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Nanomodified Solutions Based on Composite Sulphoaluminate Binding Substances

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The article deals with development of solutions and influence caused by nanoadditives and surfactants on the processes of structural formation of sulphoaluminate phases. According to the results of the research, the introduction of nanoadditives is not possible without surfactants. The influence of modifiers is determined on the basis of experimental studies of mixtures of pure C_3A and AC, AC + H minerals. Therefore, the technology of dispersion of nanoadditives and their introduction during the process of preparation of the mixture is proposed. Based on the methods of planning a full-factor experiment and conducting experimental studies, a set of experimental and statistical models are developed, a number of solution compositions based on the components of alumina and gypsum binders containing the maximum amount of ettringite are determined: 17.1% alumina cement, 7.32% gypsum, 0.4% plasticizer, 0.18% nanotubes, 75% sand, and a system strength of 40.2 MPa is provided. The optimal composition providing system strength of 37.8 MPa includes 16.7% alumina cement, 7.15% gypsum, 0.4% plasticizer, 0.75% taurite, and 75% sand. Samples with silicon dioxide (the optimal content of it is of 1%) have system strength of 42.8 MPa and consist of 16.52% alumina cement, 8.48% gypsum, 0.4% plasticizer, 1% taurite, and 75% sand. Formation of a strong structure of solutions is associated with the creation of a gel phase and hydroaluminates of cubic crystal system C_3AH_6, as well as a stable ettringite phase. With the use of nanomodifiers, the formed blocks are freely joined in the cement matrix that leads to a decrease in internal stresses in the not yet formed cement system. In addition, doping of $C_3A\dot{S}H_{32}$ and $C_3A\dot{S}H_{12}$ crystals is suggested. Internal stresses leading to a decrease in the strength of the not yet formed structure do not arise because the joining of blocks takes place in free space. In the case when the hydration process is topochemical, the rate of structure formation will depend on the granulometric composition of the components and the rate of diffusion inside the grain. By means of changing conditions for introduction of various additives into the solution system, it is possible to influence the shape, size, number of crystals, and, accordingly, formation of a spatial structure for the purpose of obtaining a product with the required properties.

В статті розглядаються питання розробки розчинів і впливу нанодобавок і ПАР на процеси структуроутворення сульфоалюмінатних фаз. За результатами дослідження введення нанодобавок є неможливим без ПАР. Вплив модифікаторів визначали на основі експериментальних досліджень сумішей чистих мінералів C_3A і ГЦ, ГЦ + Г. Тому запропоновано технологію дисперґації нанодобавок і введення їх у процесі приготування суміші. На основі методів планування повнофакторного експерименту та проведення експериментальних досліджень розроблено ряд експериментально-статистичних моделів, визначено ряд складів розчинів на основі компонентів глиноземистих і гіпсових зв'язувальних речовин, що містять максимальну кількість етрингіту (17,1% глиноземистого цементу, 7,32% гіпсу, 0,4% пластифікатора, 0,18% нанотрубок, 75% піску) та забезпечують міцність системи у 40,2 МПа. Оптимальним складом, який забезпечує міцність системи у 37,8 МПа, є: 16,7% глиноземистого цементу, 7,15% гіпсу, 0,4% пластифікатора, 0,75% тауриту та 75% піску. Зразки з діоксидом Силіцію, оптимальний вміст якого становить 1%, мають міцність системи у 42,8 МПа і складаються з 16,52% глиноземистого цементу, 8,48% гіпсу, 0,4% пластифікатора, 1% тауриту та 75 % піску. Формування міцної структури розчинів пов'язане з утворенням драглистої фази та гідроалюмінатів кубічної синґонії C_3AH_6, а також стійкої етрингітової фази. За допомогою наномодифікаторів сформовані блоки вільно зрощуються в цементній матриці, що приводить до зменшення внутрішніх напружень у ще несформованій цементній системі. Крім того, припущено леґування кристалів $C_3A\dot{S}H_{32}$ та $C_3A\dot{S}H_{12}$. Внутрішні напруження, що призводять до пониження міцности ще неутвореної структури, не виникають внаслідок того, що зрощення блоків відбувається у вільному просторі. У разі, коли процес гідратації йде топохемічно, швидкість формування структури буде залежати від ґранулометричного складу компонентів і швидкости дифузії всередині зерна. Змінюючи умови введення різних добавок у систему розчину, можна впливати на форму, розмір, кількість кристалів і, відповідно, на формування просторової структури з метою одержання продукту з потрібними властивостями.

Key words: nanomodified solutions, sulphoaluminate binders, alumina cement, carbon nanotubes, hydration, nanosystem, hardened structure.

Ключові слова: наномодифіковані розчини, сульфоалюмінатні зв'язувальні речовини, глиноземистий цемент, вуглецеві нанотрубки, гідратація, наносистема, затвердла структура.

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1. INTRODUCTION

In modern construction, there is a rather great need to use cements with special properties and solutions based on them [1–5]. Aluminate and sulphoaluminate cements belong to the group of such cements. However, the disadvantages of their properties include recrystallization during the exploitation of the ettringite phase [3, 6].

To solve this problem, a hypothesis was proposed as follows: stabilization of the ettringite phase of sulphoaluminate cements due to nanomodification.

During the research, the following tasks were set:

1. to determine the factors affecting the stability of ettringite;
2. to conduct a study of the effect of Gibbs surface energy on the order of formation of minerals;
3. to test the hypothesis of stabilization of the ettringite phase with nanoadditives (silicon dioxide, taurite, SiC, carbon nanotubes).

2. RESULTS AND DISCUSSION

An analysis of potential reserves for improving physical and mechanical properties of sulphoaluminate binders was performed.

The method of creating composite binders based on compositions of alumina cement and gypsum and the hypothesis of increasing the stability of the high-sulphate ettringite phase (calcium monosulphatoaluminate hydrate—CmSAH) and the production of solutions based on them was proposed.

Sulphoaluminate cements belong to the group of special cements with phase composition represented by calcium sulphoaluminate minerals $3CaO \cdot Al_2O_3 \cdot SO_3$ (CAS). Positive properties: firing temperature (1250–1350°C), reduced amount of CO_2 release, high hydraulic activity, rapid gain of strength, no volume changes during hardening.

However, production of sulphoaluminate cement (SAC) with C_3AC as its main material requires the use of scarce materials: bauxite ores, aluminate slags. In addition, some sulphoaluminates are not stable under certain operating conditions [7–9].

The second direction consists in development of special cements and composite binders based on the $CaO–Al_2O_3–SO_3–H_2O$ system of increased stability of ettringite due to modification with nanoadditives. This is because one of the main phases of these binders is represented as hydrosulphoaluminate $C_3As_3H_{32}$ [6].

Analysis of research results in the field of concrete science confirms that creation of a cement matrix with the regulation of structure formation processes at the macro-, micro- and nanolevel is a necessity today, as far as it will allow obtaining new construction materials with improved strength characteristics in terms of composition and structure [3, 6].

The main research work during the development of such cements is carried out in the direction of creating new compositions providing replacement of scarce components. With such a material composition, the cost of such cements is slightly higher than those of ordinary cements, but their properties make it possible to replace sulphoaluminate cements in construction. Summarizing the accumulated experience, we note that new effective sulphoaluminate compositions can be obtained on the basis of gypsum and production waste. Modification of calcium sulphates will make it possible to purposefully regulate the rate of their hydration and coordinate the structure formation of pastematrix in time.

Works of the following domestic scientists are devoted to studying technology and properties of cements: P. V. Kryvenko, R. F. Runova, L. Y. Dvorkin, V. D. Hlukhovskyi, I. V. Kryvenko, T. V. Kuznetsova, O. O. Pashchenko, T. H. Habadadze, I. H. Lugina, A. A. Saley, H. M. Shabanova, and this matter was also researched by foreign scientists: M. Polivky, J. L. Kolouseka, P. K. Mehty, H. Lakhuma, U. Yarmaki and others. Also, the generalization of scientific and technical information in the field of cements made it possible to draw a conclusion about expediency of using nanoadditives as a structuring component of the formation of calcium hydrosilicates; this matter was developed in the fundamental works by H. F. Taylor, M. V. Belov, V. V. Ilyukhin, L. H. Shpinova, M. A. Sanytskyi, H. S. Sobol.

Characterization of raw rocks and production waste, which can be used for the production of alumina and composite sulphoaluminate cements, was carried out.

Special attention is paid to the technology of manufacturing and use of composite binders (alumina cement + gypsum).

To determine the properties and structure of materials, a complex of modern physical and physical and chemical methods of analysis (chemical, x-ray phase, differential-thermal, electron-microscopic, determination of the degree of sintering and glass phase formation, micro- and macroporosity research) carried out in Ukraine were used in the work. Determination of physical and mechanical properties was carried out according to standard methods.

A research methodology was developed, which includes the following using a hypothetical method. According to the purpose of the work, it is development of special concretes based on composite binders of the $CaO–Al_2O_3–SO_3$ system, where the main mineralogical phase of such binders during the transition to the $CaO–Al_2O_3–SO_3–H_2O$ system is represented as ettringite, which is characterized by a violation of stability in certain operating conditions. Therefore, the methodology of conducting research provides for determination of influencing factors as well as dependence of stability on these factors. First, analysis of research results obtained in this direction by the following scientists was performed: P. V. Kryvenko, R. F. Runova, L. Y. Dvorkin, V. D. Hlukhovskyi, I. V. Kryvenko, T. V. Kuznetsova, O. O. Pashchenko, T. H. Habadadze, I. H. Lugina, A. A. Saley, H. M. Shabanova, V. A. Voznesensky [11–17].

Next, a study of the properties of the ettringite phase was carried out using pure minerals: C_3A and $CaSO_4 \cdot 2H_2O$.

The main goal of experimental research is to test the hypothesis of increasing phase stability due to CNT nanomodification.

Research methods were based on the use of x-ray phase and electron microscopic analysis, as well as on determination of the main properties of solidified solutions.

Due to the fact that it is difficult to organize production of sulphoaluminate cements due to the lack of bauxites in Ukraine, the hypothesis for production of composite binders of the $CaO–Al_2O_3–SO_3$ system based on alumina cement and gypsum binders is proposed.

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

Additives based on surface-active substances of the plasticizing group were used for reducing water consumption, regulating rheological properties, as well as for introducing nanomodifiers.

As a result of the research, it was established that the mineralogical composition of alumina cement is represented as 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).

Theoretical calculations of the amount of ettringite based on pure minerals C_3A and $C\dot{S}H_2$ gave a ratio of 28:72.

For the composition of alumina cement + gypsum plaster, this ratio was determined experimentally with the help of research conducted on the basis of Full Factorial Experiment (FFE-2^n).

Further investigation of the hydration processes of the $Al_2O_3–CaO–SO_3–H_2O$ system shows that the formation of ettringite can be divided into two stages. At the first stage, compounds are formed and then they interact with sulphates. The direct formation of ettringite is the reaction of C_3A aluminates and sulphates, as well as a small amount of CA and CA_2. Hydration processes, formation of hydrosulphoaluminates of highly sulphated form based on intermediate compounds create problems of internal stresses. Moreover, when the system has gained certain strength, it leads to destruction of the structure (Fig. 1, 2).

a *b* *c*

Fig. 1. Photos of the structure of composition samples of the highly sulphated hydrosulphoaluminates $C_3AS_3H_{32}$: *a*—3 days; *b*—28 days; *c*—90 days.

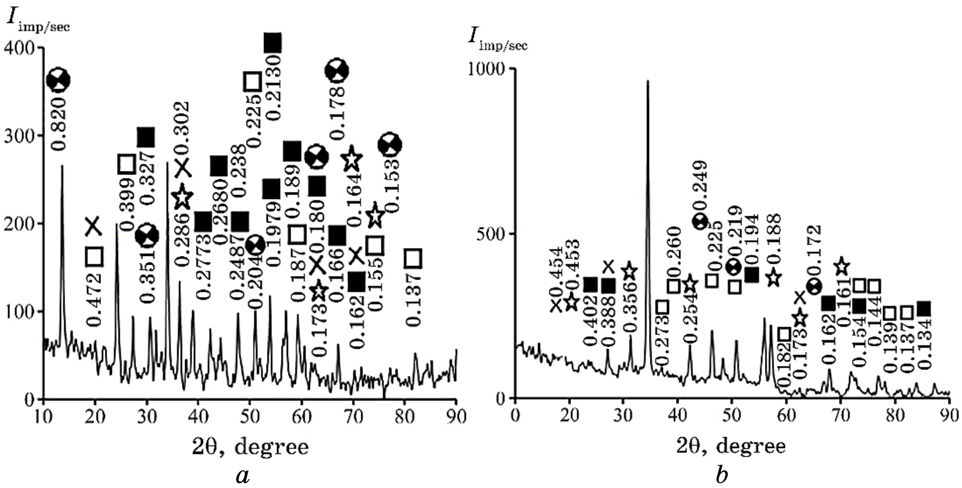

Fig. 2. Roentgenograms of the composition of alumina cement + gypsum (AC + G); during hardening periods 1–3 days (*a*) and 14–28 days (*b*); ■—ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$); □—ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}12H_2O$); ⊗—hydroaluminate ($Ca_4{\cdot}Al_2(OH)_{14}{\cdot}6H_2O$); ☆—tetracalcium nineteen-hydroaluminate ($4CaO{\cdot}Al_2O_3{\cdot}19H_2O$); ×—tetracalcium thirteen-hydroaluminate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$).

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_6, C_3AH_8, C_4AH_{13}, $Al(OH)_3$ are formed. With the presence of calcium sulphates ($CaO–Al_2O_3–SO_3–H_2O$) in the system, the hydration process is more complicated.

Ettringite or the calcium trisulphatoaluminate hydrate (CtSAH) and calcium monosulphatoaluminate hydrate (CmSAH) (accordingly, $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$ and $3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}12H_2O$) is a product of the hydration reaction in many mineralogical mixtures. Contents of crystallization water may vary. When heating the sample in dry conditions, ettringite is stable up to 65°C, and in wet conditions, it is stable up to 93°C. Within 10–12% relative humidity, the amount of crystallization water does not change, but when it decreases, 10–20 H_2O molecules are lost, which is accompanied by destruction of the ettringite structure.

Aluminous cement minerals in the presence of calcium sulphate ions also form ettringite of primary (*a*) and secondary (*b*) compounds:

$$a)\ CA + 3C\dot{S} + 2CH + 30H \rightarrow C_6A\dot{S}_3H_{32},$$
$$b)\ C_4AH_{13} + 2C\dot{S}H_2 + 16H \rightarrow C_6A\dot{S}_3H_{32}.$$

Research on the properties of ettringite obtained in the process of hydration of pure minerals ettringite (C_3A) and dihydrate calcium sulphate ($C\dot{S}H_2$) was carried out.

The process of hydration of alumina cement and the addition of calcium hydrosulphates also creates conditions for the formation of secondary ettringite (Fig. 4), the maximum amount of which is formed at the ratio of alumina cement + gypsum AC + G (70–30%) (Fig. 3, *a*).

According to the results of the research, the introduction of nanoadditives is not possible without surfactants. The influence of modifiers was determined on the basis of experimental studies of mixtures of pure C_3A and AC, AC + H minerals. Therefore, the

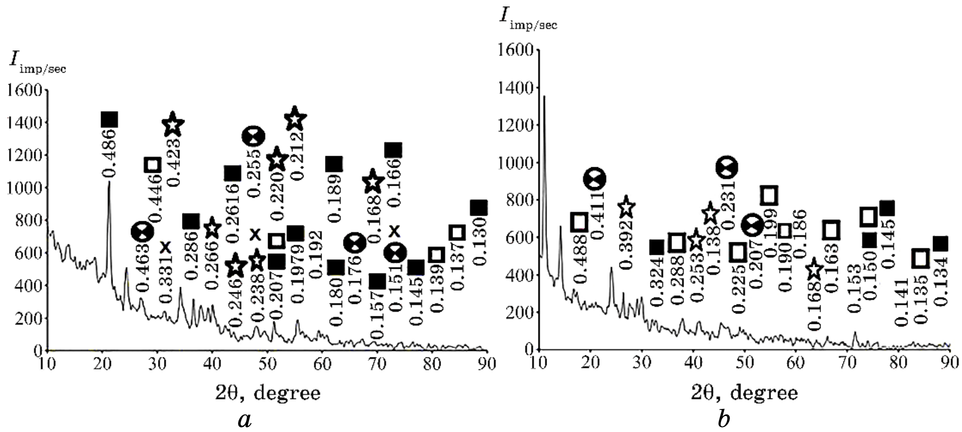

Fig. 3. X-ray diffractogram of samples made from the composition 70 AC:30 G (*a*) and 50 AC:50 G (*b*) on the 3rd day of hardening; ■—ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O$); □—ettringite ($3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}12H_2O$); ⊗— hydroaluminate ($Ca_4{\cdot}Al_2(OH)_{14}{\cdot}6H_2O$); ☆ — tetracalcium nineteen-hydroaluminate ($4CaO{\cdot}Al_2O_3{\cdot}19H_2O$); × — tetracalcium thirteen-hydroaluminate ($4CaO{\cdot}Al_2O_3{\cdot}13H_2O$).

technology of dispersion of nanoadditives and their introduction in the process of preparation of the mixture is proposed.

A method of improving the distribution and stability of solutions using carbon nanotubes was developed. This is achieved by reducing the settling of solutions with the help of Sika plasticizer and their treatment with ultrasound with a frequency of oscillations from 15 Hz to 20 Hz, as well as further mixing with water to obtain stable connections, which opens prospects for introduction of a modification technology for construction solutions. Theoretical concepts were developed and confirmed by experimental studies regarding the mechanism of the ettringite phase stabilization by introducing functional nanotubes with a diameter of 5 to 25 nm. This mechanism includes alloying and nanoreinforcement of the structure of the ettringite phase, which guarantees its stability during operation of products.

The results of the development of solutions based on nanomodified composite binders of the $CaO–Al_2O_3–SO_3$ system are shown in Fig. 4 and Table.

First, it was performed the combined ultrasound treatment of carefully dosed and mixed components of the solution, which consists of plasticizer, nanoparticles, and water. Ultrasound treatment depends on the values of the transmission coefficient and optical density and is of 4.5 min for nanotubes. After the treatment of this solution with ultrasound, it was mixed with cement, gypsum and sand until a solution of normal density was obtained. Samples 160×40×40 mm in size were formed from the paste, which hardened in air–dry conditions.

4. CONCLUSIONS

Conducted research aimed at obtaining the maximum amount of ettringite phase showed that the best ratio of C_3A i $C\acute{S}H_2$ is of 70–30.

In this way, it can be emphasized that, at the ratio of AC:G of 70–30, it is possible to replace 30% of AC with gypsum, and at the ratio of 30–70, it can be considered as a technology of modifying gypsum binders.

The results of studying nanomodified solutions containing the maximum amount of ettringite show that the optimal composition ensuring the strength of the system of 40.2 MPa is as follows: 17.1% alumina cement, 7.32% gypsum, 0.4% plasticizer, 0.18% nanotubes, and 75% sand.

The principles of dispersion and increasing the stability of solutions using carbon nanotubes by ultrasonic treatment at a frequency of 15–20 Hz and subsequent mixing with water was developed,

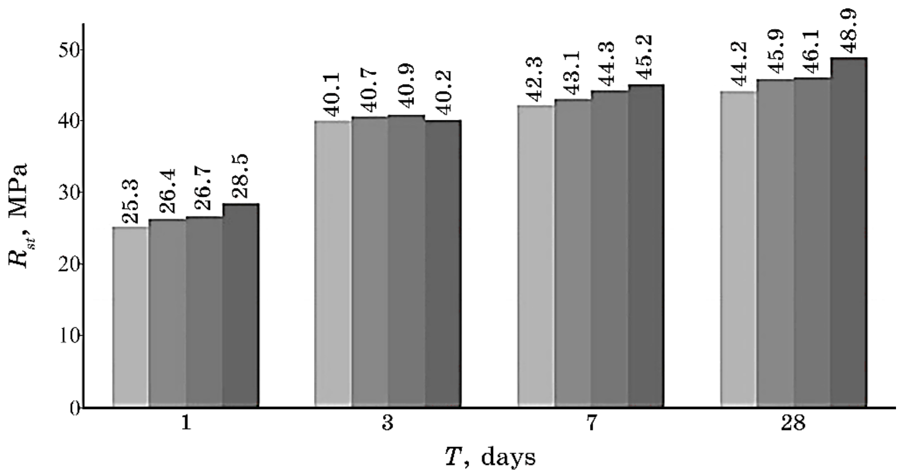

Fig. 4. Change in the compressive strength limit for AC:G solutions (7:17)% + 25% sand + 0.1–0.4% Sika + 0.035–0.18% CNT.

TABLE. Structures of research compositions and results of cement tests based on nanotubes.

Compositions of binders and their properties	Ratio of components (in wt.%) and indicators of properties			
	1	2	3	4
Alumina cement	7.47	9.88	12.28	17.1
Gypsum	17.4	14.82	12.28	7.32
Plasticizer	0.1	0.2	0.3	0.4
Nanotubes	0.035	0.1	0.14	0.18
Sand	75	75	75	75
Water/solid ratio	0.29	0.27	0.26	0.25
Compression strength, MPa				
1 day	25.3	26.4	26.7	28.5
3 days	40.1	40.7	40.9	40.2
7 days	42.3	43.1	44.3	45.2
28 days	44.2	45.9	46.1	48.9

which made it possible to develop a modified technology for production of construction solutions.

For the first time, theoretical provisions were developed and the mechanism of stabilization of the ettringite phase due to the introduction of functional nanotubes with a diameter of 5–25 nm was confirmed by means of experimental studies. The mechanism involves alloying and nanoreinforcement of the ettringite phase structure, and in this way, its stability during operation of products is ensured.

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