate Hydration Processes**

| Properties                  | Without additives | Master 81 | M-X-seed 100 | Glenium ACE 430 | Sika Private |
|-----------------------------|-------------------|-----------|--------------|-----------------|--------------|
| V/G ratio                   | 0.62              | 0.75      | 0.67         | 0.52            | 0.49         |
| $T_{si}$ – time of setting initiation, min/sec | 10 / 10          | 12 / 30   | 12 / 30      | 13 / 30         | 18           |
| $T_{fs}$ – time of final setting, min/sec        | 14 / 50          | 13 / 35   | 13 / 05      | 20 / 10         | 35           |

**Table 2. Morphology of Crystals**

| Surfactants         | Microphotography of crystals | Schematic figures | Crystal dimensions, µm |
|---------------------|------------------------------|-------------------|------------------------|
| without a plasticizer | ![Microphotography](image1) | ![Schematic](image2) | 145 0                  |
| MasterAir 81        | ![Microphotography](image3) | ![Schematic](image4) | 200 5                  |
| Master X-Seed 100   | ![Microphotography](image5) | ![Schematic](image6) | 164 0                  |
| Glenium ACE 430     | ![Microphotography](image7) | ![Schematic](image8) | 250 50                 |
| Sika (Ivate)        | ![Microphotography](image9) | ![Schematic](image10) | 300 50                 |

Adsorption on the faces of crystals plays an important role in the process of their growth. Selective absorption leads to the blockade of growth along the axis (molecules are adsorbed on the upper part of the face) and there is a tendency of growth with a low aspect ratio, and as a result crystals are formed as thickened columns.
In order to study the influence of the crystal-forming medium on the morphology of calcium sulphate dehydrate crystals they were grown using the method of counter diffusion without additives and with the addition of plasticizers. According to the results it has been shown that under identical growth conditions crystals change their shape and size depending on the type of plasticizer added. Crystals grown in the medium without adding a plasticizer are identical in their shape and size; they are evenly distributed on the lining with a thickness of 1 mm. Length of crystals is 3 mm, their width is 0.2 mm and their thickness is 0.06 mm.

Fig. 8. Photomicrographs of gypsum crystals, grown in the following ways: a) – without a plasticizer; b) – and with MasterAir 81 additive

Crystals grown in a medium with PAW: MasterAir 81 (Fig. 8), Master X-Seed 100, Master X-Seed 100, Glenium ACE 430, Sika (Fig.) change their shape, size, packing density (Fig. 8, 9).

Crystals grown in the presence of Sika plasticizer have a thickness from 0.7 to 1.5 cm, and the crystal width is 0.8-1 mm. It can also be observed that the growth of crystals begins from one point; possibly it is due to a change in surface tension. In general, all crystals formed arecuate sprouts. These crystals are larger than those grown with other plasticizers.

Fig. 9. Gypsum crystals grown with addition of: b) – Master X-Seed 100; b) Sika

In photomicrographs you can see the growth layers, you can also see how the voids between the layers grow and the crystal is compacted, i.e. the crystal growth begins at various points on the surface, these layers begin to grow before meeting other layers.

The essence of modification processes in case of using ultra- and nanoadditives: It consists in the changed energy state of the system, which can be characterized through the ratio of components, the specific surface area of interface, temperature, pressure, solubility, diffusion etc.

Hydration reaction of samples with additives (Fig. 10, 11) is more intense; the time of reaching the temperature maximum is less than that without additives.
Fig. 10. Graphs of changes in temperature of gypsum hydration process a): with the addition of Taurit (0.5%) (2), carbon white (0.5%) (3) and with a complex composition of Taurit (0.5%) and carbon white (0.5%) (4). X-ray Images of gypsum: b): without additives (1), with silicon dioxide (2), with Taurit (3), with addition of Taurit and silicon dioxide (4)
The X-ray study of samples with additives shows that there are differences in the products of hydration processes. So the Taurit additive (Fig. 11b) reduces intensity of d q 0.756, 0.379 nm peaks, while intensity of d 0.286 nm peaks (CaSO₄·2H₂O) is increased. Taurit samples contain a lesser amount of CaSO₄·2H₂O, then samples without additives, 2.5% CaSO₄·0.5H₂O і 1.0% CaSO₄ and they will not participate in hydration reaction.

Similar results are observed in the diffraction of X-ray powder (Figure 5c) with silicon dioxide plaster (silica plaster). Intensity peaks d q 0.757 (CaSO₄·2H₂O) і d 0.378; 0.305 nm (CaSO₄) do not work and peaks d q 0.286; 0.267 (CaSO₄·2H₂O). Peak d 0.348 (CaSO₄·0.5H₂O) has almost gone. Slightly more than (1.7%) CaSO₄·0.5H₂O and (1.1%) CaSO₄ was not converted to dehydrate.

Studies of the changes in electrical conductivity and heat release intensity of Calcium Sulfate Hemihydrate in the process of its hydration have shown that the curve has three typical areas (Fig. 12). The first one corresponds to saturation of the solution by ions of calcium and sulfate. The second one is related with calcium dehydrate crystallization onset. The third area indicates the completion of the calcium sulphate dehydrate structural formation.

According to studies of equilibrium morphology, surface stability is defined as a function of the directional distribution of the energy connection [14]. Adsorption on the surface of gypsum crystals
depends on the charge density as well as on the distance between adjacent groups of ions. Gypsum crystals have a layered structure with \( \text{SO}_4^{2-} \) densely distributed on the side face and \( \text{Ca}^2+ \) cations densely distributed in the upper part. Crystal faces \{010\}, \{120\}, \{011\} and \{111\} are arranged in the order of morphological value decrease. Change in the degree of solution saturation level, plasticizer adsorption on the faces as well as changes in surface energy affect the morphology of crystals.

At increase of microadditives presented in the solution up to 10% thickness of crystals reaches the level of 3 - 5 mm (Fig. 13), and their length grows up to 10-15 mm. The growth layers are more ordered, they are denser than those in crystals with lesser amounts of microadditives.

![Photomicrographs of gypsum crystals grown in the following ways: a) – with a SiC microadditive (5% solution) and Sika superplasticizer (0.2%); b) – with a SiC microadditive (10% solution) and Sika superplasticizer (0.2%)](image)

![Photomicrographs of gypsum crystals grown with the following additives to the crystal forming medium: a) – SiC nanoadditive (5%) and Sika superplasticizer; b) – SiC nanoadditive (10%) and Sika superplasticizer (0.2%)](image)

Fig. 13. Photomicrographs of gypsum crystals grown in the following ways: a) – with a SiC microadditive (5% solution) and Sika superplasticizer (0.2%); b) – with a SiC microadditive (10% solution) and Sika superplasticizer (0.2%)

Fig. 14. Photomicrographs of gypsum crystals grown with the following additives to the crystal forming medium: a) – SiC nanoadditive (5%) and Sika superplasticizer; b) – SiC nanoadditive (10%) and Sika superplasticizer (0.2%)

Theoretical and experimental studies of the influence caused by the specific surface of the components by the example of Calcium Sulfate Hemihydrate (G-5-N-II) and finely ground gypsum (G-5-N-III) gypsum indicate a change in the system energy state which is the driving factor of structure formation. So, granulometric composition of gypsum plaster sized up to 10 µm is about 10%, and in the finely ground one it is 25%. At that the ratio of surface energy (M.A. Sanitskyi as the ratio of the surface area of particles to their volume, \( S / V \)) is increased by 3-5 times.

The study of optical density and spectral directional transmission coefficient (“Expert-003” photometer) of saturated solutions indicate a sharp change in optical properties, which is associated with the appearance of the solid phase.
The spectral directional transmission coefficient \( (nk) \) in an aqueous solution of gypsum and finely ground gypsum with a change of up to 5% in the range of 99.69% to 2.63 and 1.01, respectively. Increasing the concentration of components to 10% causes reduction down to 0.06, and down to 0.7 in finely ground gypsum, i.e. more than 10 times. Change of electrical conductivity takes place in the same way (Fig. 15).

Theoretical and practical studies show the influence of faction specific surface (energy of systems) on the processes of hydration and structure, which gives an opportunity to change properties of the product.

**Conclusions**

According to the proposed hypothesis ‘Regulation of crystal morphology and structure of mineral binders by means of additives with nanoparametric characteristics’ as well as according to theoretical and experimental studies performed the nature of the influence caused by individual components of the hydration process has been determined.

1. Theoretical and experimental studies of structure formation processes during hydration of mineral binders have established the possibility of modifying their structure to achieve maximum strength. This strength depends on the degree of hydration of minerals, the number and type of crystal gaps between them, depending on the degree liquid phase saturation relative to the maximum solubility of hydrates.

2. An analysis of the effect caused by additives on the growth rate of certain crystal faces (which leads to a change in the properties of the solid body) has been performed. It has been found that there is a relationship between the directional growth of crystals and change in matrix characteristics depending on the concentration of \( \text{Ca}^{2+} \) ions in solution.

3. Changes in temperature, pressure, pH of the medium, water-gypsum ratio in the process of hydration and hardening cause changes in structural topology and rate of crystal formation.

4. Mechanisms of modification of mineral binders have been compared by means of using ultrafine additives and nanoadditives. It has been established that the difference between the results as well as the lack of clear patterns can be explained through the following factors: Nature of modifiers, parameters of synthesis, method of introduction, surface chemical composition.

5. Dependence between the growth of crystals and variable of matrix characteristics (i.e. the directed regulation concerning properties of gypsum binders) has been established;

6. The following facts have been determined: the specific surface of various anisotropic surfaces is a key parameter of growth, which regulates the shape of crystals as well as kinetics of their nucleation and growth. Introduction of nanoparticles dramatically increases the value of surface energy which in its turn influences the process of hydration by means of increasing the number of crystallization centers.
and the rate of the process as well as by means of changing the direction of growth (as indicated by hydration process thermograms B-CaSO₄·0.5H₂O) and solution electrical conductivity:

It has been established that the process of hydration and formation of gypsum binders can be regulated through the size of specific surface area, parameters of nanoadditives as well as through the change of concentration in solution.

6. By means of using the method of counter diffusion for growing crystals of saturated solutions of CaCl₂ and Na₂SO₄ without/with additives the following aspects have been determined: crystals grown without additives are thin and needle-shaped, 3-5 mm long, 0.1-0.15 mm wide and 0.05 mm thick. And, for example, in the result of introducing SiC nanoadditive to the crystal-forming medium, the length and thickness of crystals increases: their length grows up to 5-8 mm, and width grows up to 0.1-0.8 mm. Adding SiC to the crystal-forming medium leads to growth of crystals on the C axis (microadditives of 5-7 mm in length and 7-9 mm in width);

7. Based on studies aimed at determining coefficients of optical density and light transmission the influence caused by change of the surface energy of gypsum granulometric structure and finely ground gypsum as well as that of their mixture on properties of solutions has been established. The spectrum of directed light transmission and optical density depends on gypsum concentration in the solution. The change of gypsum electrical conductivity will be with different granulometric composition;

8. It has been established that: the change of the stage of saturated solution changes plasticizer adsorption on the faces of crystals as well as the surface energy, which are the main factors of influence caused on formation of crystals and on the process of crystal structural formation in general.

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