ISSN 2079-1704. Хімія, фізика та технологія поверхні. 2025. Т. 16. № 1. С. 51-62

UDC 691 doi: 10.15407/hftp16.01.051

V.M. Derevianko, H.M. Hryshko, Ye.I. Zaiats, T.M. Dubov

THEORETICAL AND EXPERIMENTAL JUSTIFICATION OF THE PRINCIPLES OF MODIFYING COMPOSITIONS OF CaO-Al_2O_3-SO_3-H_2O SYSTEMS

Ukrainian State University of Science and Technologies
Educational and scientific institute “Prydniprovska State Academy of Civil Engineering and Architecture”
24a Architect Oleh Petrov Str., Dnipro, 49005, Ukraine, E-mail: hryshko.hanna@pdaba.edu.ua
Dnipro State Agrarian and Economic University
25 Serhii Efremov Str., Dnipro, 49600, Ukraine, E-mail: dubov.t.m@dsau.dp.ua

Creation of new varieties of standard (common) cements and special cements is one of the main directions of modern developments in the technology of production of cementing agents. In the group of special cements a special place is occupied by alumina ones, sulfoaluminate ones etc. 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. Providing such a material composition, the cost of compositions with properties of alumina cements is slightly higher than that of ordinary ones, but their use improves performance characteristics of products. When summarizing the accumulated experience, we note that new effective compositions based on alumina cement, gypsum and production waste are quite effective in economic and technical terms. Purpose of the article is to determine the dependence of formation of hydrated compounds during hydration of aluminate and sulfoaluminate cements on the surface energy $\Delta G = f(AMU)$ *and the ratio* $\Delta G = f(mCaO/nAl_2O_3)$ *in the minerals of the system on the average Gibbs energy and to increase stability of the ettringite phase of the* CaO-Al_2O_3-SO_3-H_2O *system. The article considers possibilities of managing hydration processes by means of creating composites and the introduction of additives affecting the value of the Gibbs surface energy of the* CaO-Al_2O_3-SO_3-H_2O *system. As a result, the number of crystallization centers and the speed of chemical processes increase. A theoretically substantiated hypothesis of the effect caused by the ratio* $G=f(mCaO/nAl_2O_3)$ *in the minerals of the* CaO-Al_2O_3-H_2O *system on the Gibbs surface energy:* $CA_2 = 0.27$ *-* $\Delta G = 24.70$, $CA = 0.54$–51.86, $C_{12}A_7 = 0.8$–141.00, $C_3A = 1.63$–145. *The theoretical position of influence of* ΔG *during hydration of aluminate cements in the presence of gypsum received further development - the system of chemical reactions* CaO-Al_2O_3-SO_3-H_2O *can be divided into two systems (parts): a)* CaO-Al_2O_3- H_2O*; b)* CaO-Al_2O_3-SO_3-H_2O*, as a result* C_3AH_6, CAH_{10}, C_2AH_8, C_4AH_{13}, $Ca_2(OH)_2$ *is formed in the first one, and calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are formed in the second one. According to the first part and second part, there is a process of* $Al(OH)_3$ *formation. The optimal content of calcium sulfate (within 30–40 % of the composition mass) with a positive effect on the amount of ettringite formation has been theoretically determined and experimentally confirmed.*

***Keywords**: composite binder, modification, ettringite, ettringite phase stabilization, aluminate cements, sulfoaluminate cements*

INTRODUCTION

Sulfoaluminate cements belong to the group of special cements with phase composition represented by 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 gain of strength, no volume changes during hardening [1–3].

However, for the production of sulfoaluminate cements with C_3AS being their main material, it is necessary to use scarce materials: bauxite ores, aluminate slags. Cements of these types are not produced in Ukraine, despite a rather significant need for binders of this class.

The main reason consists in the lack of natural raw materials - bauxites. Although there is a fairly significant amount of secondary production products which can serve as a raw material base for the production of aluminates and sulfoaluminates [2, 4–6].

The use of imported raw materials is limited by the high cost and certain disadvantages occurring during exploitation including rapid hardening, significant heat generation, which is associated with instability of some sulfoaluminates. At the same time, it is possible to highlight the following problems in the direction of expanding possibilities of using special cements of this type: stabilization over time and operating conditions of the hydrosulfate phase based on alumina cement, as well as modification of the compositions of mineral binders based on calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) and development of binders of this class based on secondary production products. In this regard, an urgent problem is the development of a technology for stabilizing sulfoaluminate phases under the influence of various factors.

Modification of calcium sulfates will make it possible to purposefully regulate the rate of their hydration and coordinate the structure formation of pastematrix in time. Therefore, research aimed at increasing the stability of the high-sulfate ettringite phase is relevant.

METHODS OF RESEARCH

The cement matrix plays the main role in forming the main properties of composites. Alumina cement AC 400 and gypsum G-5-II were used as a binder.

Research on the physical and mechanical properties of alumina cements, gypsum and composite materials was carried out in accordance with DSTU B.V. 2.7-185:2009, DSTU B.V. 2.7-187:2009, DSTU EN 196-1:2007 and DSTU B.V. 2.7-188:2009. Terms of hardening, normal density of the water-cement paste, as well as the compressive and bending strength limits were also determined. For conducting experiments on composite binders, experimental samples with dimensions of 4×4×16 cm were made.

A methodology for investigating influence of the Gibbs surface on formation of minerals of the composite sulfoaluminate binder system is proposed. The essence consists in determining the influence of $y = f(C/A)$. For this purpose, the method of determining changes in mineral composition over time using differential thermal and X-ray structural analysis on an X-ray diffractometer under CuK_a radiation was used.

PURPOSE OF THE STUDY

To determine the dependence of formation of hydrated compounds during hydration of aluminate and sulfoaluminate cements on the surface energy $\Delta G = f(AMU)$ and the ratio $\Delta G = f(CaO/Al_2O_3)$ in the minerals of the system on the average Gibbs energy and to increase stability of the ettringite phase of the $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$ system.

THEORY

A+CA raw materials, compositions and hydration processes are marked by similarities: Aluminate cements (*a*) and sulfoaluminate cements (*b*) have the following chemical composition [6]:
a) Al_2O_3 – 35–50; CaO – 35–45; SiO_2 – 5–15; TiO_2, MgO, SO_2, K_2O from 0 to 2.5;
b) Al_2O_3 – not less than 20–25; CaO – 55; SiO_2 – 10; SO_3 – 3; Fe_2O_3 – 5–10; MgO – 2 and depending on the technology, chemical composition can be very diverse, but the main condition consists in the presence of at least 20 % of Al_2O_3, whereas SiO_2 is an undesirable component.

Mineralogical composition of cements:
a) Aluminate cement: CA, CA_2, C_3A, C_5A_3, $C_{12}A_7$;
b) Sulfatoaluminate cement: CA, C_2S, C_4AF, C_3A, $C_3A_3CaSO_4$ (C_4A_3S), $CaSO_4$.

The main factor is that during hydration of sulfoaluminates and aluminates in the presence of gypsum ($CaSO_4 \cdot 2H_2O$), a hydrosulfoaluminate phase is formed, which makes it possible to obtain a hardened cement paste structure with special properties.

When considering hydration processes of aluminate cements, we can distinguish the tendency of phase formation with C_3AH_6 [2, 6]:

$$CA \rightarrow CaOAl_2O_3 \cdot 10H_2O \rightarrow 2CaOAl_2O_3 \cdot 8H_2O + Al_2O_3 \rightarrow 3CaOAl_2O_3 \cdot 6H_2O + Al_2O_3 \cdot nH_2O.$$

In the case of CA_2, C_3AH_6 is also formed, but the reaction proceeds slowly.

$$C_{12}A_7 + H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + 2CaO \cdot Al_2O_3 \cdot 8H_2O + Ca(OH)_2 \rightarrow 3CaO \cdot Al_2O_3 \cdot 6H_2O + Al_2O_3 \cdot nH_2O.$$

In the presence of gypsum or anhydrite C_3AH_6 form ettringite:

$$3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 + 25H_2O = \\ = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O.$$

- ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$);
- ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 12H_2O$);
- tetracalcium aluminate nineteen-hydrate ($4CaO \cdot Al_2O_3 \cdot 19H_2O$).

During hydration of SA cement the first reaction is decomposition of sulfominerals. First, sulfoaluminates and sulfosilicates pass into

intermediate hydrates of the following composition:
$3(CA)\cdot CaSO_4\cdot nH_2O$ and $2(C_2S)\cdot nH_2O$ $(1 > n > 0.5)$.

Then monocalcium aluminate sulfate hydrate (hydrated calcium sulfoaluminate) turns into sulfoaluminate hydrate of the low-sulfate form $C_3A\cdot CaSO_4\cdot 12H_2O$ with the release of gibbsite $Al_2O_3\cdot 3H_2O$. Also, ettringite $C_3A\cdot CaSO_4\cdot nH_2O$ and $2(C_2S)\cdot nH_2O$ is formed and hydrated calcium silicate CSH(B) can be formed [7–9].

A common feature for hydration processes of sulfate cements in the presence of gypsum is formation of the $3CA\cdot CSH_{32}$ phase, i.e., a neoplasm that plays the main role in the modification of calcium sulfate dihydrate, or the partial replacement of alumina cement with the $CaSO_4\cdot 2H_2O$ additive.

Table 1. Approximate options for system hydration: Al_2O_3-H_2O; Al_2O_3-H_2O-$CaSO_4$

System hydration processes: (Al_2O_3-H_2O)	**System hydration processes: (Al_2O_3-H_2O-C_2SO_4)**
1. $CA \rightarrow C_3AH_6$	2. $CA \rightarrow C_3AC\dot{S}H_{12}$; $Al_2O_3\cdot 3H_2O$
$CA_2 \rightarrow C_3AH_6$ slow reaction	$CA_2 \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$
$C_{12}A_7 \rightarrow C_3AH_6$, $Al_2O_3\cdot nH_2O$	$C_{12}A_7 \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$
$C_3A \rightarrow C_4AH_{13}$, C_2AH_8	$C_3A \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O$
III. Alumina cement (CA_2)	$C_3AC\dot{S}H_{12}$; $Al_2O_3\cdot 3H_2O$
IV. Alumina cement and gypsum C_3AH_6	AC+Gypsum$\rightarrow C_3AC\dot{S}H_{12}$; $Al_2O_3\cdot 3H_2O$

Consideration of research examples of system hydration processes: Al_2O_3-H_2O; Al_2O_3-H_2O-CaO-SO_3, shows that formation of ettringite can be divided into two stages. At the first stage, intermediate compounds are formed and then they interact with sulfates. Direct formation of ettringite is a reaction of C_3A aluminates and sulfates. Hydration processes, formation of hydrosulfoaluminates (hydrated sulfoaluminates) of highly sulfated form based on intermediate compounds create problems of internal stresses. And when the system has gained certain strength, it leads to destruction of the structure. And this is confirmed by the research results (Fig. 1) [10].

Fig. 1. Photos demonstrating structure of hydrosulfoaluminates of the highly sulfated form [10]

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

Surface energy (Gibbs energy) is the main factor affecting the sequence of the hydration reaction. Calcium sulfate $CaSO_4$ – it decomposes in a salty and slightly alkaline environment, and it is a source of sulfur and calcium [11–14].

Gibbs energy [11–14]:

$$\Delta G=\Delta H-T\Delta S \quad (1)$$

where ΔG – Gibbs free energy; T – absolute temperature; ΔS – entropy change; ΔH – enthalpy change.

$$\Delta G_f=\Sigma\Delta G_{\text{prod. react}}-\Sigma\Delta G_{\text{imput-output substances}} \quad (2)$$

Surface energy levels: $\Delta G = 0$; $\Delta G < 0$; $\Delta G > 0$

In works [14–16] on the hydration process of aluminate and sulfoaluminate cements, the issue of formulation of hydrated compounds is considered: $Al_2(OH)_3$, CAH_{10}, C_2AH_8, C_3AH_6, C_4AH_{13}, $C_3AC\dot{S}_3H_{31}$, $C_3AC\dot{S}H_{12}$, $Ca_2(OH)_2$.

Table 2. Probability of reactions as dependent on the components of Gibbs energy [2, 11–13]

Δ*H*	Δ*S*	Δ*G*	Direction
-	+	-	independently
+	-	+	does not interact
-	-	±	interacts at low temperatures
+	+	±	interacts at high temperatures

On the basis of existing studies, we will consider the reactions of minerals CA, CA_2, C_3A, $C_{12}A_7$, determine the probability of forming direct and intermediate compounds which are formed during hydration of these minerals and the influence of Gibbs energy.

The reaction with $\Delta G > 0$ and at high and low temperatures was not considered.

Based on the considered Table 3, we can build dependence graphs: $\Delta G = f(AMU)$ i $\Delta G = f(CaO/Al_2O_3)$, where: Δ*G* – Gibbs free energy; f(AMU) atomic mass unit; CaO/Al_2O_3 – AMU correlation.

Table 3. The probability of the formation of direct and intermediate compounds which are formed during the hydration of minerals and influence of Gibbs energy [2, 11–13]

Minerals	Gibbs surface energy (ΔG), kJ/mol
1) $CA+10H_2O\rightarrow CAH_{10}$ $4CA+22H_2O\rightarrow C_4AH_{10}+6Al(OH)_3$	– 92.00
2) $2CA_2+17H_2O\rightarrow C_2AH_8+6Al(OH)_3$	– 4.48
$4CA_2+34H_2O\rightarrow C_4AH_{13}+14Al(OH)_3$	– 45.7
3) $C_{12}A_7+33H_2O\rightarrow 12Ca(OH)_2+14Al(OH)_3$	– 100.9
$1/3C_{12}A_7+17H_2O\rightarrow C_4AH_{13}+8/3Al(OH)_3$	– 182.0
4) $C_3A+6H_2O\rightarrow 3Ca(OH)_2+2Al(OH)_3$	– 78.7
$4/3C_3A+14H_2O\rightarrow C_4AH_{13}+2/3Al(OH)_3$	– 254.0

Table 4. Gibbs surface energy of alumina cement minerals [2]

Minerals	Surface energy ΔG), kJ/mol			Molecular mass (AMU)
	minimal	maximal	average	
$CaO\cdot 2Al_2O_3$	-11.73	-92.0	24.74	260
$CaO\cdot Al_2O_3$	-4.48	-45.0	51.86	158
$12CaO\cdot 7Al_2O_3$	-100.9	-182.0	141.00	1286
$3CaO\cdot Al_2O_3$	-74.7	-254	145.00	270.20

Analysis of dependences (Fig. 2) [17] $\Delta G = f(AMU)$ demonstrates influence of molecular masses on the value of Gibbs free energy. Influence of CaO/Al_2O_3 ratio should be especially noted (Fig. 3) [17]. The hypothesis is proposed: $\Delta G = f(CaO/Al_2O_3)$; $f(n/CaO/mAl_2O_3)$ – the Gibbs surface energy depends on the ratio of aluminum and calcium oxides.

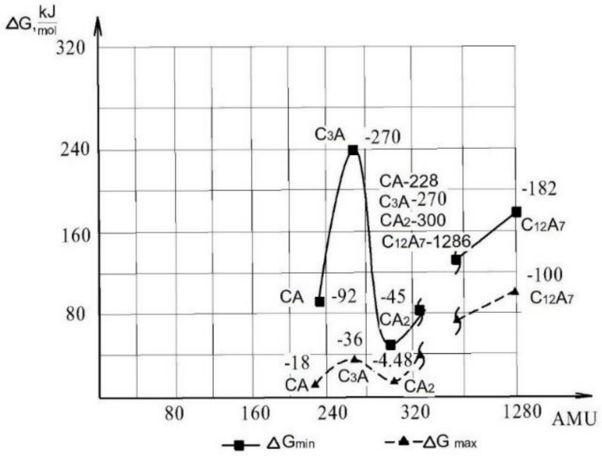


Fig. 2. Dependence graphs ΔG = f(AMU): (*1*) – ΔG_{min}; (*2*) – ΔG_{max} [17]

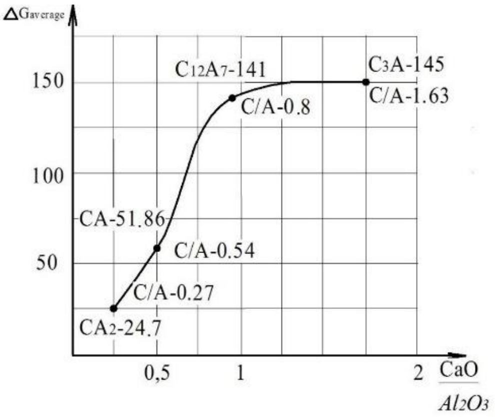


Fig. 3. Influence of the CaO/Al_2O_3 ratio in minerals on the average Gibbs energy [17]

$$K = \frac{CaO}{Al_2O_3};\ K_{CA} = \frac{CaO}{Al_2O_3} = 0.54;$$

$$K_{C_3A} = \frac{3CaO}{Al_2O_3} = 1.63;$$

$$K_{CA_2} = \frac{CaO}{2Al_2O_3} = 0.27;\ K_{C_{12}A_7} = \frac{12CaO}{7Al_2O_3} = 0.80.$$

The rate of hydration of aluminate cement minerals depends on the C/A ratio (Figs. 2, 3). This factor can be explained by comparing the structural formulas (Fig. 4). At the same time, the difference in atomic mass units (AMU) is quite insignificant and amounts to 37 AMU. Whereas the Gibbs free energy is 2.7 times higher in C_3A [2, 14–16].

Let’s consider crystal and structural models and their characteristics.

a) C_3A
ΔG = –254 kJ/mol

b) CA
ΔG = –92 kJ/mol

Fig. 4. Structural formulas: (*a*) C_3A; (*b*) CA

Sequence of hydration.

$CA \rightarrow C_3A$ (17 : 7; 1 : 1).

CA has monoclinic or rhombic syngony, and C_3A has cubic syngony. This is probably the very thing that affects the rate of hydration.

When considering formation and stability of hydroaluminates at the beginning of the reaction in the presence of (1–3), we determine the main hydroxides CAH_{10}, C_4AH_{10}, C_2AH_8, C_4AH_{13}, $Al(OH)_3$ and $Ca(OH)_2$. Their structures are presented in works [1–3].

CAH_{10} – free spatial structure. Crystals have the form of needles or plates.

C_4AH_{10} – crystallizes in the form of precise hexagonal particles. Formation $C_3ACaO \cdot CO_3H_{31}$ is possible.

C_2AH_8 – crystallization in the form of plates.

C_4AH_{13} – metastable under normal conditions hydration in the C-A-H system.

C_3AH_6 –stable hydrated phase in the $CaO\text{-}Al(OH)_3\text{-}H_2O$ system.

Over time, unstable hexagonal hydrates change, resulting in formation of stable cubic hydrates C_3AH_6 and gibbsite AH_3 [2]:

$3\ CAH_{10} \rightarrow C_3AH6 + 2\ AH_3 + 18\ H;$

$3\ C_2AH_8 \rightarrow 2\ C_3AH_6 + AH_3 + 9\ H.$

$Al(OH)_3$ – at the beginning of hydration, it is released in the form of a gel, and then it crystallizes with the formation of belite and hydrorgillite crystals.

$Ca(OH)_2$ – is anisotropic grains that increase to monocrystals (single-crystals).

$CaO \cdot Al_2O_3 \cdot 10H_2O + H_2O \rightarrow 2CaO \cdot Al_2O_3 \cdot 8H_2O + Al(OH)_3$, at elevated temperatures - more than 30 °C.

$CaO \cdot Al_2O_3 \cdot 10H_2O$ and $2CaO \cdot Al_2O_3 \cdot 8H_2O$ – change to $3CaO \cdot Al_2O_3 \cdot 6H_2O + Al(OH)_3 + H_2O$.

In the presence of gypsum:

(a) $3CaO \cdot Al_2O_3 \cdot 6H_2O + 3CaSO_4 + 25H_2O = 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

Analysis of literary sources on the formation of ettringite during hydration of aluminosilicate cements in the presence of calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$) or anhydrite ($CaSO_4$) is an intermediate product of C_3AH_6, which forms ettringite.

In the presence of C_3A, ettringite calcium trisulfoaluminate hydrate (CTSAH) is formed by direct interaction with $CaSO_4 \cdot 2H_2O$:

$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot H_2O + 25\ H_2O =$
$= 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

During hydration of the C_3A mixture to obtain calcium monosulfoaluminate hydrate (CMSAH)

$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 10H_2O =$
$= 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$.

Including calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH), $C_{12}A_7$ during hydration in the presence of gypsum, calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are also formed.

$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 0{,}5H_2O + 30.5\ H_2O =$
$= 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

$3CaO \cdot Al_2O_3 + 3CaSO_4 \cdot 2H_2O + 25H_2O =$
$= 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 31H_2O$.

During hydration of the C_3A mixture to obtain calcium monosulfoaluminate hydrate (CMSAH):

$3CaO \cdot Al_2O_3 + CaSO_4 \cdot 2H_2O + 10H_2O =$
$= 3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$.

In this way calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are formed.

$C_{12}A_7$ during hydration in the presence of gypsum calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are also formed [14–16]:

$C_{12}A_7 + 12CSH_2 + 109H_2O = 4C_3ACS_3H_{31} + 6AH_3$
$C_{12}A_7 + 4CSH_2 + 49H_2O = 4C_3ACSH_{12} + 6Al(OH)_3$

CA i CA_2 also form calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) [14–16]:

$3CA + CaSO_4 \cdot 2H_2O + 14.5H_2O = 3C_3ASH_{12} + 3Al(OH)_3$
$CA_2 – 3C_3ACS_3H_{31}$
$3CA_2 + 3CaSO_4 \cdot 2H_2O + 25H_2O = C_3ACS_3H_{12} +$
$+ 10Al(OH)_3$ -13.7 kJ/mol
$3CA_2 + 3CaSO_4 \cdot 2H_2O + 40H_2O = C_3AS_3H_{31} +$
$+ 10Al(OH)_3$ -30.2 kJ/mol
$3CA + 3CaSO_4 \cdot 2H_2O + 16H_2O = C_3ACS_3H_{12} +$
$+ 4Al(OH)_3$ -67 kJ/mol
$3CA + 3CaSO_4 \cdot 2H_2O + 31H_2O = C_3ACS_3H_{31} +$
$+ 4Al(OH)_3$ -83.8 kJ/mol
$1/4C_{12}A_7 + CaSO_4 \cdot 2H_2O + 10H_2O =$
$= C_3ACSH_{12}$ -116 kJ/mol
$1/4C_{12}A_7 + 3CaSO_4 \cdot 2H_2O + 109/4H_2O =$
$= C_3ACS_3H_{31} + 3/2Al(OH)_3$ -132 kJ/mol
$C_3A + CaSO_4 \cdot 2H_2O + 10H_2O =$
$= C_3ACSH_{12}$ -169.69 kJ/mol
$C_3A + 3CaSO_4 \cdot 2H_2O + 25H_2O =$
$= C_3ACS_3H_{31}$ -186.46 kJ/mol

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

system the hydration process is more complicated.

First, the simultaneous formation of hydroaluminates and hydrosulfoaluminates of calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH), CAH_3, i.e., this is formation of the primary structure.

Secondly, part of the hydroaluminates reacts with calcium sulfates, forming calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) - secondary minerals, and this process affects the formation of the structure, which determines such properties as strength, internal stresses, expansion, and so on. The complexity of the task consists in establishing the surface of formation and the ratio of formation at the first stage of $C_nA_mH_x$ and calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH). This makes it possible to determine the flow of physical and chemical processes of the system in time.

The average Gibbs surface energy of reactions of hydroaluminates based on CA-51.5 minerals; CA_2 = 25.9; $C_{12}A_7$ = -91.4; C_3A – 166.3 kJ/mol; sulfoaluminates based on these minerals [13–15]: CA → $C_3AC\dot{S}_3H_{31}$ -75.4; CA_2 → 31.9; $C_{12}A_7$ → 124.6; C_3A → 178.07.

Comparing the surface energy of system formation:
CaO-Al_2O_3- H_2O and CaO-Al_2O_3-SO_3-H_2O (Figs. 5, 6).

Table 5. Gibbs surface energy of alumina cement minerals

Mineral	Gibbs energy, kJ/mol	
C_3A	-166.3	-178.07
$C_{12}A_7$	-91.4	-124.6
CA	-54.5	-75.4
CA_2	-25.4	-21.9
	Hydroaluminates	Sulfoaluminates

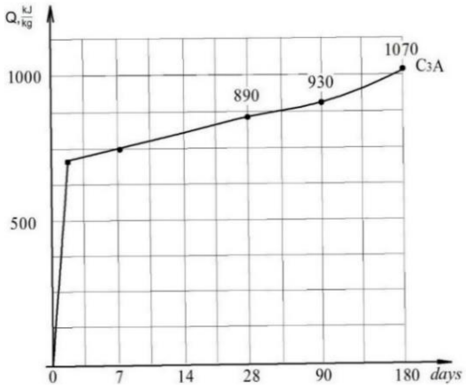


Fig. 5. Graphs of the dependence ΔG = f(c/a) of the system: *1*) CaO-Al_2O_3-$CaSO_4$-H_2O

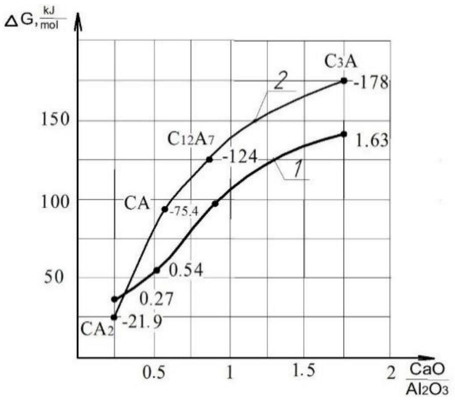


Fig. 6. Graphs of the dependence ΔG = f(c/a) of the system: *1*) CaO-Al_2O_3-H_2O; *2*) CaO-Al_2O_3-$CaSO_4$-H_2O

The process of hydration of aluminate cements in the presence of gypsum, the system of chemical reactions CaO-Al_2O_3-$CaSO_4$-H_2O can be divided into two parts: a) CaO-Al_2O_3-H_2O; b) CaO-Al_2O_3-H_2O-$CaSO_4$ (Figs. 6).

As a result, calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are formed in the second part, and in the first C_3AH_6, CAH_{10}, C_2AH_8, C_4AH_{13}, $Ca_2(OH)_2$ are formed. According to the first and second part, there is a process of $Al(OH)_3$ formation.

At the second stage, especially after hardening, the transition of hydroaluminates (except for C_2AH_6) to hydrosulfoaluminates is observed, which leads to an effect on the amount of change in the volume of the system.

Due to the low rate of calcium monosulfoaluminate hydrate (CMSAH) hydration C_2A reacts with it, so forming C_4AH_{13}. $C_3AC\acute{S}_3H_{12} + C_2A + H + 9H_2O \rightarrow C_4AH_{13} + 4Al(OH)_3 + CaSO_4 \cdot H_2O$.

And there is also a partial transition of calcium trisulfoaluminate hydrate (CMSAH) to calcium monosulfoaluminate hydrate (CMSAH) and, respectively, a reaction with C_2A.

As a result, by solving the problem of primary ettringite stability, it is possible to achieve a significant improvement of composite binders (alumina cement + gypsum), as well as sulfoaluminate binders.

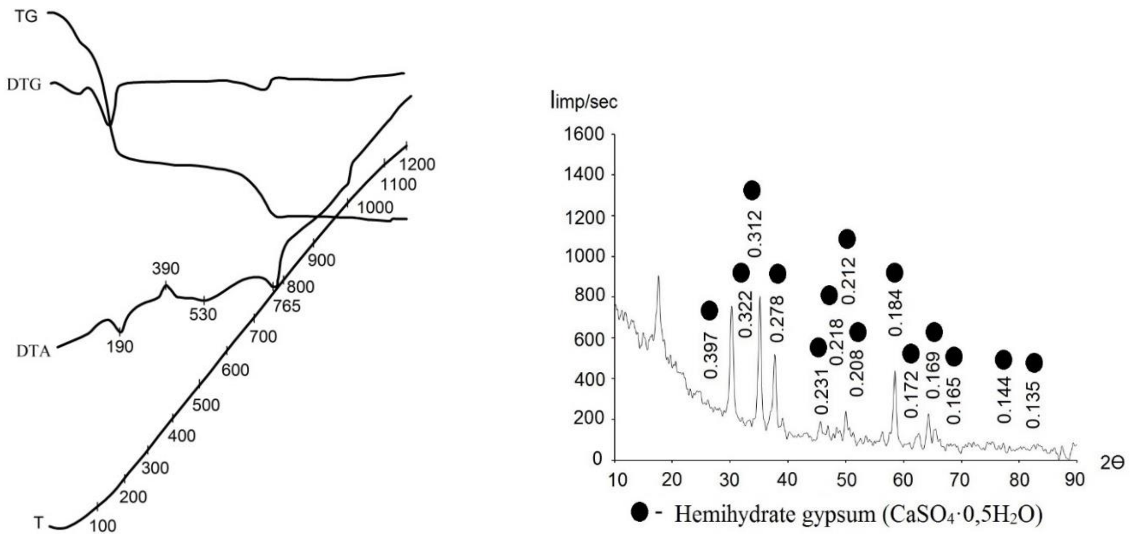
RESULTS AND DISCUSSION

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

The last option is a rather under-researched direction in connection with high energy costs for production and imparting special properties due to the formation of ettringite.

The research methodology consisted in modifying semi-aqueous gypsum with alumina cement. At the same time, the optimal amount of the modifier was determined to increase physical and mechanical properties, as well as influence of the modified binder mineralogical composition.

The research was performed with the use of Gypsum G-5-II in quantity of 30÷70 %, with semi-aqueous gypsum being the main mineral of it (Fig. 7) [18].



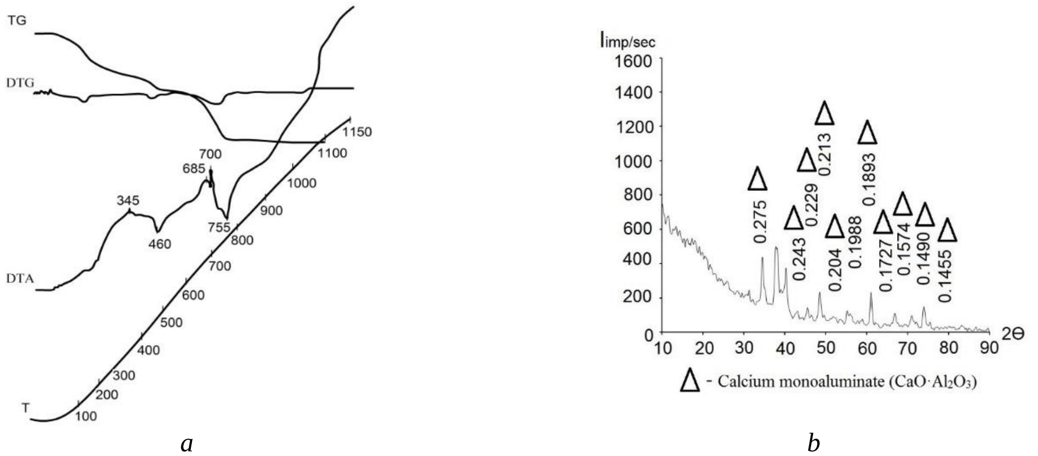
a *b*

Fig. 7. G-5-II *a*) DTA; *b*) X-ray [18]

Aluminous cement AC-500 was also used for conducting research in the amount of 30÷70 %, (DTA and X-ray of it are shown in Fig. 8).

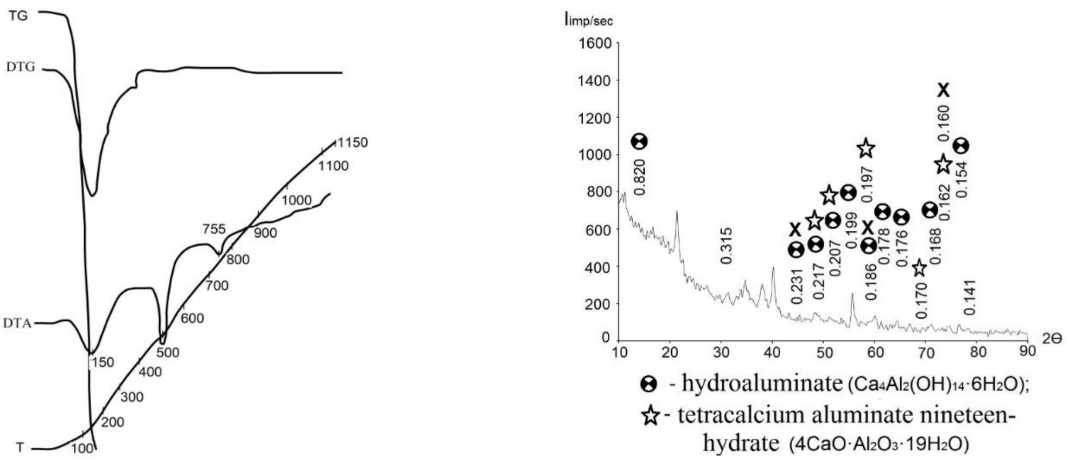
Hydrated alumina cement without additives is shown in Fig. 9 [18].

The results of studies of the composite composition of alumina cement AC-500 in the amount of 30÷70 % are shown in Figs. 10–12.



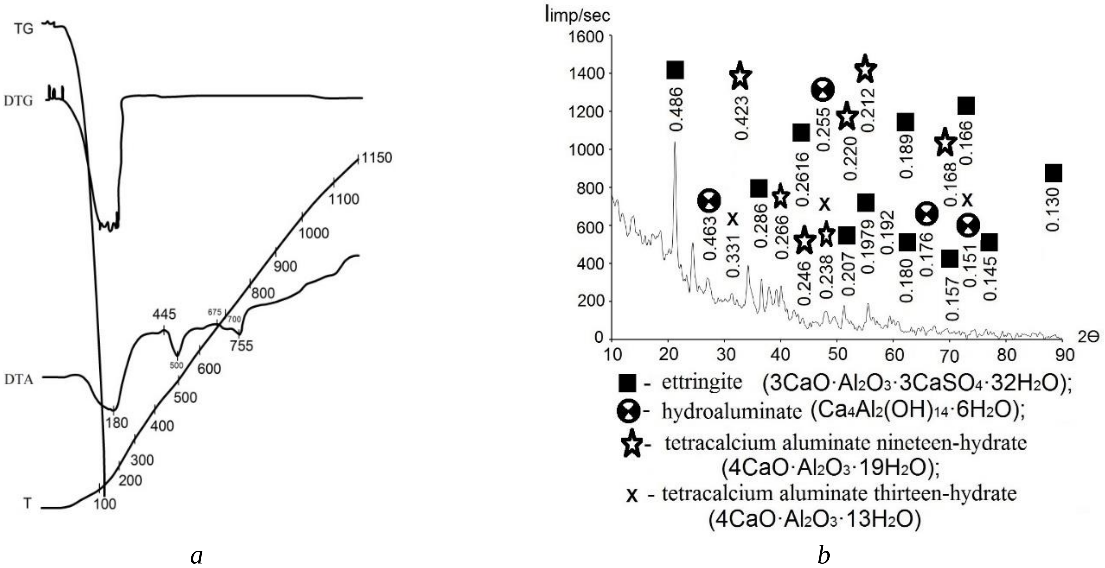
a *b*

Fig. 8. Alumina cement (AC-500) *a*) DTA; *b*) X-ray [18]



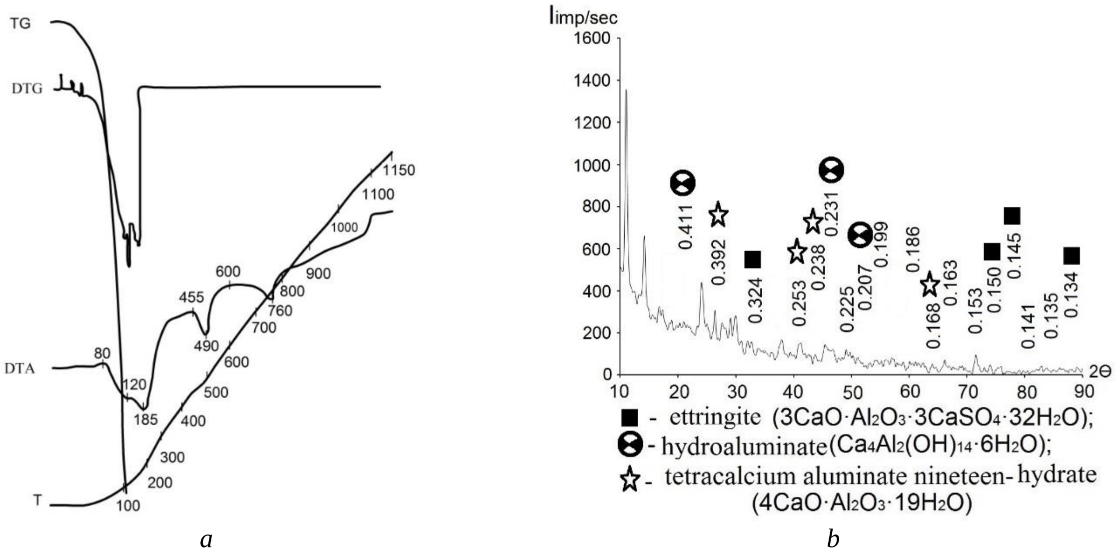
a *b*

Fig. 9. Hydrated AC-500 (without additives): *a*) DTA; *b*) X-ray



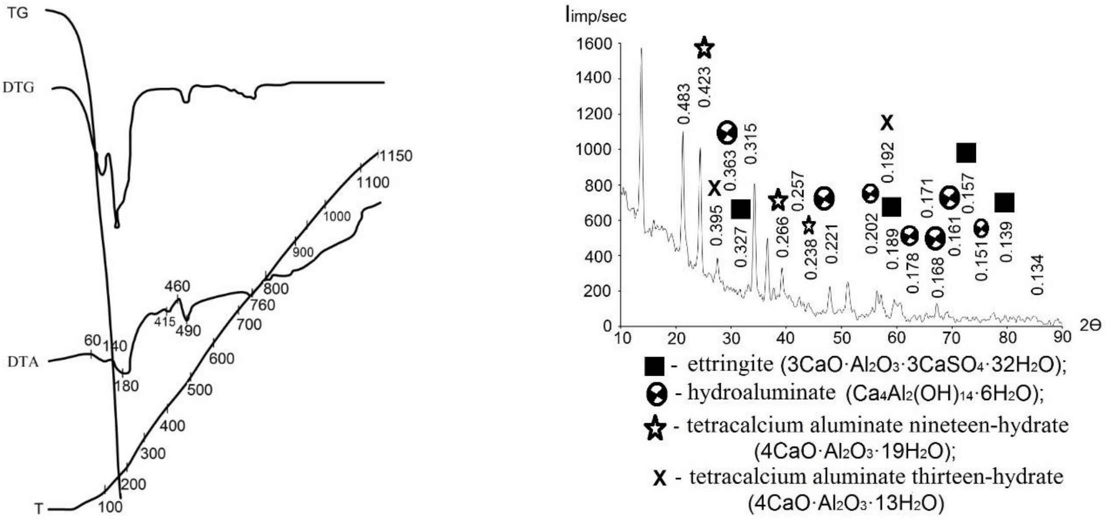
a *b*

Fig. 10. 70 % AC-500+30 % Gypsum: *a*) DTA; *b*) X-ray



a *b*

Fig. 11. 50 % AC-500+50 % Gypsum: *a*) DTA; *b*) X-ray



a *b*

Fig. 12. 30 % AC-500+70 % Gypsum: *a*) DTA; *b*) X-ray

In the process of hydration, the following interactions occur in the presence of gypsum (these interactions are associated with formation of ettringite).

X-ray phase analysis and data processing of alumina cement revealed the presence of the following hydration products. After 1 day of hardening the diffractogram of hardened AC-500 alumina cement shows the main lines of hydrated phases of hydroaluminate (d/n = 0.820; 0.231; 0.217; 0.348; 0.199; 0.186; 0.178; 0.176; 0.162; 0.154 nm), cubic aluminate hexahydrate (d/n = 0.315; 0.168; 0.160; 0.154 nm); tetracalcium aluminate nineteen-hydrate e (d/n = 0.217; 0.207; 0.197; 0.170; 0.162 nm) (Fig. 9).

With the addition of G-5 gypsum to alumina cement AC-400, after 3 days of hardening, the main interplanar distances and intensities of hydrated phases of ettringite (d/n = 0.484; 0.327; 0.324; 0.286; 0.2616; 0.189; 0.180; 0.157; 0.150; 0.145; 0.139; 0.134; 0.131 nm) appear (Fig. 10–12). Observed are lines of tetracalcium aluminate thirteen-hydrate (d/n = 0.423; 0.266; 0.246; 0.238; 0.212; 0.168 nm), tetracalcium aluminate nineteen-hydrate (d/n = 0.331; 0.238; 0.151 nm), hydroaluminate (d/n = 0.463; 0.255; 0.176; 0.151 nm), tetracalcium aluminate nineteen-hydrate (d/n = 0.331; 0.238; 0.151 nm) (Figs. 10–12).

In the process of setting and hardening, after 3 days, the intensity of the ettringite and calcium hydroxide lines increases which confirms the intensification of the hydration process (Figs. 10–12).

CONCLUSIONS

A theoretically substantiated hypothesis of the effect caused by the ratio $G = f(CaO/Al_2O_3)$ in the minerals of the $CaO\text{-}Al_2O_3\text{-}H_2O$ system on the Gibbs surface energy: $CA_2 = 0.27 - \Delta G = 24.70$, CA = 0.54–51.86, $C_{12}A_7 = 0.8–141.00$, $C_3A = 1.63–145$.

Dependence of the order of formation of hydrate compounds of the $CaO\text{-}Al_2O_3\text{-}H_2O$: C_2AH_8, C_4AH_{13}, C_4AH_{10}, CAH_{10}, $Al(OH)_3$ system during hydration of minerals of aluminate cements with Gibbs surface energy: CA_2 – 24.70, CA – 51.86, $C_{12}A_7$ – 141.00, C_3A – 145 was found theoretically and confirmed experimentally.

The theoretical position of influence of ΔG during hydration of aluminate cements in the presence of gypsum received further development – the system of chemical reactions $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$ can be divided into two systems (parts): a) $CaO\text{-}Al_2O_3\text{-}H_2O$; b) $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$, as a result C_3AH_6, CAH_{10}, C_2AH_8, C_4AH_{13}, $Ca_2(OH)_2$ is formed in the first one, and calcium trisulfoaluminate hydrate (CMSAH) and calcium monosulfoaluminate hydrate (CMSAH) are formed in the second one. According to the first part and second part, there is a process of $Al(OH)_3$ formation.

The optimal content of calcium sulfate (within 30–40 % of the composition mass) with a positive effect on the amount of ettringite formation has been theoretically determined and experimentally confirmed.

Теоретичне та експериментальне обґрунтування принципів модифікації композицій систем $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$

В.М. Дерев’янко, Г.М. Гришко, Є.І. Заяць, Т.М. Дубов

Український державний університет науки і технологій
Навчально-науковий інститут «Придніпровська державна академія будівництва та архітектури»
вул. Архітектора Олега Петрова, 24а, Дніпро, 49005, Україна, hryshko.hanna@pdaba.edu.ua
Дніпровький державний аграрно-економічний університет
вул. Сергія Єфремова, 25, Дніпро, 49600, Україна, dubov.t.m@dsau.dp.ua

Створення нових різновидів стандартних (розширених) і спеціальних цементів є одним із основних напрямів сучасних розробок у технології виробництва цементних речовин. У групі спеціальних цементів особливе місце посідають глиноземні, сульфоалюмінатні та ін. Основні науково-дослідні роботи при розробці таких цементів ведуться в напрямку створення нових композицій, що забезпечують заміну дефіцитних компонентів. При такому складі матеріалу вартість композицій з властивостями глиноземистих цементів дещо вища, ніж звичайних, але їхнє використання покращує експлуатаційні характеристики виробів. Підсумовуючи накопичений досвід, зазначимо, що нові ефективні склади на основі глиноземистого цементу, гіпсу та відходів виробництва досить ефективні в економічному та технічному відношенні. Мета статті – визначити залежність утворення гідратних сполук при гідратації алюмінатних та сульфоалюмінатних цементів від поверхневої енергії Гіббса $\Delta G = f(а.о.м)$ *та співвідношення* $\Delta G = f(mCaO/nAl_2O_3)$ *у мінералах системи на середню енергію Гіббса та підвищення стабільності етрингітової фази системи* $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$. *У статті розглянуто можливості управління процесами гідратації шляхом створення композитів і введення добавок, що впливають на значення поверхневої енергії Гіббса системи* $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$. *В результаті збільшується кількість центрів кристалізації і швидкість хімічних процесів. Теоретично обґрунтована гіпотеза про вплив співвідношення* $G = f(mCaO/nAl_2O_3)$ *в мінералах системи* $CaO\text{-}Al_2O_3\text{-}H_2O$ *на поверхневу енергію Гіббса:* $CA_2 = 0.27 - \Delta G = 24.70$, *CA = 0.54–51.86,* $C_{12}A_7 = 0.8–141.00$, $C_3A = 1.63–145$. *Теоретичні положення про вплив ΔG при гідратації алюмінатних цементів у присутності гіпсу отримали подальший розвиток – систему хімічних реакцій* $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$ *можна поділити на дві системи (частини): а)* $CaO\text{-}Al_2O_3\text{-}H_2O$*; б)* $CaO\text{-}Al_2O_3\text{-}SO_3\text{-}H_2O$*, внаслідок чого в* *першому випадку утворюється C_3AH_6, CAN_{10}, C_2AH_8, C_4AH_{13}, $Ca_2(OH)_2$, а в присутності гіпсу – трисульфатна форма гідросульфоалюмінату кальцію (ТГСАК) і моносульфатна форма гідросульфоалюмінату кальцію (МГСАК). Відповідно для першої та другої частин відбувається процес утворення $Al(OH)_3$. Теоретично визначено та експериментально підтверджено оптимальний вміст сульфату кальцію (в межах 30–40 % від маси композиції), що позитивно впливає на кількість етрингітоутворення.*

***Ключові слова**: композиційне в'яжуче, модифікація, етрингіт, фазова стабілізація етрингіту, алюмінатні цементи, сульфоалюмінатні цементи*

REFERENCES

1. Runova R.F., Dvorkin L.J., Dvorkin O.L., Nosovs'ky Yu.L. *Binders*. (Kyiv: Osnova, 2012). [in Ukrainian].
2. Pashchenko O.O. *Binding materials*. (Kyiv: Vishcha shkola, 1995). [in Ukrainian].
3. Sanytsky M., Kropyvnytska T., Fischer H., Kondratieva N. Performance of low carbon modified composite gypsum binders with increased water resistance. *Chem. Chem. Technol*. 2019. **13**(4): 495.
4. Sanytsky M., Usherov-Marshak A., Kropyvnytska T., Heviuk I. Performance of multicomponent Portland cements containing granulated blast furnace slag, zeolite and limestone. *Cement Wapno Beton*. 2020. **25**(5): 416.
5. Plank J. Concrete Admixtures Where Are We Now and What Can We Expect in the Future? 19'Ibausil. Weimar. 2015. PV03.
6. Roy D., Daimon M. Effect of Admixtures upon Electrokinetie phenomena durinq hydration of C_3S. C_3A and portland cement. *7th. International Congress of the Chemistry of Cement*. Paris. 1980. **I**: 242.
7. Plugin A.A., Plugin O.A., Fischer H.-B., Shabanova G.N. Increase of gypsum water resistance by mineral additives. In: *1 Weimarer Gipstagung*. (30-31 März 2011). Weimar, Bundesrepublik Deutscland: Tagungsbericht. Weimar: F.A. Finger - Institut fur Baustoffknude, Bauhaus - Universität Weimar. 2011. **21**: 435.
8. Land G., Stephan D. The Acceleration of the Hydration of Cements with and without supplementary cementitious materials by C-S-H seeds. In: *19 Internationale Baustofftagung*. (16-18 September, 2015). Bauhaus-Universitat Weimar. Bundesrepublik Deutschland. **2**: 1011.
9. Kryvenko P.V., Pushkariova K.K., Baranovskyi V.B., Kochevyh M.O., Hasan Ye.G., Konstantynivskyi B.Ya., Raksha V.O. *Materials Science in Construction*. (Kyiv: Lira-K Publ., 2015). [in Ukrainian].
10. Derevianko V.M., Kondratieva N.V., Hryshko H.M. Theoretical and Practical Issues of Agricultural Science: Collective Monograph / Under the general editorship of. A.S. Kobets. – Chapter 14: Nanomodified binders for ion shielding solutions. – (Dnipro: Lira, 2023). P. 276.
11. Pushkariova K.K., Kochevykh M.O. Materials Science for Architects and Designers. (Kyiv: Lira-K Publ., 2018). [in Ukrainian].
12. Kondofesky-Mintova L., Plank J. Superplasticizers and Other Chemical Admixtures in Concrete. In: *Tenth Internetional Conference*. (October 2012, Prague, Czech Republic).
13. Sanytskyi M.A., Kondratieva N.V. In: *III All-Ukrainian Science and Technology Conference "Modern Trends in the Development and Production of Silicate Materials"*. (September 5–8, 2016, Lviv).
14. Kartel M.T., Lobanov V.V. Surface Physics and Chemistry. Book I. In: *Surface Physics*. (Kyiv: O.O. Chuiko Institute of Surface Chemistry of the NAS of Ukraine –Interservis LLC, 2015). [in Russian].
15. Shishkin A., Shishkina A., Vatin N. Low-shrinkage alcohol cement concrete. *Applied Mechanics and Materials*. 2014. **633–634**: 917.
16. Shishkina A., Shishkin A. Study of the effect of micellar catalysis on the strength of alkaline reactive powder concrete. EEJET. 2018. **3**(6(93)): 46.
17. Hryshko H., Derevianko V., Vatazhyshyn O., Dubov T. 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.* International Scientific and Practical Conference Innovations in Construction and Smart Building Technologies for Comfortable, Energy Efficient and Sustainable Lifestyle. ICSBT. 2024. 534(01005). https://doi.org/10.1051/e3sconf/202453401005.
18. Derevianko V.M., Hryshko H.M., Dubov T.M. Stabilizatsiia etrynhitovoi fazy. *Building Materials and Products*. 2023. **1–2**(103): 18.

Received 07.06.2024, accepted 05.03.2025