

# Researching the influence of the CaO/Al<sub>2</sub>O<sub>3</sub> ratio on ettringite formation and obtaining the structure of a cement paste with special properties

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**Abstract.** The hypothesis of the dependence of the value of the Gibbs surface energy on the ratio of molecular masses  $m\text{CaO}/n\text{Al}_2\text{O}_3$  ( $\Delta G=f(m\text{CaO}/n\text{Al}_2\text{O}_3)$ ) is confirmed, and it is proposed to determine the effectiveness of its influence on the hydration process of minerals of composite sulfoaluminate systems by means of the mineral coefficient  $KCA = C_m/A_n$ , where  $C_m/A_n$  is the Gibbs surface energy,  $KCA$  is the mineral coefficient of the system. This makes it possible to arrange the minerals of the CaO-Al<sub>2</sub>O<sub>3</sub> system in the following order: CA<sub>2</sub>, CA, C<sub>12</sub>A<sub>7</sub>, C<sub>3</sub>A respectively with surface energy, kJ/mol – 24.7; 51.86; 141; 145 and later use the coefficients for researching multicomponent systems. Research on the influence of nanodisperse additives in the composition of the system (Al<sub>2</sub>O<sub>3</sub>-CaO-SO<sub>3</sub>-H<sub>2</sub>O) is aimed at managing the hydration. Formation of a strong structure is associated with the creation of a gel phase and hydroaluminates of cubic crystal system – C<sub>3</sub>AH<sub>6</sub>, as well as a stable ettringite phase. With the help of nanomodifiers, the formed blocks are freely joined in the cement matrix, which leads to a decrease in internal stresses in the not yet formed cement system. In addition, there is an assumption on doping of C<sub>3</sub>AŠH<sub>32</sub> and C<sub>3</sub>AŠH<sub>12</sub> crystals.

## 1 Problem Statement

Special-purpose cements are widely used in the sphere of construction. Aluminate and sulfoaluminate cements belong to the group of such cements [1-4]. Alumina cement is one of the types of aluminate cements, production of alumina cement is absent in our country. Therefore, imported alumina cement is used.

Up-to-date prices for 1 ton of alumina cement are within the limits UAH 25-30 thousand, and this makes the problem of partial replacement of alumina cement with gypsum and modification of gypsum with alumina cement to be relevant.

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Disadvantages of cements with a special purpose, as well as other cements include recrystallization during operation of the highly basic hydrosulfoaluminate phase. And also the formation of the ettringite phase in the presence of gypsum based on secondary minerals (hydroaluminates) [5-8].

In order to solve this problem, a hypothesis of the effect caused by surface energy on the stability of the ettringite phase of sulfoaluminate cements due to nanomodification was proposed and the following tasks were set: 1) Test the hypothesis of the effect of surface energy on stability of the ettringite phase due to nanomodification; 2) Conduct a study of Gibbs surface energy on the order of formation of minerals; 3) Determine the factors affecting stability of the ettringite phase.

### 1.1 Objective

Establishing the formation process and influence of the C/A ratio on formation of  $C_nA_mH_x$  and calcium trisulphato aluminate hydrate (CtSAH), calcium monosulphato aluminate hydrate (CmSAH) at the first stage and obtaining the structure of cement paste with special properties.

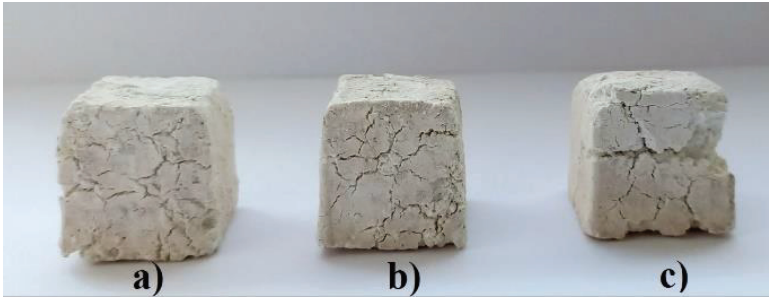
## 2 Main part

During the analysis of literary sources of the hydration processes of the CaO-Al<sub>2</sub>O<sub>3</sub>-SO<sub>3</sub>-H<sub>2</sub>O and CaO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O systems, the similarity of the hydration process of aluminate cements and sulfoaluminate cements was revealed (Table 1) [9-11].

**Table 1.** Approximate options for system hydration: CaO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O; CaO-Al<sub>2</sub>O<sub>3</sub>- SO<sub>3</sub>-H<sub>2</sub>O.

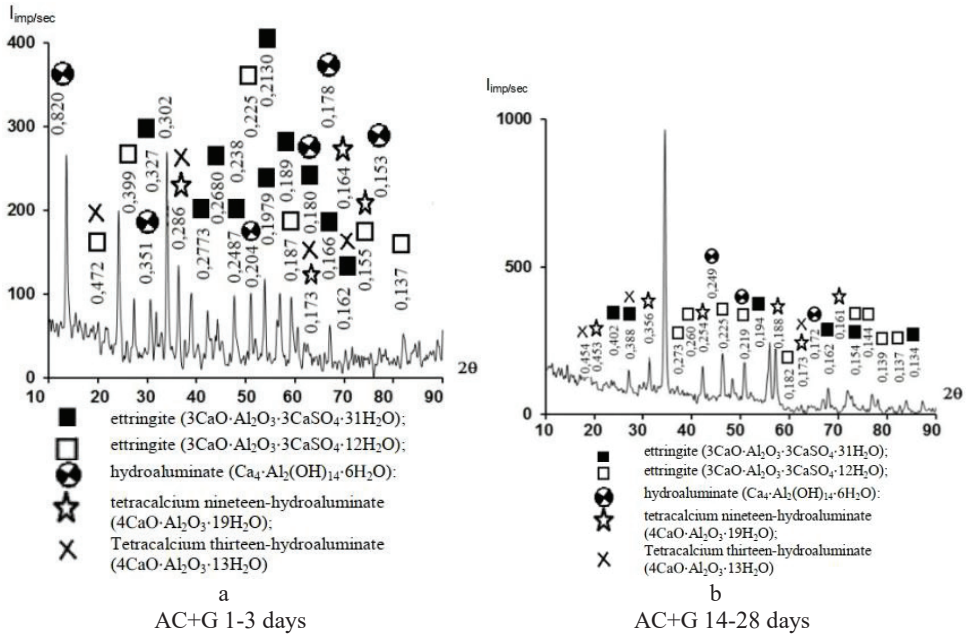
System hydration processes: CaO-Al <sub>2</sub> O <sub>3</sub> -H <sub>2</sub> O	System hydration processes: Al <sub>2</sub> O <sub>3</sub> -CaO-SO <sub>3</sub> -H <sub>2</sub> O
1. CA → C <sub>3</sub> AH <sub>6</sub>	2. CA → C <sub>3</sub> A <sub>3</sub> CSH <sub>12</sub> ; Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O
CA <sub>2</sub> → C <sub>3</sub> AH <sub>6</sub> slow reaction	CA <sub>2</sub> →3CaO·Al <sub>2</sub> O <sub>3</sub> ·3CaSO <sub>4</sub> ·31H <sub>2</sub> O
C <sub>12</sub> A <sub>7</sub> → C <sub>3</sub> AH <sub>6</sub> , Al <sub>2</sub> O <sub>3</sub> ·nH <sub>2</sub> O	C <sub>12</sub> A <sub>7</sub> →3CaO·Al <sub>2</sub> O <sub>3</sub> ·3CaSO <sub>4</sub> ·31H <sub>2</sub> O
C <sub>3</sub> A → C <sub>4</sub> AH <sub>13</sub> , C <sub>2</sub> AH <sub>8</sub>	C <sub>3</sub> A→3CaO·Al <sub>2</sub> O <sub>3</sub> ·3CaSO <sub>4</sub> ·31H <sub>2</sub> O
III. Alumina cement C <sub>3</sub> AH <sub>6</sub> + CaSO <sub>4</sub> ·H <sub>2</sub> O	AC+Gypsum→C <sub>3</sub> ACSH <sub>12</sub> ; Al <sub>2</sub> O <sub>3</sub> ·3H <sub>2</sub> O

The process of hydration of the CaO-Al<sub>2</sub>O<sub>3</sub>-H<sub>2</sub>O system can occur by means of a direct reaction, when minerals of alumina cement interact with gypsum and on the basis of secondary minerals: first, hydroaluminates and gel CAH<sub>10</sub>, C<sub>4</sub>AH<sub>10</sub>, C<sub>3</sub>AH<sub>6</sub>, C<sub>3</sub>AH<sub>8</sub>, C<sub>4</sub>AH<sub>13</sub>, Al(OH)<sub>3</sub> are formed [9-13], then, in the presence of gypsum in the system, they form a high-sulfate form of hydrosulfoaluminate already in the hardened structure, and this causes internal stresses and subsequent destruction (Fig. 1).



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

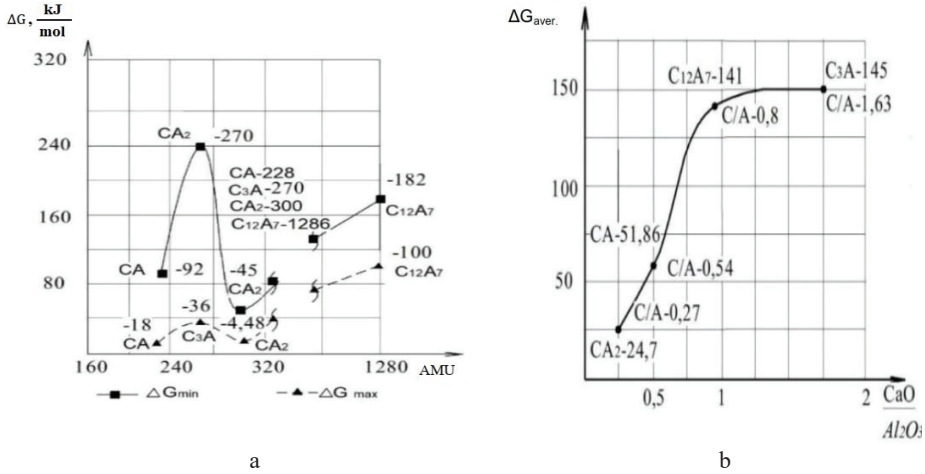
For example, destruction of samples shown in Fig. 1 occurred as a result of the formation of ettringite on the basis of secondary minerals and it is confirmed by the X-ray structural analysis shown in Figure 2.



**Fig. 2.** Roentgenograms (a), photographs (b) of samples of the composition of Alumina cement + Gypsum (AC+G); during hardening periods

Confirmation of the hypothesis of the effect caused by the surface energy on stability of the ettringite phase was carried out by means of plotting the dependence of the Gibbs surface energy on atomic molecular masses, which did not yield results (Fig. 3a).

Therefore, dependence of the Gibbs surface energy on the ratio of molecular masses  $mCaO/nAl_2O_3$  was constructed (Fig. 3b) and for each mineral coefficients showing the order of formation of minerals were calculated. The higher the coefficient, the faster the mineral enters the hydration process.



**Fig. 3.** Graphs of the dependence of  $\Delta G$ : a)  $\Delta G = f(\text{AMU})$ ; b)  $\Delta G = f(\text{C/A})$

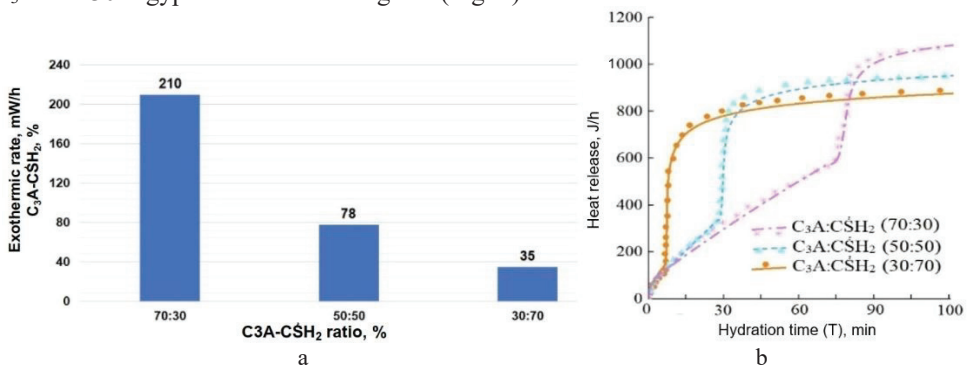
Calculation of K coefficients (CaO/Al<sub>2</sub>O<sub>3</sub> ratio) shows a direct relationship:

$$\Delta G = f(\text{CaO}/\text{Al}_2\text{O}_3) \text{ (Fig. 3b): } K = \frac{\text{CaO}}{\text{Al}_2\text{O}_3}; K_{\text{CA}_2} = \frac{\text{CaO}}{2\text{Al}_2\text{O}_3} = 0,27; K_{\text{CA}} = \frac{\text{CaO}}{\text{Al}_2\text{O}_3} = 0,54;$$

$$K_{\text{C}_{12}\text{A}_7} = \frac{12\text{CaO}}{7\text{Al}_2\text{O}_3} = 0,80. \quad K_{\text{C}_3\text{A}} = \frac{3\text{CaO}}{\text{Al}_2\text{O}_3} = 1,63. \quad (1)$$

Due to the fact that the cost of pure minerals is quite high (for example, 100 g of C<sub>3</sub>A costs EUR 100-120) further research was carried out on artificially created ettringite by calculating its formation from the minerals of alumina cement and gypsum according to the equation of the hydration process, based on molecular weights, and based on AC 40 alumina cement.

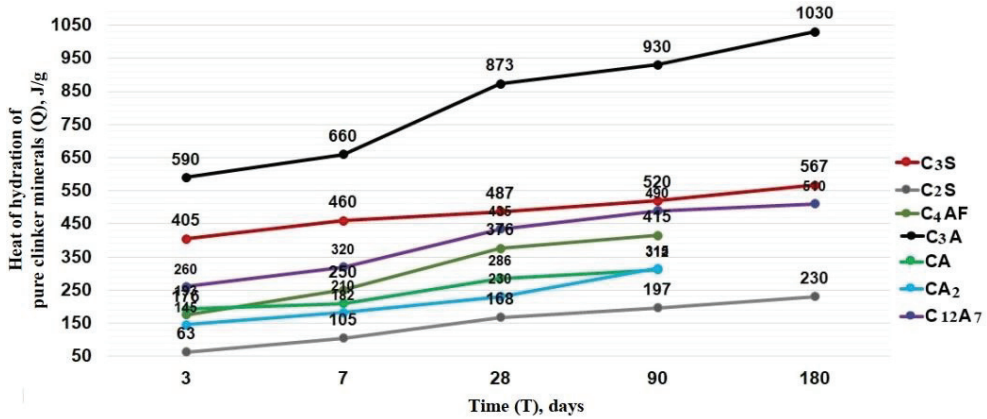
The heat release and exothermic rate of artificial ettringite with an optimal content of 70% C<sub>3</sub>A and 30% gypsum will be the highest (Fig. 4).



**Fig. 4.** The rate of heat release (a) and heat release (b) during hydration of C<sub>3</sub>A in the C<sub>3</sub>A-C<sub>3</sub>SH<sub>2</sub> system with different C<sub>3</sub>SH<sub>2</sub> content

Confirmation of the idea of influence caused by Gibbs surface energy on the order of formation of minerals is shown in Figure 5. The graphs show that change in the heat of hydration of pure clinker minerals over time and change in their degree of hydration depend on the value of the coefficients. For example, the coefficient K (mCaO/nAl<sub>2</sub>O<sub>3</sub> ratio) is the largest for C<sub>3</sub>A mineral – 1.63, and the heat of hydration is correspondingly the highest in

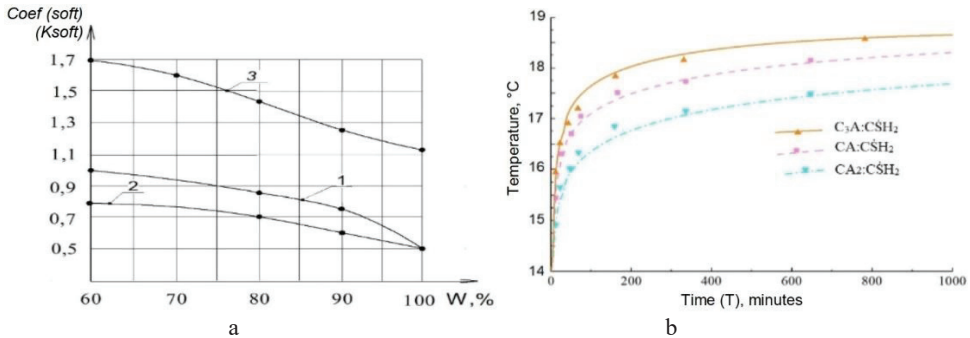
$C_3A$  mineral and is 873 J/g on the 28th day; therefore, accordingly,  $C_3A$  mineral will enter the hydration reaction the fastest.



**Fig. 5.** Change in heat of hydration of pure clinker minerals over time

Next, the factors affecting stability of the ettringite phase were determined (Fig. 6). An increase in temperature was detected for artificially formed ettringite in the  $C_3A+C\dot{S}H_2$  system followed by  $CA+C\dot{S}H_2$  and  $CA_2+C\dot{S}H_2$ , which confirms the main idea of the experiments.

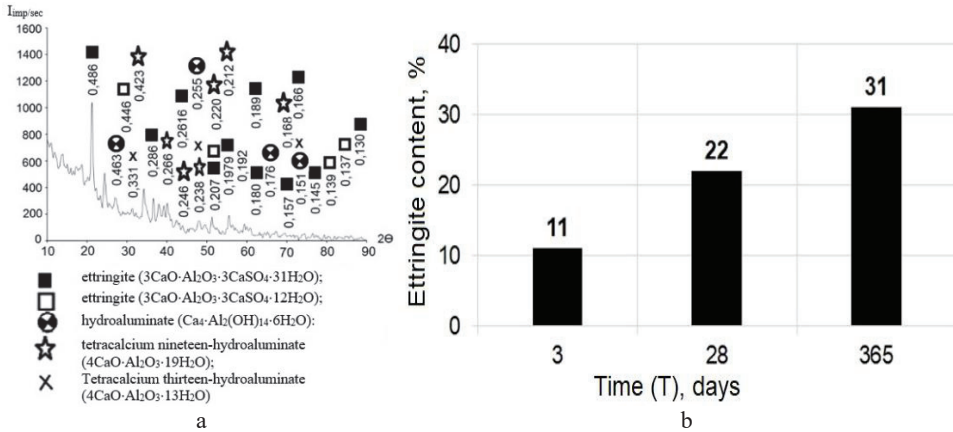
The composite based on the AC:G ratio has the highest softening coefficient, which in a wet environment is 1.15. Artificially created ettringite has the lowest values of the softening coefficient at 100% humidity – 0.5.



**Fig. 6.** Graphs of dependence: Coefficient of softening  $K(soft)$  (a) on the medium with variable humidity of samples over time, containing: 1)  $C_3AH_6$  hydrate, 2)  $C_3AS_3H_{32}$  mineral; 3) AC:G and graphs of temperature changes over time during hydration of  $CA+C\dot{S}H_2$ ,  $CA_2+C\dot{S}H_2$ ,  $C_3A+C\dot{S}H_2$  systems under normal conditions (b)

The results of basic physical and mechanical experiments and X-ray structural analysis confirm the possibility of replacing alumina cement with gypsum and modifying gypsum with alumina cement: on the 3rd and 28th day of hardening in the  $C_3A-C\dot{S}H_2$  system, in the AC:G system, the formation of an ettringite phase occurs, and this is confirmed by the kinetics of changes in the ettringite phase of nanomodified samples under normal conditions (Fig. 7).

The process of hydration of alumina cement and the addition of calcium hydrosulfates also creates conditions for the formation of secondary ettringite (Fig. 7), the maximum amount of which is formed at the ratio of Alumina Cement + Gypsum AC+G% (70÷30%).



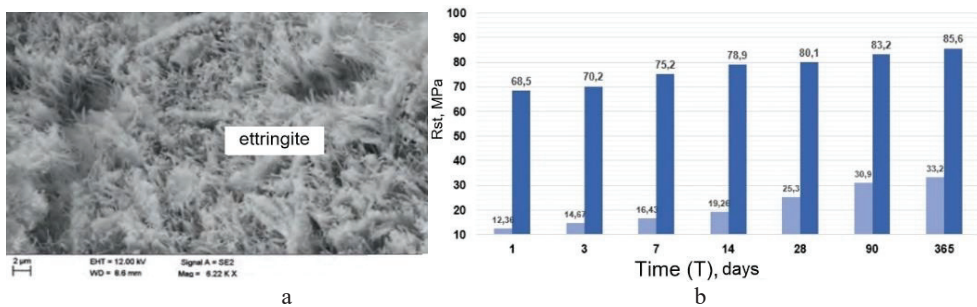
**Fig. 7.** X-ray diffractogram (a) of samples made from the composition of Alumina cement: Gypsum - AC:G (70:30) after 90 days of curing and the kinetics of changes in the ettringite phase over time of nanomodified samples under normal conditions (b)

The study of changes in structure during the analysis of diffractograms and the results of differential thermal analysis shows an increase in the amount of ettringite during the hardening process up to 28 days.

According to the proposed working hypothesis, stabilization of the ettringite phase occurred due to nanomodification: with carbon nanotubes (CNTs), taurite, silicon dioxide.

Due to nanomodifiers with a specific surface of 80-100 g/m<sup>2</sup>, the following occurs: 1) Increase in the centers of crystallization of a part of the mineral hydrated according to the soluble scheme; 2) Changing the rate of the hydration process; 3) Changing the structure of minerals, which makes it possible to purposefully obtain a structure with determined properties.

The results of the research presented in Figure 8 show a 5-fold increase in strength indicators, a change in the softening factor depending on the type of nanomodifier and systems with different plasticizers and nanotubes.



**Fig. 8.** Photomicrograph of the ettringite surface (a) and Change in compressive strength for the composition AC:G (70:30) % + 0.4 % Sika + 0.18 % CNT

According to the results of the research, the introduction of nanoapplications is not possible without surfactants. The influence of modifiers was determined on the basis of experimental studies of mixtures of pure C<sub>3</sub>A and AC, AC+G minerals. Therefore, the technology of dispersion of nano-additives and their introduction in the process of preparation of the mixture is proposed in the work.

### 3 Conclusions

On the basis of consideration of the structure of minerals and determination of thermodynamic characteristics, a hypothesis of the dependence of the Gibbs surface energy ( $\Delta G = f(\text{CaO}/\text{Al}_2\text{O}_3)$ ) on the ratio of molecular masses of chemical elements of minerals is proposed.

Conducted studies of the thermodynamic characteristics of the specified minerals confirm the hypothesis of the effect caused by surface energy on the rate of formation of minerals.

The idea of studying the sequence of formation of sulfoaluminates on the basis of intermediate compounds makes it possible to obtain the structure of solutions of high strength or with special properties. Calculation of K coefficients ( $\text{CaO}/\text{Al}_2\text{O}_3$  ratio) shows a direct relationship  $\Delta G = f(\text{CaO}/\text{Al}_2\text{O}_3)$  (Fig. 2b):  $K_{\text{CA}_2} = 0,27$ ;  $K_{\text{CA}} = 0,54$ ;  $K_{\text{C}_{12}\text{A}_7} = 0,80$ ;  $K_{\text{C}_3\text{A}} = 1,63$ .

Experimental studies of the thermodynamics of pure minerals confirmed the proposed hypothesis.

The paper presents the results of research into the properties of ettringite obtained in the process of hydration of pure minerals ( $\text{C}_3\text{A}$ ) and Calcium sulfate dihydrate ( $\text{C}_2\text{SH}_2$ ).

The process of hydration of alumina cement (AC) with the addition of calcium hydrosulfates (Gypsum) also creates conditions for formation of already secondary ettringite to a greater extent, the maximum amount of which is formed at the ratio of AC+G% (70-30%).

The study of changes in structure during the analysis of diffractograms and the results of differential thermal analysis indicates an increase in the amount of ettringite during the hardening process up to 28 days.

The hypothesis of the dependence of the value of the Gibbs surface energy on the ratio of molecular masses  $m\text{CaO}/n\text{Al}_2\text{O}_3$  ( $\Delta G = f(m\text{CaO}/n\text{Al}_2\text{O}_3)$ ) is confirmed, and it is proposed to determine the effectiveness of its influence on the hydration process of minerals of composite sulfoaluminate systems by means of the mineral coefficient  $K_{\text{CA}} = C_m/A_n$ , where  $C_m/A_n$  is the Gibbs surface energy,  $K_{\text{C}_m\text{A}_n}$  is the mineral coefficient of the system. This makes it possible to arrange the minerals of the  $\text{CaO}-\text{Al}_2\text{O}_3$  system in the following order:  $\text{CA}_2$ ,  $\text{CA}$ ,  $\text{C}_{12}\text{A}_7$ ,  $\text{C}_3\text{A}$  respectively with surface energy, kJ/mol – 24.7; 51.86; 141; 145 and later use the coefficients for researching multicomponent systems.

Research on the influence of ultra- and nanodisperse additives in the composition of the system ( $\text{Al}_2\text{O}_3-\text{CaO}-\text{SO}_3-\text{H}_2\text{O}$ ) is aimed at managing the hydration and stabilization processes of sulfoaluminate phases of composite binders.

Formation of a strong structure is associated with the creation of a gel phase and hydroaluminates of cubic crystal system –  $\text{C}_3\text{AH}_6$ , as well as a stable ettringite phase.

With the help of nanomodifiers, the formed blocks are freely joined in the cement matrix, which leads to a decrease in internal stresses in the not yet formed cement system. In addition, there is an assumption on doping of  $\text{C}_3\text{A}\text{SH}_{32}$  and  $\text{C}_3\text{A}\text{SH}_{12}$  crystals.

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