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DETERMINATION OF THE DEPENDENCE OF ETTRINGITE PHASE STABILITY IN NANOMODIFIED CEMENT SYSTEMS UNDER THE INFLUENCE OF VARIOUS FACTORS

The object of research is the stabilization of the ettringite phase in cement systems containing gypsum-alumina cement and nanoparticles. One of the most problematic areas is the instability of the ettringite phase, which affects the durability and mechanical characteristics of materials. The main problems are insufficient consideration of transitions between macro-, micro- and nanolevels when forming the structure of the hardening system. Multicomponent mixtures cannot be calculated using existing models, since a significant number of initial parameters and characteristics are not taken into account. The transition of systems from one level to another is not taken into account, namely the transition of systems from macro- to micro- and to nanolevel. The study used nanomodification of cement systems based on gypsum-alumina cement by introducing synthesized composites (carbon nanoparticles) into the hardening matrix. The influence of the raw material mixture components on the correction of the factors of instability of the ettringite phase, the processes of structure formation was studied, which allows in the future to eliminate these shortcomings and control the structure formation at different levels of the hardening matrix system. The optimal amount of calcium sulfate for the formation of ettringite was obtained – 30–40 % of the composition mass. This is due to the fact that the proposed composition of GC-40/G – 70/30 % has a significant amount of calcium hydroaluminates in the hydration process, the compressive and bending strengths are, respectively, 14 and 10 MPa. In particular, a dispersed medium resistant to delamination is formed, the water release of which is stabilized within 3 hours. Obtaining such values is ensured due to the fact that ettringite is formed in the early stages of hardening and provides an increase in the strength of the stone at a high speed. Compared with similar known gypsum-alumina cements, this provides advantages in the formation of high-basic ettringite. The results obtained are recommended for use in the construction of tunnels, restoration of hydraulic structures and transport infrastructure.

Keywords: *binder, solution, ettringite, ettringite stabilization, aluminate cements, sulfoaluminate cements.*

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1. Introduction

Ettringite binders are represented by sulfoaluminate (gypsoaluminate) cements [1]. The latter belong to the group of special cements, the phase composition of which includes calcium sulfoaluminate minerals $3CaO{\cdot}Al_2O_3{\cdot}SO_3(C_3AS)$. Positive properties: firing temperature: 1250–1350 °C, reduced amount of CO_2 release, high hydraulic activity, rapid strength gain, no volume changes during hardening.

However, the production of sulfoaluminate cements requires the use of scarce materials: bauxite ores, aluminate slags. In addition, the formation of ettringite during hydration in sulfoaluminate cements creates an uneven structure, since ettringite is less thermodynamically stable in the conditions of the porous electrolyte of cement stone. It is prone to recrystallization into a more thermodynamically stable monosulfate form of trihydrosulfoaluminate (AFt-phase) into monohydrosulfoaluminate (AFm-phase), also known as $C_3A{\cdot}CaSO_4{\cdot}12H_2O$. Also, some sulfoaluminates are not stable under certain operating conditions.

The second direction is the development of special cements and composite binders based on aluminosulfates of increased stability of ettringite due to modification with nanoadditives.

The creation of new varieties of Portland cements for general construction and special purposes is one of the main directions of modern developments in the technology of binder production. In the group of special cements, a special place is occupied by gypsum-alumina, sulfoaluminate and other special cements [1–5]. The main research work during the development of such cements is carried out in the direction of creating new compositions of scarce components. With such a material composition, the cost of gypsum-alumina cements slightly exceeds ordinary ones, but their use improves the performance characteristics of products, in particular, mechanical strength, frost resistance and water resistance increase. Summarizing the accumulated experience, it is possible to note that new effective gypsum-alumina compositions can be obtained on the basis of gypsum and production waste. Modification of calcium sulfates will allow to purposefully regulate the rate of its hydration and to coordinate the structure formation of cement stone in time. Therefore, studies aimed at studying the influence of additives of various nature on the hydration activity of the $CaO\text{-}SO_3\text{-}H_2O$ system and the ability to regulate stresses in the structure of cement stone are relevant from the point of view of theory and practice.

Sulfoaluminate cements, which can be effectively used as binders in the manufacture of products without steaming and to accelerate construction times, and to reduce the time of heat-moisture treatment, have an unstable structure of the ettringite phase.

The paper [1] presents the results of studies of the properties of sulfoaluminate cement aggregates with the addition of Portland cement and limestone. It was shown that the addition of Portland cement (up to 30 %) to sulfoaluminate cements significantly worsens their mechanical properties due to the rapid hydration of elemi, which leads to limited access of water to the cement particles. However, the addition of limestone did not have a negative effect on hydration and even contributed to its acceleration. However, the issues related to the decrease in strength when adding large amounts of both Portland cement and limestone remained unresolved. The reason for this may be the limitation of water access to the cement particles or the dilution effect. An option to overcome the corresponding difficulties may be to reduce the amount of impurities or use other compositions. This is the approach used in the paper [5], but the results require further study, especially with regard to long-term strength. All this allows to state that it is advisable to conduct a study dedicated to optimizing the compositions to ensure better rheological and stronger characteristics of aggregates based on sulfoaluminate cements.

In [2], the results of studies on the influence of alumina-rich bauxite ore on the mineralogical composition of sulfoaluminate cement (CSA) clinker and its performance are presented. It is shown that the Al_2O_3-rich bauxite ore of Minim-Martap contributes to the increase in the performance of CSA cements, providing high compressive strength after 28 days (up to 28 MPa). However, the issues related to the influence of high gypsum content on hydration reactions and microstructural changes in cement remain unresolved. The reason for this may be the rapid formation of ettringite and microcracks in the cement structure. An option to overcome the corresponding difficulties may be to regulate the amount of gypsum or change the clinker processing temperature. This is the approach used in [1], but the studies still require a more in-depth assessment of the rheological properties of the cement paste. All this allows to state that it is advisable to conduct a study devoted to optimizing the composition of CSA cements to achieve better mechanical and microstructural properties.

In the work [3], the results of studies on the influence of different types of cement, curing age and humidity of concrete samples on the ultrasonic pulse velocity (UPV) are presented. It is shown that with curing time, the ultrasonic pulse velocity increases, and this increase depends on the type of cement: cements with additives of pozzolanic materials demonstrate a greater increase in velocity at later stages of hydration. However, issues related to the influence of the geometry of the samples on the test results, especially for CPV type cement, remain unresolved. The reason for this may be the heterogeneity of the samples and the difficulty of accurate alignment of ultrasonic sensors. An option to overcome the relevant difficulties may be the use of more standardized geometries or the adaptation of alignment methods. All this allows to state that it is advisable to conduct a study devoted to the standardization of testing methods for samples of different geometries for determining the ultrasonic characteristics of concrete.

The paper [4] presents the results of studies of the AFm phase of cements, which is a family of hydrated calcium aluminates based on the hydrocalumite structure. It is shown that the replacement of hydroxide by anions such as sulfate or carbonate significantly affects the stability of AFm phases at a temperature of 25 °C. Carbonate contributes to the stabilization of AFm, displacing hydroxide and sulfate under conditions commonly encountered in cement systems. However, issues related to the existence of incomplete solid solutions between hydroxide and sulfate AFm phases, which affects the mineralogical balances of hydrated cement paste, remain unresolved. The reason for this may be the difficulties in the synthesis of some precursors and variable experimental conditions. An option to overcome these difficulties may be to more precisely regulate the hydration conditions and study the composition of cement under real operating conditions. All this allows to argue that it is advisable to conduct a study devoted to studying the influence of various anions on the stability of AFm phases in cement systems.

In [5], the results of studies of the microstructure of hydration phases in the AFm-AH_3 and AFt-AH_3 systems formed during the hydration of calcium sulfoaluminate cement (CSA) are presented. It is shown that the AH_3 phase has a micro- or nanocrystalline structure, with the average crystal size in the AFt-AH_3 system being about 20 nm. However, questions related to the influence of different hydration conditions on the microstructure and stability of the AH_3 phase, as well as on its interaction with other hydration products, such as AFm and AFt, remain unresolved. The reason for this may be the complexity of the analysis due to the low crystallinity of the phases and possible fluctuations in the composition depending on the reaction conditions. An option to overcome the corresponding difficulties may be to conduct more detailed studies of the AH_3 microstructure under different hydration conditions. All this allows to state that it is advisable to conduct a study devoted to the detailed characterization of the AH_3 phase microstructure and its influence on the properties of cement.

The paper [6] presents the results of studies on the use of gypsum as an OPC component to improve the mechanical properties of very soft clays with a high initial water content and the utilization of industrial gypsum waste. It is shown that increasing the gypsum fraction (G/C) to a certain threshold has a positive effect on reducing the final water content and increasing the dry density of the treated clays, as well as on increasing their strength under uniaxial compression (UCS). However, issues related to the long-term stability of the treated clays, taking into account the sulfate content in the soil, remain unresolved. The reason for this may be objective difficulties associated with the difficulty of predicting the effect of sulfates on the durability of the material. An option to overcome these difficulties may be additional control over the sulfate content during the soil strengthening process. This is the approach used in the paper, but further research is needed to study the effect of sulfates on the long-term stability of CBSC.

Calcium sulfoaluminate cements are well-known alternatives to ordinary Portland cement (OPC). They were developed in China in the 1970s. Developed by the China Building Materials Academy (CBMA), they were intended for the production of self-stressing concrete pipes due to their expansion properties.

In [7], the results of studies on the electrical properties of ettringite binders as repair materials are presented. It was shown that the electrical resistance of ettringite binders is higher compared to ordinary Portland cement (OPC), which indicates lower transport properties, but at the same time, the increased porosity and lower alkalinity of the pore solution can contribute to the corrosion of reinforcement. However, the issues related to the precise determination of the influence of hydration and degree of saturation on the electrical properties remain unresolved. The reason for this may be the objective difficulties associated with the difference in water content and degree of saturation, which affect the electrical conductivity. An option to overcome these difficulties may be to take saturation into account during electrical resistance measurements. All this suggests that it is advisable to conduct a study devoted to the long-term stability of such binders under operating conditions and their influence on transport properties.

In [8], the results of studies on the mechanisms of slowing down hydration by citric acid in ettringite binders are presented. It is shown that citric acid acts as an inhibitor of ettringite formation, promoting the formation of monosulfate and gypsum. However, questions related to the exact influence of citric acid on the structure of the ettringite crystal lattice remain unresolved. The reason for this may be objective difficulties associated with the interaction of organic acids with binders, which creates a kinetic barrier for ettringite precipitation. An option for overcoming the relevant difficulties may be to adjust the rate of dissolution of phases in the models. All this allows to argue that it is advisable to conduct a study on the influence of organic impurities on the hydration processes and phase composition of ettringite binders. In [9], the results of studies on the use of nanomodified ettringite to improve the characteristics of photopolymer epoxy acrylate resins are presented. It has been shown that modification of ettringite with silane agents (KH-550 and KH-570) improves its dispersion in the resin and contributes to increased tensile strength and reduced shrinkage. However, issues related to further improvement of the compatibility of the nanomaterial with the resin matrix remain unresolved, which may affect the accuracy and stability of the composite properties. This may be due to limitations in the uniformity of the distribution of nanoparticles or the difficulty in maintaining stable interfacial interaction. An option to overcome these difficulties may be the use of alternative modification methods or new types of silanes to ensure better adhesion. All this suggests that it is advisable to conduct research devoted to further improving the mechanical properties and stability of photopolymer composites using modified ettringite.

In [10], the results of studies on the influence of the hardening temperature, chloride concentration and nano-metakaolin content on the formation of Friedel salts and ettringite in cement pastes mixed with seawater are presented. It is shown that an increase in the chloride concentration promotes the formation of Friedel salts and ettringite, which can negatively affect the strength of the material. An increase in the hardening temperature reduces the amount of ettringite formed, and nano-metakaolin reduces the negative impact of delayed ettringite formation. However, issues related to optimizing the composition of cement composites with seawater to minimize the risk of cracking remain unresolved. The reason for this may be the difficulties with the uniformity of the distribution of nanomaterials and maintaining the stability of hydration processes at different temperatures. An option to overcome these difficulties may be to modify the content of nanometakaolin to achieve a balance between the strength and durability of the material. All this allows to state that it is advisable to conduct additional studies devoted to the study of the composition of cement composites with seawater and nano-metakaolin to increase their durability.

In [11], the results of studies of the thermal properties of cement based on calcium sulfoaluminate (CSA) as an alternative to ordinary Portland cement (OPC) are presented. It is shown that the hydration of CSA cement is significantly different from OPC, in particular, in that the main hydration product is formed – ettringite, which provides a short setting time and high early strength. However, issues related to the thermal effect on hydration and the final characteristics of the material remain unresolved, especially in massive structures, where uneven heat distribution can lead to cracks. The reason for this may be the high heat of hydration and a sharp increase in temperature in the first hours after mixing. An option to overcome the corresponding difficulties may be controlled hydration at reduced temperatures or the use of modified cement compositions. All this allows to argue that it is advisable to conduct a study dedicated to optimizing the thermal properties of CSA cement to prevent the appearance of early cracks in massive concrete structures.

In [12], the results of studies on the influence of lime powder on the properties of the composite system of Portland cement (PC) and sulfoaluminate cement (CSA) at low temperatures are presented. It is shown that the addition of lime powder significantly increases the compressive strength of the PC–CSA system and reduces the hardening time. However, issues related to the long-term stability of such systems at sub-zero temperatures and the mechanisms of acceleration of hydration remain unresolved. The reason for this may be objective difficulties associated with the chemical complexity of hydration processes and limited possibilities of long-term temperature control. An option to overcome these difficulties may be the use of additional heat sources or changing the proportions of the components of the cement mixture. This is the approach used in [5], but the feasibility of such changes requires further research. All this allows to state that it is advisable to conduct a study devoted to optimizing the composition of cement systems to increase frost resistance with minimal energy costs.

In [13], the results of studies on the influence of different types of fine aggregate and cooling methods on the engineering properties of cement mortar based on sulfoaluminate cement after heating are presented. It is shown that water immersion cooling (WIC) or the use of a fire extinguisher (FEC) contribute to better restoration of cement mortar strength compared to natural cooling (NGC). However, issues related to the influence of temperature on the microstructure of cement and interaction with different types of aggregate remain unresolved. The reason for this may be objective difficulties associated with complex dehydration processes and structural changes at high temperatures. An option to overcome the relevant difficulties may be to optimize the composition of aggregates and cooling modes to increase the stability of the material. All this allows to state that it is advisable to conduct a study devoted to the influence of different types of aggregates and cooling modes on the microstructure of cementitious materials after thermal exposure.

Considering the prospects for the development of building products, one of the current directions of modern research can be distinguished – the creation of multicomponent binder systems, as a result of the hydration of which insoluble or slightly soluble substances with special properties are formed. Among them, the properties associated with the expansion of cement stone, due to the formation of ettringite, which creates the problem of composition stability, stand out. In recent years, a significant number of studies of this mineral have been conducted, but there is no final solution to the issue [11–13]. In this regard, the use of cement binders (Portland cement, sulfate-resistant, modification of sulfate and alumina binders) requires special measures in the manufacture of building productSolving the problem of theoretical generalization of the stabilization of the ettringite phase and complex processes that determine the formation of the structure and physical and mechanical properties, their relationship with the composition of the starting materials and the technological process of obtaining products will allow creating a promising series of composite cements.

The development of sulfoaluminate compositions based on calcium sulfates and gypsum-alumina cement makes it possible to significantly expand the raw material base and scope of application, and to develop new technologies for the production of building materials.

The aim of research is to identify the dependence of the stability of the ettringite phase under the action of various factors of nanomodified gypsum-alumina cement. This will allow to ensure improved performance characteristics of special concretes, in particular their durability and resistance to aggressive environments.

2. Materials and Methods

The object of research is the stabilization of the ettringite phase in cement systems containing gypsum-alumina cement and nanoparticles.

According to the research methodology, the main properties of raw materials GC-400, GC-500 (Turkish and Polish manufacturers) and gypsum binders (dihydrate gypsum stone, gypsum G-5 Kamianets-Podilsk and Ivano-Frankivsk) were determined according to the methods of DSTU.

The main characteristics of alumina cement (GC) are given in Table 1 [14, 15].

The main physical and mechanical properties of alumina cements, according to [15], include: fineness of grinding, hardening time and strength properties.

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

Table 1

Physical and mechanical properties of alumina cement [14, 15]

Aluminous cement S_{sp}, m^2/kg	A_{008}, %	NDD, %	Curing time, hours-minutes		Compressive strength, MPa, at age, days		
			begin	end	1	3	28
398	92	33	60 min 56 sec	12 hours 5 min 10 sec	30.52	36.42	41.23

Note: NDD – normal dough density

In studies to create composite binders in order to stabilize the ettringite phase, semi-aqueous gypsum of the G-5 brand was used, the quality indicators of which correspond to [15].

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).

In the research and quality of modifiers were used: carbon nanotubes, silicon dioxide, Koksu shungite rocks, SiC.

The purity of carbon nanotubes is more than 92 %, outer diameter 8–28 nm, inner diameter 5–10 nm, length 10–35 μm. The density determined by the nanotube sedimentation method is 0.15 g/cm^3, the true density is 2.2 g/cm^3, the specific surface area is 220 m^2/g.

Silicon dioxide is highly dispersed silica manufactured by LLC "Zavod DK Orisil", Zaporizhzhia, Ukraine (TU U 24.1-31695418-002:2008). The content of silicon dioxide in mass terms for the calcined substance is 99.9 %. The specific gravity according to the BET method is 220 m^2/g. The bulk weight is 49 kg/m^3. The pH value (4 % suspension) is 3.9.

Koksu shungite rocks (trademark "Taurit") are powders with a carbon content of 95 %, which contain grains of a fraction of 5 microns up to 90 %.

The determination of the physical and mechanical properties of alumina cement and nanomodified compositions based on it was carried out in accordance with DSTU B.V. 2.7-187:2009, DSTU EN 196-1:2019 (EN 196-1:2016, IDT), DSTU B.V. 2.7-185:2009, and DSTU B.V. 2.7-188:2009. The following indicators were determined: normal density, hardening times of alumina dough and composite binders, ultimate compressive and flexural strength, fineness of grinding of alumina cement and modified nanocompositions. For the experiments, samples measuring 4x4x16 cm were manufactured. The addition of plasticizer additives to alumina composites, as well as concrete mixtures based on them, was carried out in accordance with DSTU B V.2.7-175:2008, DSTU B V.2.7-69-98 and DSTU EN 934-2:2019 (EN 934-2:2009+A1:2012, IDT).

The introduction of nanoparticles was carried out by dispersing them in a water-plasticizer medium by ultrasonic treatment for 4.5–6 minutes with subsequent mixing of the components with gypsum-alumina cement.

To assess the influence of the components and ensure stabilization of the ettringite phase, alumina cement was mixed with semi-aqueous gypsum of the G-5 brand in different ratios. The optimal ratio was determined by the maximum ettringite content using the simplex lattice method of experimental planning. The optimal component ratios were established taking into account the influence of each component on the physical and mechanical characteristics.

Uniform placement of experimental points in the (q–1)-dimensional simplex was ensured using simplex plans. Nodes (q, n), which contain simplex lattices, are points of the plans.

For each component in each lattice, n+1 uniform equations with an interval from 0 to 1 (x_i=0.1/n....1) were used and existing combinations of combinations were used. The mathematical model is described by the following formula:

$$\sum_{i=1}^{q} X_i = 1;\ 0 \le X_i \le 1;\ i = 1,3....q. \quad (1)$$

For this system, a second-order model was described by a third-degree polynomial. To estimate the coefficients of the second- and third-degree approximating polynomial, experiments were conducted and the system responses were determined at all points of the plan.

When calculating the strength value at each point of the model, response surface curves were constructed.

A full factorial experiment (PFE 2^n) allowed to determine the influence of individual variables (gypsum content, nanomodifiers, water-cement ratio) on the formation of the phase composition and strength properties of composite cements.

To determine the composition with the optimal content of the ettringite phase, studies were conducted using physicochemical analysis, diffraction X-ray analysis, thermogravimetric analysis and electron microscopy.

To identify the phase composition of the studied samples, an X-ray diffractometer DRON-3 was used with CuKα radiation. The intensity of X-rays was recorded using a scintillation quantum counter.

To determine the chemical composition, X-ray fluorescence analysis (XRF) was performed and an ARL 9800 XP X-ray spectrometer was used. The method involved analyzing the composition of the material by exciting characteristic X-ray radiation and subsequent registration of the spectrum using a spectrometer. This allowed determining the qualitative and quantitative composition of elements in the samples.

PEM-106И and JEOL JSM-T 220A devices were used to conduct scanning electron microscopy. To highlight the zones and surface relief of the cleavages, the samples were covered with a gold film using vacuum thermal evaporation. The study was carried out in a high-vacuum mode or a variable pressure mode. The obtained images of the sample surface at different magnifications were analyzed to identify microstructural features, including determining porosity, phase composition and the nature of the distribution of components.

The ARL 9800 XP X-ray spectrometer was used to conduct X-ray fluorescence analysis (XRF). The wave intensities of all elements were calculated by software.

During electron probe microanalysis, X-ray spectra from the inner shells emit electrons and energy is emitted in the form of X-ray waves.

The Rietveld method is based on a comparison of two X-ray diffraction patterns – experimental and simulated using regression analysis. After taking the diffraction pattern, the background, intensity and broadening of the peaks are corrected. After that, a model of the structure is created that includes the grain size distribution, relief effects and structural characteristics of the phases. In order to find the optimal agreement with the experimental data, the least squares method was used. For calculations of the quantitative phase composition, the correlation of the integral value of the peak intensity of each phase was used using the GSAS-II, FullProf, TOPAS or MAUD software.

3. Results and Discussion

Initially, studies were conducted on the influence of the ratio of components of gypsum-alumina cement on the compressive strength at the age of 1–3 days depending on the value of the water-hardness ratio, which depends on the specific surface area, the number of active crystallization centers and the mobility of the initial components. Therefore, in order to increase ettringite, the activation of alumina cement was carried out by adding gypsum and the water demand of composite binders based on alumina cement, gypsum was determined (Table 2–7).

Table 2

Determination of the normal density of the paste consisting of: 70 % alumina cement and 30 % gypsum [16]

No.	Cement mass, g	Gypsum mass, g	Water mass, ml	W/C	Immersion depth, mm
1	245	105	115.5	0.33	10
2	210	90	90	0.3	6
3	210	90	156	0.52	40
4	210	90	147	0.49	40
5	210	90	135	0.45	40
6	210	90	126	0.42	40
7	210	90	114	0.38	40
8	210	90	120	0.4	39
9	210	90	117	0.39	38
10	210	90	111	0.37	38
11	210	90	108	0.36	37

Note: Start of binder hardening – 4 min 56 s. End of binder hardening – 6 min 39 s

Table 3

Determination of the normal density of a paste consisting of: 50 % alumina cement and 50 % gypsum [16]

No.	Cement mass, g	Gypsum mass, g	Water mass, ml	W/C	Immersion depth, mm
1	150	150	117	0.39	36
2	115	150	120	0.45	37
3	150	150	118.5	0.4	37

Note: Start of binder hardening – 4 min 40 s. End of binder hardening – 6 min 5 s

Table 4

Determination of the normal density of a paste consisting of: 30 % alumina cement and 70 % gypsum [16]

No.	Cement mass, g	Gypsum mass, g	Water mass, ml	W/C	Immersion depth, mm
1	90	210	117	0.39	20
2	90	210	126	0.42	39
3	90	210	123	0.41	36÷37

Note: Start of binder hardening – 4 min 53 s. End of binder hardening – 6 min 23 s

Table 5

Average values of the main properties of samples hardened in tap water

No.	Composition	Sample size, cm			m_{dr}, g	ρ, kg/m^3	m_{wat}, g	W, %	$R_{pr\ dr}$, MPa	$R_{pr\ wat.}$, MPa	K_p
1	C_3A	2.0	2.0	2.0	14.83	1854	6.78	6.78	6.86	4.03	0.59
2	C_3A+ dihydrate gypsum	2.0	2.0	2.0	14.92	2139	15.92	6.73	8.66	5.25	0.60
3	100 % GC	16	4	4	518	2040	529	1.9	36.41	36.41	1.0
4	GC:G (70:30) %	16	4	4	486	1841	495	4.6	18.75	19.43	1.04

Note: m_{dr} – mass of dry sample; ρ – density of sample; m_{wat} – mass of wet sample; W – water absorption of sample; $R_{pr\,dr}$ – compressive strength of dry sample; $R_{pr\,wat}$ – compressive strength of wet sample; K_p – stability coefficient

Table 6

Compressive strength of binders of the GC:G system [17]

No.	Composition	Sample size, cm			M_{dr}, g	ρ, kg/m^3	R_{pr1}, MPa	R_{pr2}, MPa	$R_{pr\ tot.}$, MPa	$R_{bend.}$, MPa	$R_{bend.\ tot.}$, MPa
1	Aluminous + 0 % additives	16.0	3.9	3.9	499	2050	32.55	32.55	36.41	7.43	7.92
		16.1	3.9	3.9	499	2040	38.52	40.0		9.71	
		16.1	4.0	4.0	527	2050	37.48	37.33		6.63	
2	Aluminous cement, brand	16.1	4.0	3.9	547	2190	16.00	17.96	15.19	7.59	7.66
		16.1	3.9	3.9	557	2280	14.07	14.84		7.79	
		16.1	4.0	3.9	551	2190	15.36	12.77		7.59	
3	GC:G (70:30)	16.1	4.0	4.0	487	1890	16.00	13.5.48	14.37	6.06	8.74
		16.1	4	3.9	487	1940	16.13	14.71		10.07	
		16.3	4	3.8	495	2000	13.56	14.84		10.1	
4	GC:G (50:50)	16	3.9	4.1	471	1840	8.77	10.84	10.8	7.29	7.36
		16	3.9	4	463	1860	12.00	11.36		6.76	
		16.1	3.9	4	466	1860	11.61	10.19		8.04	
5	GC:G (30:70)	16	3.9	4	453	1820	8.34	10.32	10.4	6.47	6.76
		16	4	3.9	433	1740	9.67	10.45		6.33	
		16.1	3.9	3.9	440	1800	10.57	10.32		7.48	

Note: M_{dr} – mass of dry sample; ρ – density of sample; R_{pr1} – compressive strength of the first half of the beam of the dry sample; R_{pr2} – compressive strength of the second half of the beam of the dry sample; $R_{pr.\,tot}$ – average value of compressive strength of the dry sample; R_{bend} – bending strength of the dry sample; $R_{bend.\ tot}$ – average value of bending strength of the dry sample

Table 7 [17] shows the average values of the main properties of the samples that hardened in the tap water environment. The main physical and mechanical properties of the binders are given in Table 7 [17], Table 8.

Table 7

Water absorption of binders of the GC:G system [17]

No.	Sample mass in water-saturated state, g	Mass of dry samples, g	Water absorption, %	Water absorption, %
Aluminous cement + 0 % additives				
1	508.000	499.000	1.80	1.90
2	509.000	499.000	2.00	
3	537.000	527.000	1.90	
Alumina cement + 0 % additives. brand				
4	562.000	547.000	2.74	2.84
5	573.000	557.000	2.87	
6	567.000	551.000	2.90	
70 % Alumina cement + 30 % gypsum				
7	509	487	4.52	4.63
8	510.000	487.000	4.72	
9	518.000	495.000	4.65	
50 % Alumina cement + 50 % gypsum				
10	498.000	471.000	5.73	6.00
11	492.000	463.000	6.26	
12	494.000	466.000	6.01	
30 % Alumina cement + 70 % gypsum				
13	490.000	453.000	5.73	6.00
14	464	433	6.26	
15	475	440	6.01	

The use of modifier additives and the study of their influence on the thermodynamic and hydrodynamic stability of the hardening structure of ettringite $3CaOAl_2O_3 \cdot 3CaSO_4 32H_2O$ will lead to an increase in water resistance, improvement of technological factors. This, in turn, will contribute to the expansion of the scope of application of composites based on them.

The composition of the raw material mixture based on GC:C (70:30) has the greatest water separation, which is explained by its smaller specific surface compared to the compositions of the raw material mixture based on: GC:G (30:70) and GC:G (50:50). Significant water separation is observed within 2 hours.

At the second stage, studies were conducted on the influence of plasticizers on the water resistance and structure formation of the solution based on gypsum-alumina cement.

The work focuses on the study of the stability of the ettringite phase of the GC:C (70:30) system. As an aluminate system, alumina cement GC-40 was used, and as sulfates, gypsum G5. Stabilization was carried out with nanomodifiers – taurite, silicon dioxide, nanotubes, SiC after studying the influence of surfactants. The following additives were used as plasticizers: Sika Viscocrete G, MC Bauchemie 2695, Stachemie STP 156. The smallest decrease in W/T and the best indicators of the main physical, mechanical and technological properties are achieved with the use of the Sika Viscocrete G additive. W/T for the composition GC:G (70:30) is 0.27 compared to 0.32 without a plasticizer, compressive and flexural strengths are 19 MPa and 14 MPa, respectively (Fig. 1).

During the third stage of research, binders with an increased amount of chemically bound water were developed – composite cements of the system $CaO–Al_2O_3–SO_3–H_2O$ [1, 2]. The development of such binders makes it possible to form a solution with a high content of ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) during the hydration process, a mineral in which the amount of chemically bound water reaches 46 %.

At the third stage, to create a barrier for ions of aggressive environments, enhance the pozzolanic reaction and increase the strength of gypsum-alumina cement, it is possible by nanomodifying its structure with nanoadditives.

The dependence of the strength of nanomodified gypsum-alumina cement on different hardening temperature conditions is shown in Fig. 2.

GGC is significantly resistant to long-term exposure to elevated temperatures. And it can be used at temperatures from 30 °C to 70 °C and humidity, where alumina cement is destroyed.

From studies of changes in the strength of gypsum-alumina cement in aggressive environments (Table 8), it was established that gypsum-alumina cement is resistant to the effects of seawater environments and magnesium solutions. The stability of GGC is determined not by the stability of hydrosulfoaluminate, but by the stability of alumina cement from which it was made. Initially, the strength decreased somewhat. But over time it increased compared to the strength at 28 days of age (Table 8).

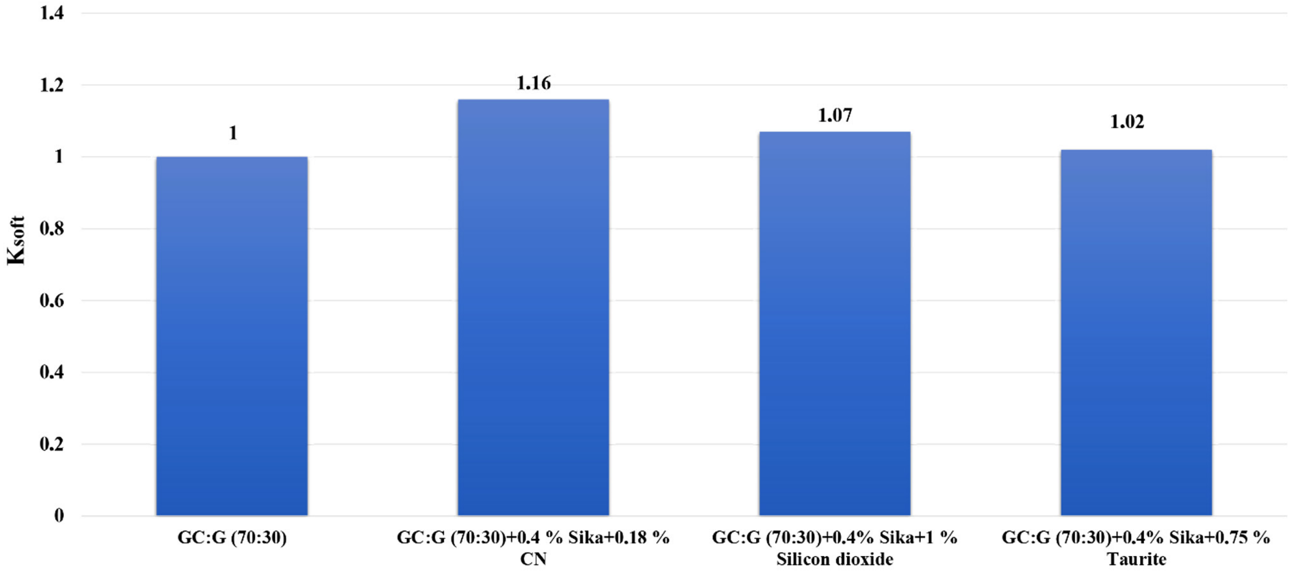
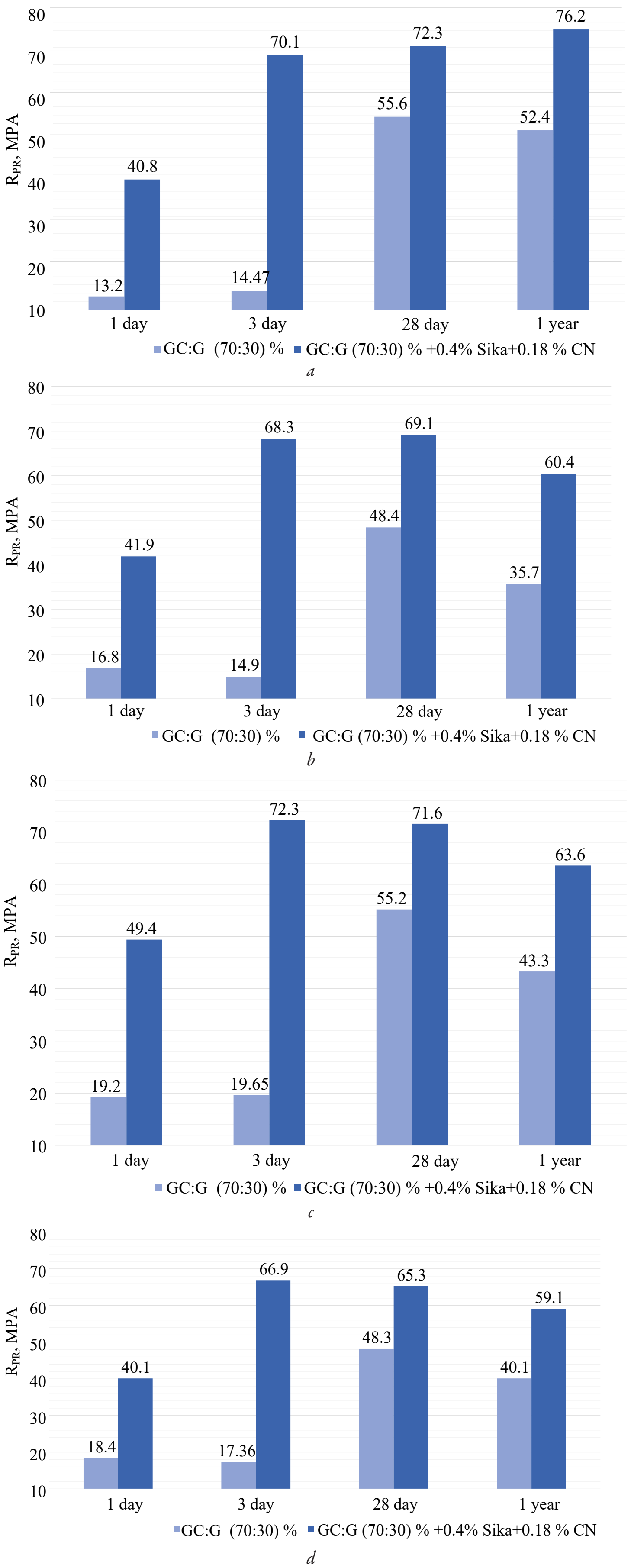


Fig. 1. Dependence of the softening coefficient for the system GC:G (70:30) + Sika on the type of nanomodifier



a

b

c

d

Fig. 2. Dependence of the strength of nanomodified gypsum-alumina cement on different temperature conditions of hardening: *a* – 15–18 °C; *b* – 35–37 °C; *c* – 40–50 °C; *d* – 60–70 °C

Table 8

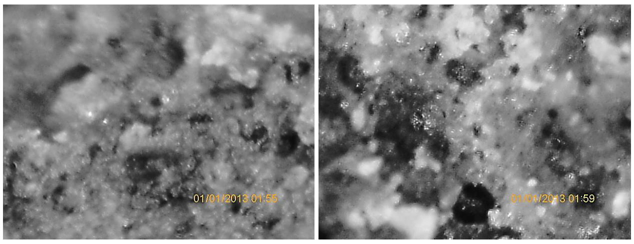
Change in the strength of nanomodified gypsum-alumina cement in aggressive environments

Aggressive environment	1 day	3 days	28 days	6 months	1 year
GC:G (70:30) % + 0.4 % Sika + 0.18 % CN					
Tap water	40.8	70.16	72.3	74.1	76.2
Sea water	46.4	73.2	78.6	76.3	80.5
10 % $MgSO_4$ solution	39.2	70.8	51.5	36.9	destroyed
5 % $MGCl_2$ solution	36.8	70.6	65.3	59.6	50.1
1 % Na_2SO_4 solution	40.5	70.3	62.1	59.6	59.5
5 % Na_2SO_4 solution	37.5	70.3	62.1	destroyed	

Note: GC – alumina cement; G – gypsum; CN – carbon nanotubes

The stability of ettringite crystals depends on the morphology of crystals formed under different conditions, for example, on the pH value. The pH range of 11–12 provides an acicular shape of ettringite [14]. With increasing pH value, the length and thickness of acicular ettringite fibers decrease. At pH more than 13, ettringite has an X-ray amorphous gel-like structure [14].

The specific surface area and surface energy have an influence on the formation of ettringite crystals (Fig. 3). On the 3rd day of hardening, the formation of the ettringite phase occurs in the nanomodified system based on gypsum-alumina cement, which is justified by its kinetic characteristics under normal conditions [18].



a *b*

Fig. 3. Micrographs of ettringite formation in nanomodified gypsum-alumina cement (×3000): *a* – on the 3rd day of hardening; *b* – on the 28th day of hardening

Formation of ettringite, which occurs on the third day and leads to an increase in the strength properties of cement stone [14]. Needle-shaped ettringite crystals provide reinforcement of the cement stone structure and, when combined with aluminum hydroxide gel, a decrease in internal stresses due to increased elasticity of bonds with crystals occurs (Fig. 3).

In the hardening process, after 3 days, the intensity of ettringite and calcium hydroxide lines increases, which confirms the intensification of the hydration process (Fig. 4).

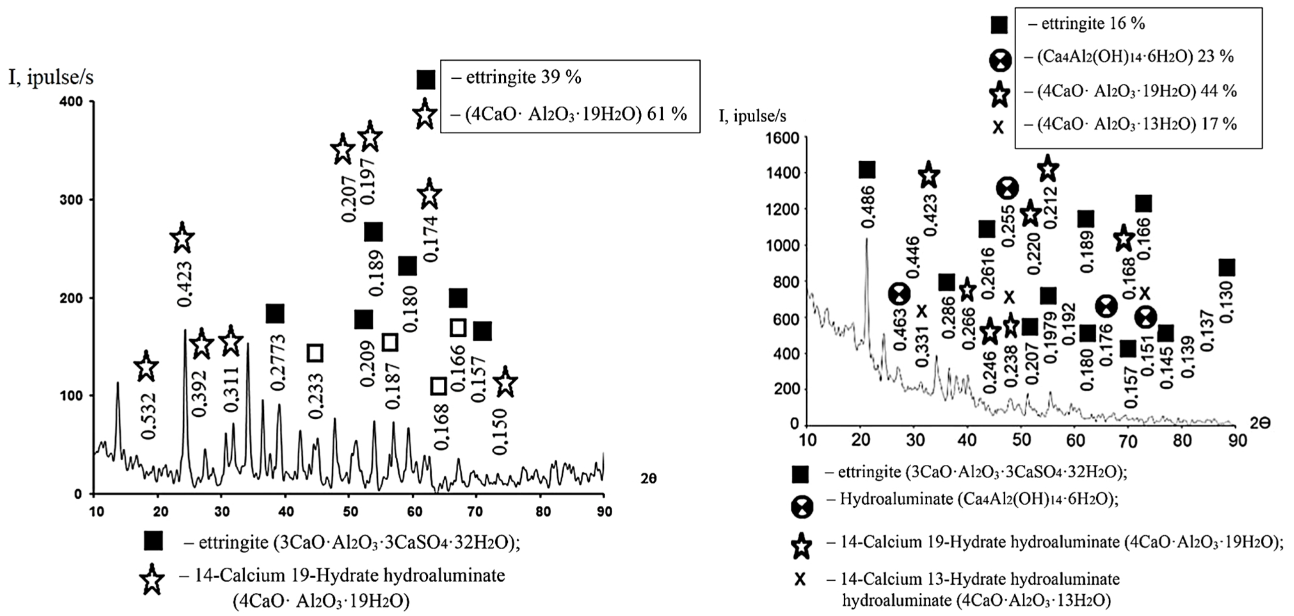
In compositions based on gypsum-alumina cement, after three days of hardening, the main interplanar distances and intensities of the hydrated phase $3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$ ($d/n=0.973$; 0.561; 0.388; 0.348; 0.256 nm) are formed (Fig. 4). The lines $4CaO \cdot Al_2O_3 \cdot 13H_2O$ ($d/n=0.423$; 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), Fig. 4. The compressive and flexural strength limits are 14 and 10 MPa, respectively.

The mechanism of influence on the structure and properties of gypsum-alumina cements is to accelerate the coagulation of solid phase particles and reduce the disintegrating effect of water.

The use of nanotubes for modified concrete mixtures. Nanotubes in the cement mortar behave as "nuclei" of crystals, but since they have not a point shape, but an extended one, the crystals are formed elongated. Growing, the crystals intertwine, partially germinate into each other, form a spatial network, penetrating and binding the entire cement stone into a single whole. Similarly, when using gypsum-alumina cements modified with carbon nanostructures, the mixing water consumption is reduced, which leads to increased strength. Thus, the introduction of carbon nanotubes and nanoparticles creates the potential for increasing strength, which occurs due to the directed regulation of crystallization processes.

Summarizing the accumulated experience, it is possible to note that work has been carried out on stabilizing the ettringite phase [2–4, 13, 14], but the problem is currently unresolved, which hinders the creation of a promising range of binders with eliminated factors of instability of the ettringite phase.

Solving the problem of stability of the ettringite phase is possible due to the reinforcement of the concrete mixture with carbon nanotubes and nanoparticles.



a *b*

Fig. 4. The influence of the ambient temperature on the structure and morphology of samples made from the composition GC:G (70:30): *a* – for 3 days of hardening under normal conditions in running water; *b* – for 3 days of hardening at a temperature of 100 °C

The presence in the composition of cement stone of formations of extended structures with a length of hundreds of microns is nothing more than microdispersed self-reinforcement of cement stone, and will lead to the corresponding strengthening of concretes based on such nanoadditions.

The introduction of carbon nanotubes into the modified cement matrix will ensure the structuring of the cement matrix with the formation of a dense defect-free shell of calcium hydrosilicates on the surface of the solid phases, giving better adhesion to the surface. In this case, self-bridged cracks will be observed due to stimulation of growth of new formations in defects of the cement matrix. The 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 strengthening of the structure due to the formation of spatial packing [12–14].

Obtaining new high properties of building composites modified with nanotubes and surfactants is possible through the use of these modifying additives, which perform versatile tasks:

- inhibit crystal growth;
- affect the shape of crystals;
- change the modification of crystals;
- affect the habit of crystals;
- change the surface tension.

Stabilization of the ettringite composition in the binder modified with nanotubes leads to an increase in strength indicators of up to 50 % compared to samples modified with nanotubes without ettringite stabilization.

At a nanotube content of 0.18 %, an increase in strength of up to 30 % is observed. Chemical functionalization of the surface of carbon nanotubes helps to reduce the sedimentation effect inherent in nanoparticles, allows for more uniform dispersion of nanostructures throughout the volume of the modified material and ensures chemical interaction between the nanotube and the matrix of the substance.

The results of the study of the hydration processes of building gypsum in the presence of carbon nanomodifiers are presented. The interaction of a dihydrate gypsum molecule with a graphene-like surface is a chemical process, which is confirmed by quantum-chemical analysis methods. The increase in the strength of a gypsum composite containing CNTs is due to the accelerated crystallization process of dihydrate gypsum near the graphene surface.

Analysis of the microstructure of gypsum-alumina cement samples showed that without a modifying additive, a fragile structure of gypsum samples with a significant number of pores is formed. It can be assumed that nanodispersed CNT additives play the role of «crystallization centers», on the surface of which the structuring of the gypsum matrix occurs with the achievement of increasing the strength of the gypsum composition.

Practical significance. The results of the study have a wide range of practical applications in the construction industry, in particular in the production of high-strength concretes and cement compositions with increased performance characteristics. The use of carbon nanotubes (CNs) in the cement matrix improves its structural integrity, making the materials more resistant to mechanical loads, reduces their porosity and increases crack resistance. This opens up prospects for the use of such materials in the construction of high-rise buildings, bridge structures, tunnels and other objects where strength and durability are critically important. In addition, modified cement mixtures can be used to restore and strengthen existing structures, especially in aggressive environments, such as chemical plants, hydraulic structures and transport infrastructure. The improved properties of gypsum-alumina cements with the use of nanotubes also make them suitable for the manufacture of specialized building materials, such as self-healing coatings and composite panels.

Research limitations. Despite significant advantages, the use of carbon nanotubes in building materials has limitations. It is necessary to evenly disperse nanotubes in the cement matrix by ultrasonic treatment for 4.5 minutes. This requires additional technological solutions. It is also necessary to take into account the use of nanomaterials, which requires regulation of regulatory standards.

Martial law in Ukraine has significantly affected the conduct of scientific research, including in the field of building materials. One of the key factors was the restriction of access to specialized laboratory equipment and materials necessary for conducting experiments. Due to disruptions in logistics and the import of high-tech components (in particular, carbon nanotubes), research could be delayed. Changes in the education system and scientific activity, in particular the transition to a remote work format, also had a certain impact on the coordination of research processes and the conduct of laboratory experiments. Despite these limitations, martial law stimulated the search for alternative solutions, the adaptation of research to new conditions and the emphasis on the development of building materials with increased resistance to mechanical loads and extreme operating conditions.

Prospects for further research. The solved problems of theoretical generalization of the stabilization of the ettringite phase and complex processes that determine the formation of the structure and physical and mechanical properties, their relationship with the composition of the starting materials and the technological process of obtaining products allow creating a promising series of composite cements. Further research in this area can be aimed at the development of new types of modified nanocomposites based on alternative nanomaterials, such as graphene nanoplatelets or oxide nanoparticles. In general, the results obtained are the basis for further research in the direction of creating high-tech building materials that can provide increased reliability, durability and safety of building structures in the future.

4. Conclusions

By adjusting the water-hardness ratio, it is possible to control the properties of the initial composite: to obtain the required structure and water resistance. The study of the effect of additives on composites of the $CaO–Al_2O_3–SO_3–H_2O$ system and the subsequent development of their compositions will make it possible to control the hydration processes, to form highly basic ettringite, the amount of chemically bound water in which reaches 46 %. Studies have established that an increase in the calcium sulfate content has a positive effect on the amount of ettringite formation and the optimal value is within 30–40 % of the composition weight. According to Fig. 3, at the ratio of GC-40/G – 70/30 %, a fairly significant amount of calcium hydroaluminates remains, the compressive and flexural strengths are, respectively, 14 and 10 MPa. Gypsum has a higher water requirement than alumina cement, and the resulting dispersed medium will be much more resistant to delamination. Water release for compositions containing 30 % alumina cement and 70 % gypsum, as well as 50 % alumina cement and 50 % gypsum is stabilized within 3 hours.

The factors influencing the stability of ettringite of two forms of formation have been established: 1 – based on pure minerals $C_3A+C\check{S}H_2$; 2 – gypsum-alumina expansion cement from changes in humidity and pH of the environment, temperature, operating conditions. Thus, the formation of ettringite, which occurs in the early stages of hardening at a high speed, ensures an increase in the strength of the stone:

- ettringite with needle-shaped crystals provides good reinforcement of the cement stone structure;
- aluminum hydroxide gel helps reduce internal stresses during crystal growth due to more elastic bonds with crystals. As a result, the hardening structure retains high strength and integrity in the process of increasing crystalline phases. The highest effect is achieved when $C_6A\check{S}_3H_{32}$ and AN_3 are used simultaneously, which occurs during the hydration of $C_4A_3\check{S}$.

Studies have shown that the use of nanomodifiers (carbon nanotubes, silicon dioxide) helps stabilize the ettringite phase and improve the properties of gypsum-alumina cement materials. The introduction of nanoadditives increases the compressive strength, reduces water absorption and prevents the transition of ettringite to the monosulfate form. The optimal concentration of carbon nanotubes (0.18 %) provides an increase in strength of up to 30 % compared to unmodified samples. Chemical functionalization of nanotubes promotes uniform distribution of particles in the cement matrix, increasing its density and crack resistance. Thus, nanomodification not only stabilizes the ettringite phase, but also significantly improves the performance characteristics of cement materials, expanding the possibilities of their use in construction.

Conflict of interest

The author declares that she has no conflict of interest regarding this research, including financial, personal, authorship or other nature, which could affect the research and its results presented in this article.

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Data availability

The manuscript has linked data in the data repository.

Use of artificial intelligence

The author confirm that she did not use artificial intelligence technologies when creating the presented work.

References

1. Gołaszewski, J., Gołaszewska, M. (2021). Properties of mortars with Calcium Sulfoaluminate cements with the addition of Portland cement and limestone. *Archives of Civil Engineering, 67 (2),* 425–435. https://doi.org/10.24425/ace.2021.137177
2. Yanze, G. A. N., Nana, A., Lemougna, P. N., Kaze, R. C., Tome, S., Rahier, H. et al. (2024). Development of calcium sulfoaluminate cements from rich-alumina bauxite and marble wastes: Physicochemical and microstructural characterization. *International Journal of Ceramic Engineering & Science, 6 (3).* https://doi.org/10.1002/ces2.10216
3. Godinho, J. P., De Souza Júnior, T. F., Medeiros, M. H. F., Silva, M. S. A. (2020). Factors influencing ultrasonic pulse velocity in concrete. *Revista IBRACON de Estruturas e Materiais, 13 (2),* 222–247. https://doi.org/10.1590/s1983-41952020000200004
4. Matschei, T., Lothenbach, B., Glasser, F. P. (2007). The AFm phase in Portland cement. *Cement and Concrete Research, 37 (2),* 118–130. https://doi.org/10.1016/j.cemconres.2006.10.010
5. Zhang, Y., Chang, J., Ji, J. (2018). AH3 phase in the hydration product system of AFt-AFm-AH3 in calcium sulfoaluminate cements: A microstructural study. *Construction and Building Materials, 167,* 587–596. https://doi.org/10.1016/j.conbuildmat.2018.02.052
6. Wu, J., Liu, L., Deng, Y., Zhang, G., Zhou, A., Xiao, H. (2022). Use of recycled gypsum in the cement-based stabilization of very soft clays and its micromechanism. *Journal of Rock Mechanics and Geotechnical Engineering, 14 (3),* 909–921. https://doi.org/10.1016/j.jrmge.2021.10.002
7. Tuinukuafe, A., Noor, L., Ideker, J. H., Isgor, O. B. (2022). Factors Influencing the Electrical Properties of Ettringite Binders as Repair Materials. *MATEC Web of Conferences, 364,* 02005. https://doi.org/10.1051/matecconf/202236402005
8. Nguyen, H., Kunther, W., Gijbels, K., Samyn, P., Carvelli, V., Illikainen, M., Kinnunen, P. (2021). On the retardation mechanisms of citric acid in ettringite-based binders. *Cement and Concrete Research, 140,* 106315. https://doi.org/10.1016/j.cemconres.2020.106315
9. Cao, W., Zhu, H. (2024). A Study on the Application Performance of High-Aspect-Ratio Nano-Ettringite in Photocurable Resin Composites. *Materials, 17 (14),* 3492. https://doi.org/10.3390/ma17143492
10. Fang, Z., Zhang, S., Qi, W., Fan, Y., Shah, S. P., Zheng, J. (2024). Study on the Binding Behavior of Chloride Ion and Ettringite in Nano-Metakaolin Cement by Seawater Mixing and Curing Temperatures. *Materials, 17 (16),* 3943. https://doi.org/10.3390/ma17163943
11. Gołaszewska, M., Klemczak, B., Gołaszewski, J. (2021). Thermal Properties of Calcium Sulphoaluminate Cement as an Alternative to Ordinary Portland Cement. *Materials, 14 (22),* 7011. https://doi.org/10.3390/ma14227011
12. Zhang, G., Zhang, B., Hao, Y., Pang, Q., Tian, L., Ding, R., Ma, L., Wang, H. (2024). Effects of Lime Powder on the Properties of Portland Cement-Sulphoaluminate Cement Composite System at Low Temperature. *Materials, 17 (15),* 3658. https://doi.org/10.3390/ma17153658
13. Jacques, K. T. J., Zengyao, W., Shoude, W., Shifeng, H., Xin, C. (2023). The influence of different fine aggregate and cooling regimes on the engineering properties of sulphoaluminate cement mortar after heating. *Case Studies in Construction Materials, 18,* e01866. https://doi.org/10.1016/j.cscm.2023.e01866
14. Derevianko, V., Hryshko, A., Dubov, T. (2019). Etringite phase stabilization. *Building Materials and Products, 1-2 (103),* 18–25. https://doi.org/10.48076/2413-9890.2023-103-04
15. *EN 197-1:2011 – Cement – Part 1: Composition, specifications and conformity criteria for common cements.* Available at: https://standards.iteh.ai/catalog/standards/cen/64d327b1-d5ac-45e3-8b04-fafec9e0698e/en-197-1-2011?srsltid=AfmBOoqv2RY7WzBOfeH7aNVKxNM8xyXmYwWuFQTpSbLrU3_cxEfXCpTs
16. Derevianko, V. M., Hryshko, H. M., Dubov, T. M. (2024). Forming hydrate compounds system $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}32H_2O$ during the aluminate cement minerals hydration. *Ukrainian Journal of Civil Engineering and Architecture, 5 (23),* 66–76. https://doi.org/10.30838/ujcea.2312.301024.66.1094.1
17. Derevianko, V. M., Kondratieva, N. V., Hryshko, H. M.; Kobets, A. S. (Ed.) (2023). Nanomodyfikovani zviazuvalni rechovyny dlia rozchyniv zakhystu ioniv. *Teoretychni ta praktychni pytannia ahrarnoi nauky*. Dnipro, 276–292.
18. Hryshko, H., Derevianko, V., Vatazhyshyn, O., Dubov, T. (2024). Researching the influence of the CaO/Al_2O_3 ratio on ettringite formation and obtaining the structure of a cement paste with special properties. *E3S Web of Conferences, 534,* 01005. https://doi.org/10.1051/e3sconf/202453401005

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