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IDENTIFYING THE INFLUENCE OF NANOMODIFIERS ON THE STRUCTURE FORMATION PROCESS REGULARITIES IN THE GYPSUM-ALUMINA CEMENT SYSTEM

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Gypsum alumina cement is resistant to magnesium solutions, seawater, and concentrated Na_2SO_4 and Mg_2SO_4 solutions, but it is less resistant to sodium chloride solutions. One of the ways to improve the gypsum alumina cement durability and enable its use in aggressive calcium chloride waters is to design a composition by incorporating modifiers. Thus, the composite is applicable for well-casing under conditions involving aggressive water exposure. However, such cements have their limitations: they are not suitable for processing at high temperatures in autoclaves. Up to now, the ettringite phase stability dependence on curing conditions and temperature has remained an unresolved issue.

It has been theoretically proven and experimentally confirmed that the optimal calcium sulfate content in gypsum alumina cement and gypsum grade G-5 (GAC+G5) compositions, according to calculations, ranges from 28 % to 38 % of the mass of the alumina binder. That makes it possible to increase ettringite formation and obtain cement stone structure with predefined characteristics. As a result of modification with nano additives, the strength indicators of the composite materials have been improved: gypsum alumina cement GAC gypsum grade G-5:G (70:30) %+0.18 % nanotubes+0.4 % Sika – up to 70.2 MPa compared to 14.67 MPa in the reference composition.

The scope of practical application includes the development of road surfaces and waterproofing materials, as well as hydraulic engineering. A condition for the practical implementation of results is the temperature range from –15 to 80 °C. Expected effects of application are shrinkage deformation reduction, improved crack resistance, increased strength, and enhanced durability of concrete articles under challenging operating conditions

Keywords: composite binder, mortar, ettringite, ettringite stabilization, aluminate cements, sulfoaluminate cements, nanomodifier

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1. Introduction

Aluminate and sulfoaluminate binders are widely used, in particular alumina cement. However, it is not widely used in construction because of unstable expansion, shortage of raw materials, high cost, and low setting times.

In addition, binders based on gypsum, slag, ash, and alumina cement have been developed. Thus, in the composition of cement stone within gypsum-alumina cement, compared to Portland cement, the main factors that cause low sulfate resistance – $Ca(OH)_2$, high amounts of highly basic calcium hydroaluminate – are absent. Instead, the basic components of expansive gypsum-alumina cements are aluminum hydroxide, calcium hydrosulfoaluminate, and low-basic calcium aluminates.

In the process of hydration of minerals of the $CaO-Al_2O_3-H_2O$ system, hydroaluminates and gel CAH_{10}, C_4AH_{10}, C_3AH_8, C_4AH_{13}, $Al(OH)_3$ and $Ca(OH)_2$ are formed, while in the $CaO-Al_2O_3-SO_3-H_2O$ system the hydration process is more complex.

Firstly, hydroaluminates and hydrosulfoaluminates of the AFt-phase and AFm-phase, CAH_3, are simultaneously formed, that is, this is the formation of the primary structure.

Secondly, part of the hydroaluminates reacts with calcium sulfates, forming AFt- and AFm-phases – secondary minerals; this process affects the formation of the structure, which determines such properties as strength, internal stresses, expansion, and so on. The complexity of the task is to establish the formation surface and the ratio of formation at the first stage of $C_nA_mH_x$ and AFt-, AFm-phases. This makes it possible to determine the course of physicochemical processes in the system over time.

Common to the hydration processes of sulfate cements in the presence of gypsum is the formation of the AFt phase, i.e., a new formation that plays a major role in the modification of calcium sulfate dihydrate, or partial replacement of aluminous cement with the $CaSO_4 \cdot 2H_2O$ additive – ettringite.

Consideration of examples of research on the hydration processes of the system Al_2O_3-H_2O; Al_2O_3-H_2O-CaO-SO_3 reveals that the formation of ettringite can be divided into two stages. At the first stage, intermediate compounds are formed and then interact with sulfates. Direct formation of ettringite is the reaction of calcium aluminates and sulfates. Hydration processes, the formation of hydrosulfoaluminates of a highly sulfated form based on intermediate compounds create problems of internal stresses. And when the system has gained a certain strength, this leads to the destruction of the structure.

The idea of studying the sequence of formation of sulfoaluminates based on intermediate compounds makes it possible to obtain a structure of high strength.

Research on expansive gypsum-alumina cements is relevant because it makes it possible to use components of alumina cement and dihydrate gypsum to design new binders. They also stabilize the hydrosulfoaluminate phase by modifying the structure. This, in turn, could make it possible not only to design a structure with specified properties but also obtain special-purpose mortars and concretes with high technical and operational indicators. That is why, given the significant number of buildings and structures that require restoration and reconstruction, it is relevant to develop a binder with special properties based on gypsum-alumina cement.

2. Literature review and problem statement

In [1], the results of studies on the reduction of corrosion caused by Cl^- and SO_4^{2-} ions in concrete based on blast furnace cement when mixed with seawater are reported. It is shown that the addition of small mineral components, such as alkali metal compounds, calcium aluminate cement, and clinoptilolite, improves the early strength of concrete, increases the density of the structure, and reduces the corrosion of steel reinforcement. However, the issues related to the long-term characteristics of concrete under the influence of an aggressive environment, the mechanism of binding Cl^- and SO_4^{2-} ions, and the economic feasibility of using the proposed additives on an industrial scale remain unresolved. The likely reason is difficulties associated with the variability of the composition of seawater, the high cost of special additives, and insufficient research into the influence of different types of alkali metals on the structure of cement stone. The option to overcome these difficulties is a further study of the interaction of cement with seawater at the molecular level, development of alternative cheaper activators, and improvement of methods for assessing the durability of concrete under real operating conditions. All this allows us to state that it is advisable to conduct a study aimed at devising optimal formulations of concrete based on blast furnace cement for aggressive environments, which would ensure its durability and cost-effectiveness [2].

Paper [3] reports the results of research on the use of industrial waste as cement substitutes in permeable concrete to increase its environmental sustainability. It was confirmed that replacing up to 20 % of cement with fly ash (FA), metakaolin (MK), silicate dust (SF), and blast furnace slag (GGBS) makes it possible to reduce the porosity and permeability of concrete, increase the strength up to 35 MPa. The use of these materials also reduces the carbon footprint of cement production. However, the problems associated with the durability of such concretes under aggressive conditions, the economic feasibility of introducing alternative cement substitutes on an industrial scale, as well as the development of standardized methods for assessing their strength and durability remain unresolved. Possible factors are obstacles associated with the variability of the waste composition, the complexity of quality control over the resulting concrete mixtures, and the need for additional research on the mechanisms of binding of Cl^- and SO_4^{2-} ions in such concretes. One way to overcome these difficulties is to devise an approach to modifying cement compositions by combining different additives, as well as to introduce new methods for assessing the environmental benefits of using alternative cement substitutes. This method was used in [4]; however, the impact of changing environmental conditions on the behavior of these materials in the long term has not yet been sufficiently studied. Based on this, we can conclude that it is advisable to conduct a study aimed at devising new compositions of permeable concrete with an optimal combination of industrial waste, which would ensure its durability [5].

In [4], the results of studies on the ecotoxicity of building materials containing steel slag (SS) by assessing the phytotoxicity of its leached solutions are reported. It was confirmed that neither steel slag nor concrete with its partial replacement have a significant toxic effect on plants since no significant decrease in root length was observed in the studied samples. In some cases, stimulation of root growth was detected, which indicates a possible positive effect of leached elements on plant development. In addition, the mitotic index of onion root cells did not undergo significant changes, which indicates the absence of genotoxic effects of the studied materials. However, there are open questions related to the long-term ecological stability of concretes containing steel slag, as well as to the possible gradual release of potentially harmful elements into the environment. This is due to the difficulties associated with the variable chemical composition of steel slag, different conditions of its storage and use, as well as the lack of regulatory standards for assessing the long-term environmental impact of such materials. A possible way to overcome the obstacles is to conduct research on leaching and modeling of metal migration processes in concrete mixtures, as well as standardization of methods for assessing ecotoxicity for building materials containing secondary resources. All this suggests that it is advisable to conduct research on long-term environmental monitoring of concretes containing steel slag, which would enable the safe use of these materials in construction [4].

In [6], the results of studies on partial replacement of cement with red mud (RMD) in the production of ecological concrete are reported. It is shown that the use of up to 25 % RMD improves the mechanical properties and durability of concrete, as well as reduces its negative impact on the environment. Studies have confirmed that RMD reduces the permeability of concrete, improves its strength, and promotes the formation of hydrated phases that increase the adhesion between the cement matrix and the aggregate. However, some questions remain open, related to the long-term behavior of concrete containing RMD, the optimal concentration of cement replacement, and standard methods for assessing its mechanical and durability characteristics. This is explained by the obstacles associated with the variable chemical composition of RMD, the need for pre-treatment to reduce alkalinity, and the limited number of studies addressing the long-

term impact of aggressive environments on such concretes. One of the approaches to overcome the difficulties is to devise methods for pre-treatment of RMD to stabilize its composition, to study new concrete compositions with cement substitutes, and introduce environmentally friendly standards for assessing durability. This approach is indicated in [5]; however, there is no data on the optimal temperature and chemical treatment of RMD before use in cement compositions. All of the above confirms that it is advisable to conduct a study aimed at devising effective methods for preparing and modifying RMD, which would make it possible to improve the quality and durability of concretes based on it [6].

In [7], the results of studies on the use of industrial waste for the synthesis of geopolymer concrete are reported. It is shown that concrete created on the basis of fly ash, blast furnace slag (GGBS), red mud, and rice husk can reach a strength of up to 70 MPa and demonstrates increased resistance to acidic and alkaline environments. However, certain aspects still need to be addressed, related to the long-term strength and durability of geopolymer concrete, the optimization of alkaline activators and their cost, as well as the influence of changing environmental conditions on the behavior of the material. This may be due to obstacles related to the need to devise uniform standards for geopolymer materials, the high energy intensity of obtaining alkaline activators, and the lack of sufficient research on the long-term characteristics of the material. The way to overcome these obstacles may be to use industrial waste, such as Bayer process liquids, to obtain cheaper alkaline activators, as well as to conduct detailed studies on the durability and stability of concrete. All this allows us to state that it is advisable to conduct a study aimed at devising an integrated approach to the standardization of geopolymer materials, their durability, and cost-effectiveness in industrial and construction applications [7].

Solving the problem of the stability of an ettringite component is possible by using state-of-the-art technologies and techniques for obtaining a binder – by modifying calcium sulfoaluminates.

Thus, the binder to be designed, with improved technological, physical-mechanical, and operational properties, could be used for the repair of concrete coatings.

Our review of the literature reveals a number of unresolved issues related to the development and research of products based on binders of the $CaO-Al_2O_3-SO_3$ system, obtained from production waste, as well as composite binders of this system. In particular, the influence of additives of various nature on the hydration activity of the $CaO-Al_2O_3-SO_3-H_2O$ system, its ability to regulate stress, as well as other properties of the hardened structure, remains insufficiently studied. These aspects constitute a general task that requires further research.

3. The aim and objectives of the study

The aim of our study is to determine the regularities of processes related to structure formation in the gypsum-alumina cement system in the presence of nanomodifiers. This will make it possible to increase the stability of the ettringite phase (the main component of cement stone), purposefully regulate the hydration rate, and coordinate the process of structure formation in time.

To achieve the goal, the following tasks were set:

– to investigate the influence of factors on the genesis of the structure of the ettringite phase;

– to build a mathematical model of modifying compositions based on gypsum-alumina cement with ultra- and nanoadditives, surfactants;

– to stabilize the ettringite phase by nanomodification.

4. The study materials and methods

The object of our study is the process of structure formation and control over initial factors in the gypsum-alumina cement system in the presence of nanomodifiers.

The hypothesis of the study assumes that it is possible to stabilize the formation of the ettringite phase (AFt) by eliminating the factors of ettringite instability by nanomodification.

Basic assumptions adopted are that the creation of a cement matrix with the regulation of the structure formation processes at the macro-micro and nano levels could make it possible to obtain new building materials with improved strength characteristics in terms of composition and structure.

The accepted simplifications relate to the fact that due to the introduction of carbon nanotubes, a dense defect-free shell of calcium hydro silicates is formed on the surface of solid phases and self-healing of cracks is observed through the stimulation of the growth of new formations in the defects of the cement matrix.

To study the factors of instability of the ettringite phase, gypsum-alumina cement was used (ratio of alumina cement and gypsum: 70:30). The chemical and granulometric compositions of the raw materials are given in Tables 1–3 [8] and Fig. 1.

Table 1

Chemical composition of alumina clinker GC-400, PAT "Volyn-cement" [8]

Oxide content, wt. %			
Al_2O_3	CaO	SiO_2	Fe_2O_3
50	35	10	5

The cement matrix plays a major role in the formation of the structure of building composites and strength properties. In the process of conducting research, alumina cement GC-400, GC-500, PAT "Volyn-cement" (Ukraine), was used as the initial binder.

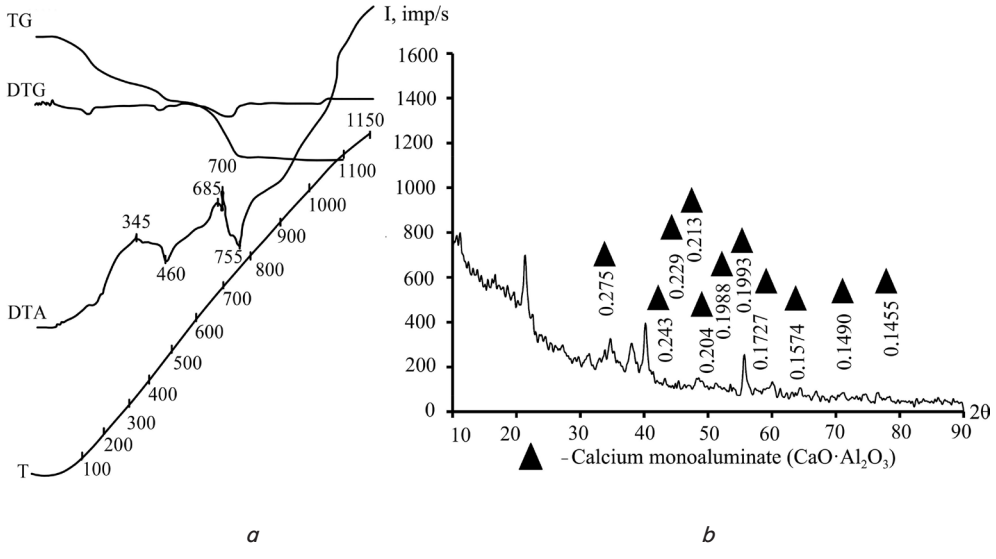
Basic physical-mechanical properties of alumina cements, according to [9], include fineness of grinding, setting time, and strength properties. Based on [9], we investigated the specified characteristics (Table 2 [8]).

Table 2

Determining ND of cement slurry (Alumina cement) [8]

No. of entry	Cement mass, g	Water mass, ml	W/C	Depth of immersion of the pestle, mm
1	400	160	0.4	40
2	400	120	0.3	25
3	350	115,5	0.33	33
4	350	112	0.32	23
5	350	108,5	0.31	25
6	350	122,5	0.35	40
7	350	119	0.34	40

Mineral and differential thermal analyses of alumina cement are shown in Fig. 1.



a *b*

Fig. 1. Mineral analysis curves for alumina cement: *a* — differential thermal; *b* — X-ray diffractogram

The mineral composition of alumina cement is represented by monalbite (d/n=0.275; 0.243; 0.229; 0.213; 0.204; 0.1988; 0.1893; 0.1727; 0.1574; 0.1490; 0.1455).

To stabilize the ettringite component, mineral studies were conducted. The chemical composition of the C_3A mineral is given in Table 4 [8].

Table 4

Chemical composition of the mineral C_3A [8]

Oxide content, wt. %					
Al_2O_3	CaO	Free CaO	SiO_2	Fe_2O_3	l.o.i.
37,36	61,80	0,38	сл.	сл.	0,28

In accordance with DSTU, the main characteristics of the C_3A mineral were investigated (Table 5).

Table 5

Physical-mechanical properties of the mineral C_3A

Alumina cement S_{sp}, m^2/kg	A_{008}, %	NDD, %	Setting time, h-min		Compressive strength, MPa, age, days		
			beginning	end	1	3	28
390	93	35	5 min 36 s	10 min 12 s	40.23	41.67	43.24

In studies to design composite binders for the purpose of stabilizing the ettringite phase, semi-aqueous gypsum of the G-5 brand was used. Basic physical-mechanical properties are given in Table 6 [8].

The normal density of gypsum slurry is determined in Table 6 [8].

Table 6

Determining ND of gypsum slurry [8]

No. of entry	Gypsum mass, g	Water mass, ml	W/G	Slurry spread, mm
1	300	168	0.56	215
2	300	153	0.51	175
3	300	156	0.52	180
4	300	159	0.53	190

The beginning of gypsum slurry setting is 7 min 45 sec. The end of gypsum slurry setting is 14 min 5 sec.

Table 7 gives the compressive strength of gypsum binder [8].

Table 7

Compressive strength of gypsum binder without additive [8]

No. of entry	Sample size, mm						m, g	ρ, kg/m^3	*Rcomp*, MPa	*Rbend*, MPa
	Top edge			Bottom edge						
1	16.0	4.0	4.0	16.0	4.0	4.0	444	1,756	4.07	3.55
2	16.0	4.0	4.0	16.0	4.0	4.0	462	1,805	3.67	4.04
3	16.0	4.0	3.9	16.0	4.0	3.9	447	1,791	3.54	3.94
4	15.9	4.0	4.1	15.9	4.0	4.1	456	1,749	3.81	3.92
5	15.9	4.0	4.1	15.9	4.0	4.1	456	1,749	3.76	3.84
6	16.1	4.0	4.0	16.1	4.0	4.0	452	1,755	4.11	3.61

The mineral composition of semi-aqueous gypsum is shown in Fig. 2 [8].

The mineral composition of semi-aqueous gypsum is represented by semi-aqueous gypsum (d/n=0.397; 0.322; 0.312; 0.278; 0.231; 0.218; 0.212; 0.184; 0.172; 0.169; 0.165; 0.144; 0.135).

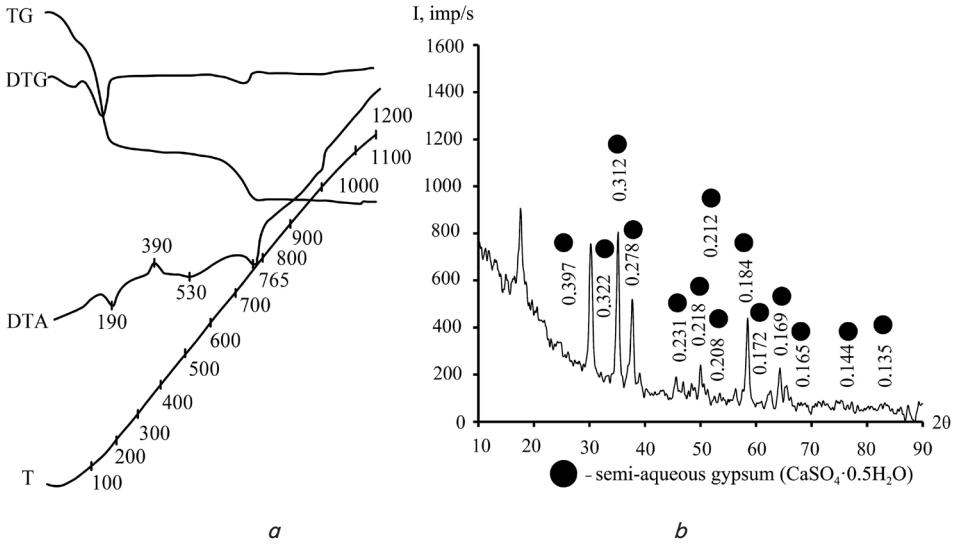
To increase the specific surface area, as well as active crystallization centers, gypsum binders were modified with carbon nanotubes.

Table 8 gives the properties of gypsum binder modified with multi-walled carbon nanotubes with functional groups.

Rietveld diagrams of gypsum hardening are shown in Fig. 3, *a*, *b* [8].

The results of quantitative X-ray phase analysis by the Rietveld method are given in Table 9 [8].

The research methodology involved modifying semi-aqueous gypsum with alumina cement. In this case, the optimal amount of modifier was determined to improve the physical-mechanical properties, as well as the influence of the mineralogical composition of the modified binder.



a *b*

Fig. 2. Mineral analysis curves for semi-aqueous gypsum [8]: *a* – differential thermal; *b* – X-ray diffractogram

Table 8

Properties of gypsum binder modified with multi-walled carbon nanotubes with functional groups

No. of entry	% SAS	% CNT	ND, %	Setting time, min		Strength, MPa	
				Beginning	End	Compression	Bending
Functional group – COOH							
1	0.4	–	58	16	24	5.5	3.2
2	0.4	0.015	58	9	13	8.0	3.85
3	0.4	0.035	58	8	13	8.1	3.6
4	0.4	0.09	58	8	12	8.45	3.95
5	0.4	0.18	58	11	17	7.86	3.6
Functional group – OH							
6	0.4	–	58	16	24	4.6	2.1
7	0.4	0.015	58	9	13	5.6	2.2
8	0.4	0.035	58	8	13	5.9	2.2

Table 9

Quantitative X-ray diffraction analysis by the Rietveld method [8]

Curing process cycles	$CaSO_4 \cdot 0.5H_2O$	$CaSO_4 \cdot 2H_2O$	$CaSO_4$	Impurities
Mineralogical composition after 1 curing cycle of semi-aqueous gypsum, curve 1	24	67	4	5
Mineralogical composition after 18 curing cycles of semi-aqueous gypsum, curve 2	5	86	4	5
Mineralogical composition after 1 curing cycle of modified semi-aqueous gypsum, curve 1	14	77	4	5
Mineralogical composition after 18 curing cycles of modified semi-aqueous gypsum, curve 2	1	93	1	5

When conducting experiments, a set of modern methods of X-ray diffractometry, scanning electron microscopy, low-temperature dilatometry, etc. was used. When determining the main physical-mechanical and construction and technical properties of nanomodified composites based on alumina cement and concretes based on them, current regulatory documents and methodologies were used. When optimizing nanomodified compositions based on alumina cement, experimental and statistical methods of experiment planning were used.

For X-ray diffractometry, a DRON-3 diffractometer was used with CuKa radiation, and the intensity of X-rays was recorded using a scintillation counter. The tape moved simultaneously with the rotation of the counter and recorded the curve of the dependence of the intensity of diffraction maxima on angle of reflection. When performing scanning electron microscopy, the devices REM-106I and JEOL JSM-T 220A were used. Before the study, the samples were covered with a thin film of gold by vacuum thermal evaporation in order to highlight the surface relief of contact chips and zones.

For X-ray fluorescence analysis (XRF), an ARL 9800 XP X-ray spectrometer was used. The intensity of the waves of all elements was determined by the software.

The principle of operation of electron probe microanalysis is as follows: X-ray spectra are characterized by the emission of electrons from the inner shells. The energy released is released in the form of X-rays.

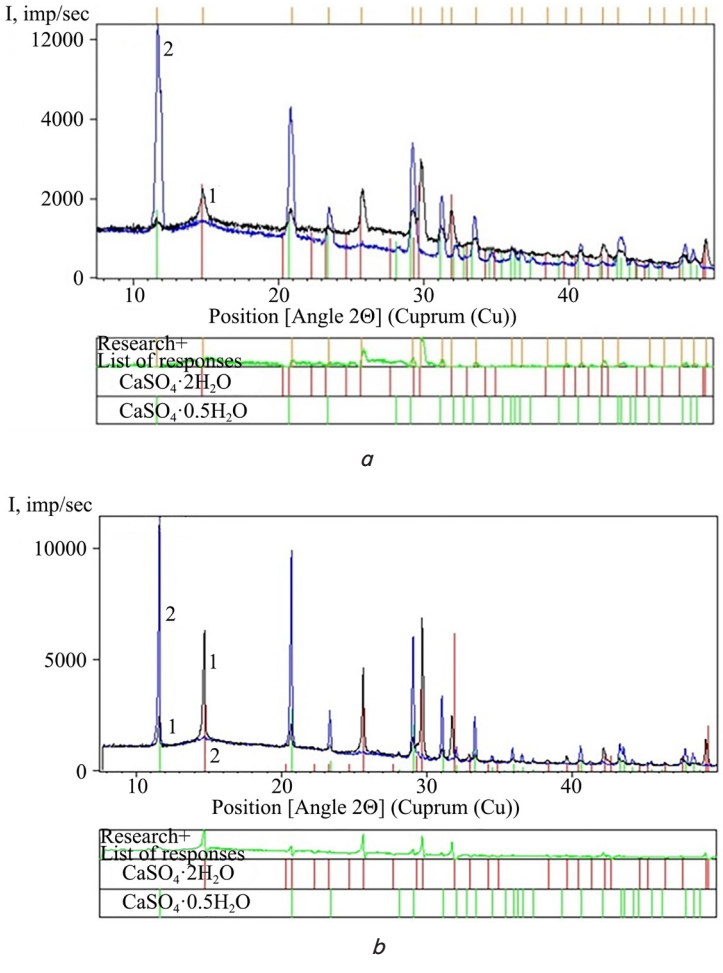


Fig. 3. Rietveld diagram of hardening over time: *a* – gypsum *G*-5 [8]: 1 – after 1 cycle; 2 – after 18 cycles; *b* – gypsum *G*-5 modified with CNT: 1 – after 1 cycle; 2 – after 18 cycles

The Rietveld method is based on comparing the experimental X-ray diffractogram with the simulated one obtained by regression analysis. First, the diffractogram is photographed, after which background correction, intensities normalization, and instrumental broadening of peaks are performed. Next, a model of the material structure is built, which includes crystallographic parameters of the phases, grain size distribution, and textural effects. The least squares method is used to refine the parameters and find the optimal fit to the experimental data. The quantitative phase composition is determined based on the ratio of the integral intensity of the peaks of each phase. GSAS-II, FullProf, TOPAS, or MAUD software packages are used for calculations.

This method allows for high-precision analysis of the phase composition of complex materials, including cement composites and nanomodified materials.

Swelling and shrinkage deformations of composite concretes were determined on 4x4x16 cm samples using a comparator with an indicator.

5. Results of research on the processes of structure formation in the gypsum-alumina cement system

5. 1. Influence of factors on the genesis of the ettringite phase structure

In order to increase ettringite, gypsum-alumina cement was prepared by activating alumina cement by adding gypsum and forming the system: alumina cement+gypsum.

In our studies, to design composite binders in order to stabilize the ettringite phase, semi-aqueous gypsum of the G-5 brand and dihydrate gypsum were used, the quality indicators of which correspond to [9].

The stability of ettringite is necessary when using PC, SAC, composite binders based on GC+Gypsum, as well as when modifying gypsum binders with alumina cement.

For the research, gypsum G-5-II was used in the amount of 30÷70 %, the main mineral of which is semi-aqueous gypsum and dihydrate gypsum.

Dependence plots: Kp (*a*) [10] on the environment with variable humidity of the samples over time, as well as dependence plots pH (*b*) [8], *t*, °C (*c*) [8], are shown in Fig. 4.

The results of physical-mechanical studies and X-ray structural analysis confirm the possibility of using gypsum-alumina cement. On the 3rd and 28th day of hardening, an ettringite phase is formed in the GC:G system, which is confirmed by its kinetics under normal conditions (Fig. 5) [10].

The monosulfate form is formed later as a result of the interaction of ettringite with anhydrous calcium aluminates. The formation of ettringite is initially accompanied by the compaction and strengthening of the cement stone, and then – as a result of the interaction of gypsum and calcium hydroaluminates, ettringite causes the expansion of the cement stone, as well as its destruction depending on its amount.

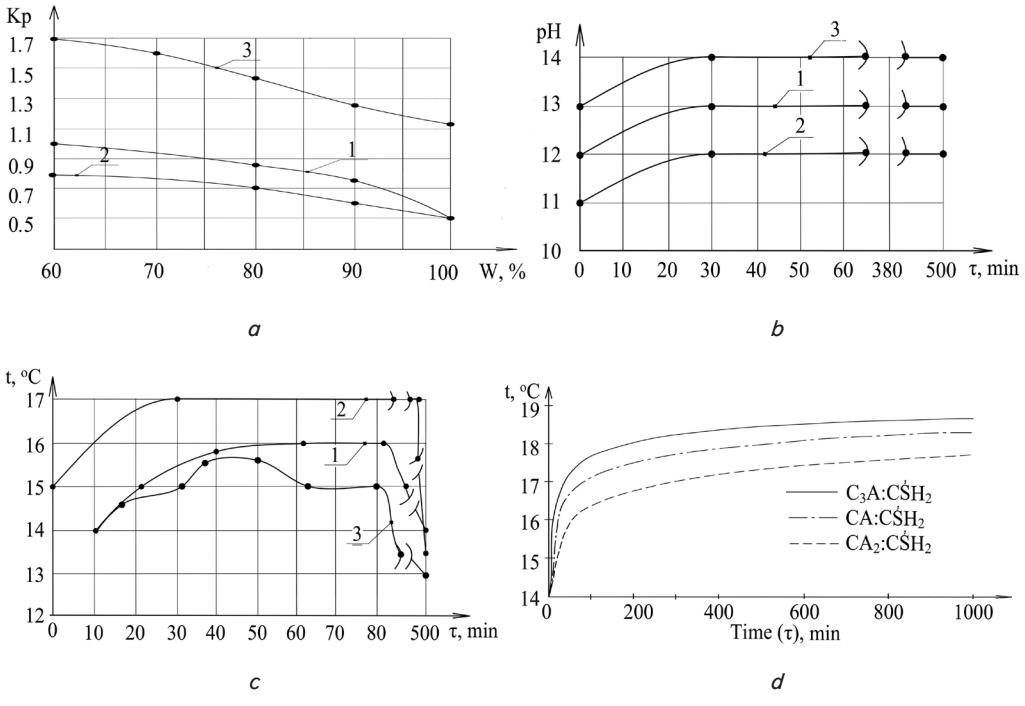


Fig. 4. Dependence plots: *a* — Kr on the environment with variable humidity of samples over time; *b* — dependence plots of Ph [8]; *c* — *t*, °C [8], containing: 1 — hydrate C_3AH_6, 2 — mineral $C_3AS_3H_{32}$; 3 — GC:G; *d* — plots of temperature change over time during hydration of the systems $CA+C\bar{S}H_2$, $CA_2+C\bar{S}H_2$, $C_3A+C\bar{S}H_2$ under normal conditions [10]

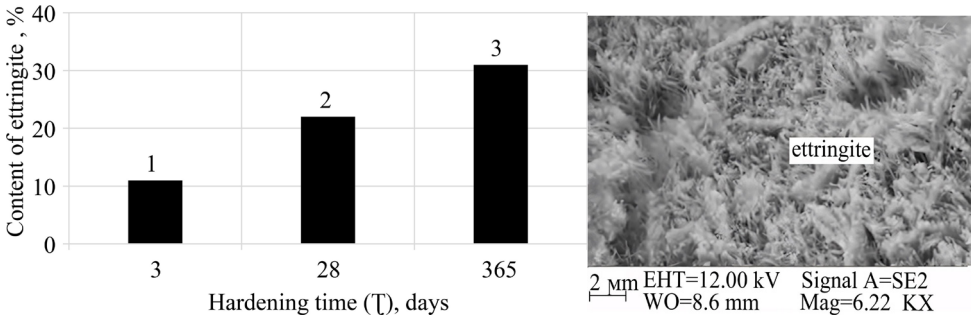


Fig. 5. Plots of change in the ettringite phase over time in samples under normal conditions [10]: *a* — kinetics; *b* — micrographs of the structure of GC+Gypsum (30:70) depending on the heat release of the system

5. 2. Construction of a mathematical model for modifying compositions based on gypsum-alumina cement

A composition containing the optimal content of ettringite was developed; the optimal content of components in the compositions of GC+G5, carbon nanotubes was determined. The results of the studies are given in Table 10 and Fig. 6.

The results of studies on the nanomodified building composites containing the maximum amount of ettringite show that the optimal composition, which provides the strength of the system of 43.8 MPa, is 70 % alumina cement and 30 % gypsum.

Table 10

Results of research on three-component raw material mixtures

Planning matrix and initial parameters of the material using cement, gypsum G-5, nanomodifier						
Components content at coded scale			Natural content of components, % by weight			Compressive strength of the material, MPa
X_1	X_2	X_3	C	G	CNT	
1	0	0	30	70	0.035	28.03
0	1	0	40	60	0.108	31.01
0	0	1	50	50	0.12	36.54
0.5	0.5	0	70	30	0.18	43.83
0.5	0	0.5	85	15	0.9	45.07
0	0.5	0.5	20	80	1.63	24.89
0.333	0.333	0.333	83.6	13.3	3.10	24.55

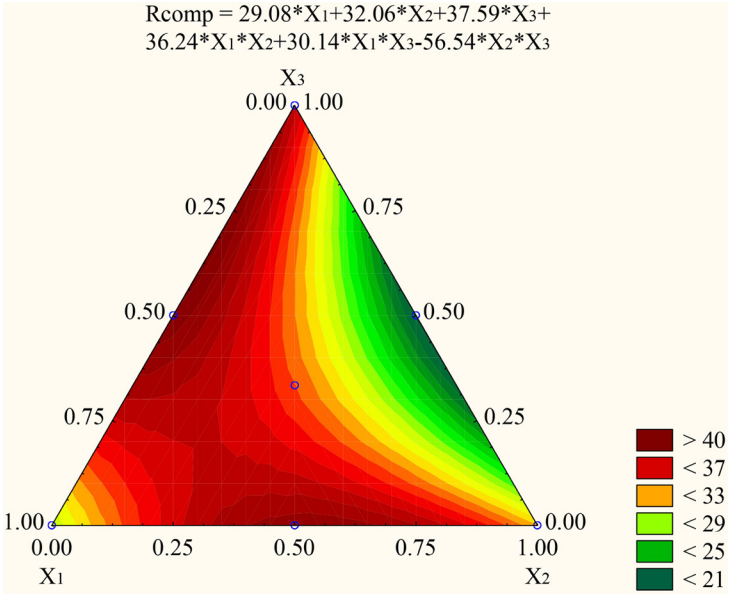


Fig. 6. Composition-compressive strength diagram for a material based on cement, gypsum G-5, and nanomodifier

5. 3. Stabilization of the ettringite phase by nanomodification

Studies on stabilization of the ettringite phase by nanomodification were conducted. The stability of ettringite crystals depends on the morphology of crystals formed under different conditions, for example, on the pH value.

The amount of ettringite phase formation was determined for the composition $C_3A+C\check{S}H_2$ under normal conditions in running water (*a*) and on day 3 of hardening at a temperature of 100 °C (*b*) (Fig. 7). An increase in the amount of ettringite phase was established.

The best physical, mechanical, and technological properties are achieved with the use of the Sika Viscocrete G additive: W/T for the $C_3A+C\check{S}H_2$ composition is 0.48 (versus 0.65 without plasticizer), compressive strength is 8.66 MPa.

In the $C_3A+C\check{S}H_2$ compositions, after three days of hardening, the main interplanar distances and intensities of the $C_3AS_3H_{32}$ hydrated phases appear after 3 days of hardening (d/n=0.973; 0.561; 0.388; 0.348; 0.256 nm) (Fig. 7). The lines $4CaO{\cdot}Al_2O_3{\cdot}13H_2O$ (d/n=0.423; 0.266; 0.246; 0.238; 0.212; 0.168 nm), $4CaO{\cdot}Al_2O_3{\cdot}19H_2O$ (d/n=0.331; 0.238; 0.151 nm), $Ca_4{\cdot}Al_2(OH)_{14}{\cdot}6H_2O$ (d/n=0.463; 0.255; 0.176; 0.151 nm) are observed (Fig. 7, 8).

Being in a saturated solution, ettringite will initially be released in a colloidal, highly dispersed state and simultaneously settle on the surface of the CA and C_2A particles, causing the entire system to slow down the setting time and the hydration process.

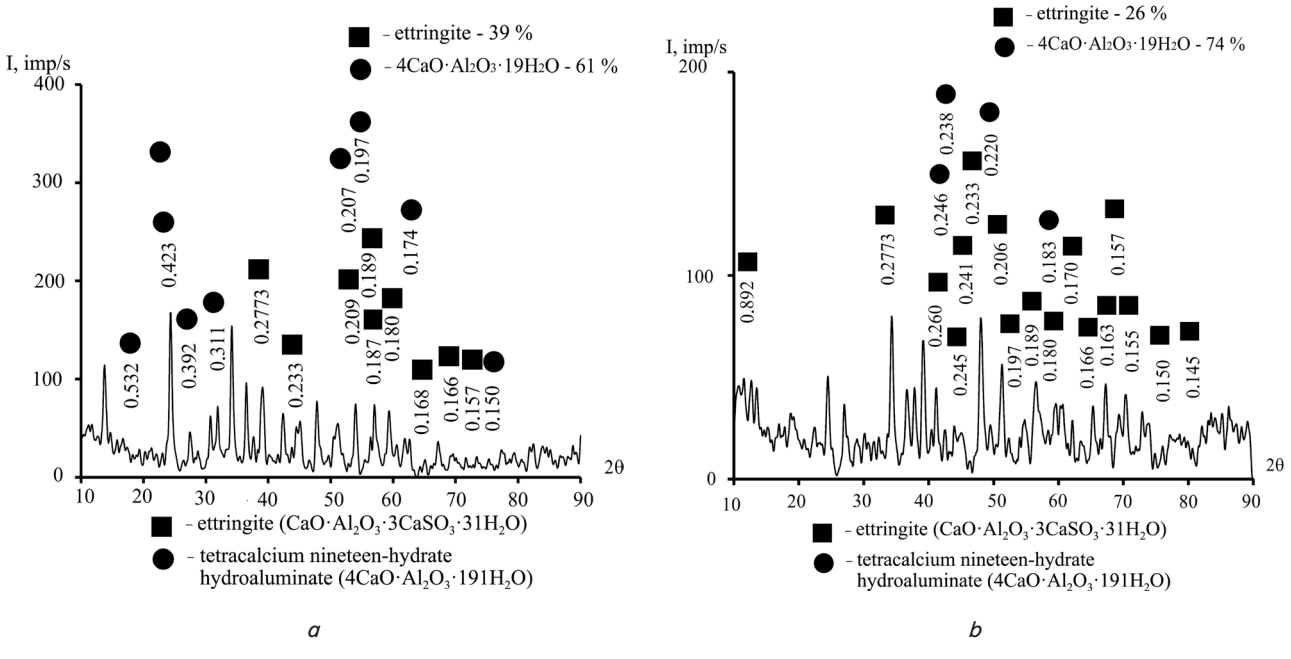


Fig. 7. The influence of ambient temperature on the structure and morphology of samples made from the composition $C_3A+C\acute{S}H_2$ on day 3 of hardening in running water: *a* — under normal conditions; *b* — at a temperature of 100 °C

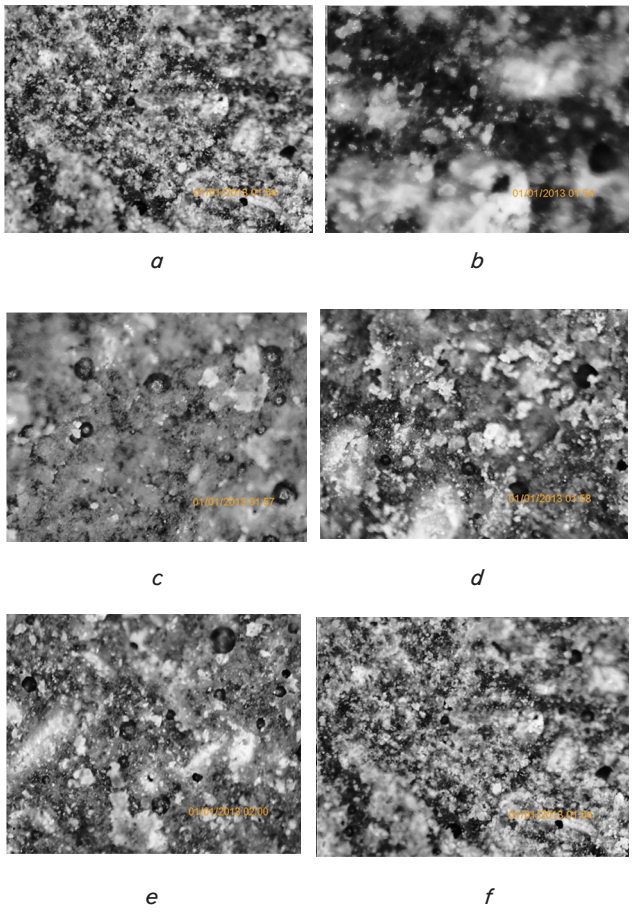


Fig. 8. Micrographs of ettringite formation in the C_3A+dihydrate gypsum system (×3000): *a* — on day 1 of hardening; *b* — on day 3 of hardening; *c* — on day 7 of hardening; *d* — on day 14 of hardening; *e* — on day 28 of hardening; *f* — on day 90 of hardening

6. Discussion of results based on investigating structure formation in the gypsum-alumina cement system and stabilization of the ettringite phase

Our results regarding the influence of factors on the genesis of ettringite phase structure are explained by the fact that the stability of ettringite crystals depends on their morphology, formed under different conditions, for example, on the pH value (Fig. 4). The pH range of 11–12 provides an acicular shape of ettringite (Fig. 4, 5, *b*). With an increase in the pH value, the length and thickness of acicular ettringite fibers decreases. At a pH of more than 13, ettringite has an X-ray amorphous gel-like structure. The formed structure of cement stone (Fig. 5, *b*) makes it possible to note the very important role of ettringite and aluminum hydroxide among other hydrates. The positive role of these hydrates in ensuring the properties of cement stone is explained as follows: the formation of ettringite occurs in the early stages of hardening at a high speed, which ensures an increase in the strength of the stone. Ettringite, with its elongated needle-like crystals, provides good reinforcement of the cement stone structure (Fig. 5, *b*). In the process of ettringite formation, a significant amount of water is involved and the volume of the solid phase increases significantly, thereby achieving structural strengthening in the early stages of hardening.

The results of the constructed mathematical model of the composition based on gypsum-alumina cement (Fig. 6) confirm the optimal content of ettringite (Fig. 5, *a*, 7) since the construction of a frame with the highest strength (Fig. 6, 8) can be achieved by adjusting the size of the hard surface and crystallization centers, which affect the initial spatial structure. Internal stresses that lead to weakening of the structure that has not yet formed do not arise due to the fact that the fusion of blocks occurs in free space.

The measure of change in the characteristic function at constant parameters and masses (concentrations) of all substances except the mass (concentration) of the component whose amount changes in the system is the chemical potential. In the case when the hydration process proceeds topochemically, the rate of structure formation will depend on the granulometric composition of the components and the rate of diffusion inside the grain.

The ettringite phase can be stabilized by eliminating the factors of its instability by nanomodification. As a result, ettringite has a higher stability compared to other hydrates and is less confirmed by phase transformation, which ensures the stability of the hardening structure (Fig. 7, 8). Aluminum hydroxide gel helps reduce internal stresses during crystal growth due to more elastic bonds with crystals, as a result of which the hardening structure retains high strength and integrity (Fig. 8). In the process of increasing the number of crystalline phases based on AH_3, other hydrated phases, including ettringite, are formed more. AH_3 fills pores and capillaries (Fig. 8), provides high density of the hardening structure.

In contrast to [11, 12], in which the experiments of scientists were aimed for a long time at developing a non-shrink cement, which is resistant to the action of aggressive environments and prevents the development of corrosion phenomena in concrete. The results of the study of concrete structures of 15 years of age in the Netherlands [11, 12] established only that the cause of the formation of shrinkage deformations is the instability of the structure of the ettringite phase. That is why the shrinkage temperature joints of roads are the weakest place to the action of corrosion [11, 12]. It is worth noting that the problem of instability of the ettringite phase is not solved for binders based on calcium sulfoaluminates [10, 13–17].

Solving this problem is possible by eliminating the factors of instability of the ettringite phase by nanomodification of expanding and non-shrinking cements (Fig. 6, 7), which are used to achieve waterproofing in the construction of hydraulic structures. The latter are also used for the construction of roadbeds, airfield self-tensioning slabs, and the production of pressure reinforced concrete pipes.

Our solutions completely resolve the issue of stability of the ettringite phase and increase the structural integrity of the gypsum-cement matrix due to the introduction of carbon nanotubes. This ensures the structuring of the cement matrix with the formation of a dense defect-free shell of calcium hydro silicates on the surface of the solid phases (Fig. 7, 8), giving better adhesion to the surface. In this case, self-healing of cracks will be observed due to stimulation of the growth of new formations in the defects of the cement matrix. An increase in contact interactions of structured boundary layers will lead to the formation of spatial framework cells in the structure of the modified cement matrix, which will cause the structure to be strengthened due to the formation of spatial packing (Fig. 8).

The conditions for applying the proposed solutions and the results obtained with their use are that the binder must be manufactured using ultrasonic treatment. The latter is required for uniform distribution of nanotubes in water with a plasticizer. The duration of ultrasonic treatment is 4.5 minutes. Subsequently, the resulting colloidal system is mixed with gypsum-alumina cement.

The disadvantages of the study are the impossibility of uniform distribution of nanotubes in a colloidal solution without the use of ultrasound.

The areas of application of the proposed nanomodified cement compositions are the construction of high-strength building structures, hydraulic engineering, when constructing road surfaces, self-stressed slabs, and waterproofing materials.

At the same time, the conditions for applying the research results are a temperature range from – 15 to 80 °C.

The expected effects of their implementation are primarily the improvement of the crack resistance of materials, the increase of mechanical strength, the reduction of shrinkage deformations, the increase in the durability of concrete and cement articles under difficult operating conditions.

Our research may in the future focus on designing a number of promising composite materials with a stable structure of the ettringite phase. This is due to the fact that the formation of ettringite during the hydration of nanomodified binders based on gypsum-alumina cement makes it possible to form the necessary structure and basic physical-mechanical properties.

7. Conclusions

1. The influence of factors on the genesis of the ettringite phase structure has been investigated. It was established that its formation in the early stages of hardening contributes to the strengthening of cement stone due to needle-shaped ettringite crystals, which provide structural reinforcement. The difference from the known research data is the determined role of aluminum hydroxide gel in reducing internal stresses due to elastic bonds with ettringite crystals. This is explained by the increased stability of the structure in the process of enhancing crystalline phases.

2. A mathematical model of modifying compositions based on gypsum-alumina cement with the use of ultra- and nano-additives and surfactants has been built. It connects the input variables such as the content of components of the nanomodified raw material mixture and the output variable – the ultimate compressive strength. With an increase in the content of carbon nanotubes exceeding 0.18 % and gypsum exceeding 30 %, there is a decrease in strength indicators. The isoline of the general form of the response surface takes a value of 43.8 MPa with coordinates (X_1=0.5; X_2=0.5; X_3=0). More significant from the point of view of the influence on the resulting (output) variable is the content of carbon nanotubes. A feature of this model is the ability to control the structure of the hardening system at the macro-, micro-, and nano-levels to obtain composites with the predefined physical-mechanical properties. This is explained by the correction of kinetics of ettringite formation and its interaction with other phases.

3. Stabilization of the ettringite phase and the formation of the required structure during hydration of binders based on gypsum-alumina cement have been achieved by modification with nanoadditives. The use of nanoadditives leads to an increase in the specific surface area of the solid phase and contributes to the production of crystal hydrates with an excessive amount of water without varying its fraction in the crystal structure and the transition of the AFt phase to the AFm phase. During hydration, elongated crystal hydrates and an aluminum hydroxide gel appear in the process of interaction of hydrosulfoaluminates. The formation of crystals with a spatial network, filamentous crystals and hydrates in an amorphous state occurs. The stability of the structure of the ettringite phase is confirmed by data on the kinetics of change in the ettringite phase on day 28 – 22 %, and by the rentrenostructural analysis. After boiling at a temperature of 100 °C, the ettringite content decreased by 13 % compared to the reference sample. The difference from existing data on ettringite stabilization is the construction of a spatial defect-free structure that prevents the material from breaking down upon further hydration. This is explained by the uniform distribution of nanoactivated crystallization centers.

Conflicts of interest

The authors declare that they have no conflicts of interest in relation to the current study, including financial, personal, authorship, or any other, that could affect the study, as well as the results reported in this paper.

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Data availability

The manuscript has associated data.

Use of artificial intelligence

The authors confirm that they did not use artificial intelligence technologies when creating the current work.

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