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DEVELOPMENT OF SOLUTIONS CONCERNING REGULATION OF PROPER DEFORMATIONS IN ALKALI-ACTIVATED CEMENTS

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Проаналізовано сутність проблеми власних деформацій лужних цементів (ЛЦ), ускладнення якої пов'язано з підвищеним вмістом гелеподібних гідратних новоутворень. Як приклади розглянуто типи цементів діаметрально протилежні за композиційною будовою і відповідно за вмістом гелеподібних фаз при гідратації – лужний портландцемент (ЛПЦ) і шлаколужний цемент (ШЛЦ). Запропоновано підходи до формування ефективної структури штучного каменя, протидіючою деформаціям усадки, шляхом втручання в структуроутворення при використанні комплексів мінеральних і органічних сполук. Такі сполуки в складі комплексних органо-мінеральних добавок сумісно впливають на інтенсифікацію кристалізаційних процесів, формування ефективної порової структури та морфологію гідратних фаз при зменшенні вмісту води в штучному камені. В якості інгредієнтів запропонованих комплексних добавок-модифікаторів розглянуто солі-електроліти різного аніонного типу та аніоноактивні поверхнево-активні речовини.

Виявлено, що для модифікації ЛПЦ найбільш ефективною є система «сіль-електроліт – поверхнево-активна речовина». Показано, що модифікація ЛПЦ комплексною добавкою цієї системи на основі $NaNO_3$ забезпечує зменшення усадки з 0,406 до 0,017 мм/м. Натомість використання Na_2SO_4 забезпечує цьому типу лужного цементу здатність до розширення в межах 0,062 мм/м. Показано, що ефект компенсованої усадки модифікованого ЛПЦ пов'язаний з більшою кристалізацією низькоосновних гідросилікатів (CSH(B)) і гідроалюмінатів кальцію ($CaO \cdot Al_2O_3 \cdot 10H_2O$). Додатковий ефект пов'язаний з утворенням сульфатвміщуючого натрієво-кальцієвого гідроалюмінату (для системи на основі Na_2SO_4) та кристалічного гідронітроалюмінату кальцію (для системи на основі $NaNO_3$) з відповідним напруженням мікроструктури.

В розвиток для модифікації ШЛЦ запропоновано комплексну добавку системи «портландцементний клінкер – сіль-електроліт – поверхнево-активна речовина», яка забезпечує зменшення усадки з 0,984 мм/м до 0,683 мм/м. Мінімізація усадки модифікованого ШЛЦ пояснено формуванням поряд з низькоосновними гідросилікатами кальцію гідроалюмосилікату натрію типу гмеліниту ($(Na_2Ca) \cdot Al_2 \cdot Si_4 \cdot O_{12} \cdot 6H_2O$) з підвищеним ступенем закристалізованості. При цьому відмічено, що структура цементного каменя характеризується підвищеною щільністю, однорідністю і монолітністю гідратних новоутворень

Ключові слова: лужний цемент, сіль-електроліт, комплексна органо-мінеральна добавка, структуроутворення, власні деформації, усадка

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1. Introduction

The relevance of using cements containing mineral admixtures of both natural and artificial origin is determined by compliance with current trends in sustainable mankind development in terms of efficient consumption of raw materials and energy and responsible attitude to the environment. From the environmental point of view, partial replacement of cement clinker with mineral admixtures contributes to the reduction of CO_2 emissions. In addition, materials based on such cements are characterized by high quality, functionality and durability. For example, efficiency of using blast furnace slag, zeolite and limestone in composite eco-cements with high initial strength has been demonstrated [1]. Replacement of clinker with zeolite promotes higher strength of concrete and its freeze/thaw resistance and crack resistance [2].

Improvement of concrete performance attributes is possible through joint use of several mineral admixtures due to optimization of granulometric composition of cement [3]. The principle of raising performance attributes by the use of multi-component cement systems can be applied to various materials, that is decorative mortars (plasters for restoration and finishing works, etc.) [4].

Various types of activation (calcium, sulphate, alkaline, sulphate-alkaline, etc.) are used to raise initial strength of cements with mineral admixtures [5]. Alkaline activation is realized in alkali-activated cements (AAC) by adding compounds of alkali metals to the aluminosilicate component.

Environmental benefits of AAC are associated with the possibility of ensuring the highest content of by-products and production wastes, such as slag, fly ash, red mud, etc. [6]. Possibility of utilization of industrial wastewater in production of safe building materials on AAC basis has also been shown [7]. Such cements are characterized by high heat-resistance [8], corrosion resistance [9] and freeze/thaw resistance [10] in comparison with those based on conventional clinker cements for general and special construction purposes.

However, along with advantages, AACs have their own features. These features include high proper deformations that can intensify crack formation and reduce durability of structures if a right choice of approach to warehouse design and surveillance of the process of mortar and concrete hardening was not made. High proper deformations of AAC is explained by high content of gel phase which depends on cement composition [11].

Principles of designing AAC composition were proposed and implemented in the national standard of Ukraine DSTU B V.2.7-181:2009 [12]. Content of granular blast furnace slag (GBS) from 0 % (type II, AAPC) to 100 % (type I, AASC) in composition of the aluminosilicate component can be considered the cause of variation in composition of five AAC types.

Alkali metal compounds in such cements are considered as structure-forming components whose content depends on the AAC type. Increase in GBS content and, accordingly, alkaline component in AAC causes increase in content of the gel phase and, hence, higher shrinkage deformations [13]. This is explained by growth of the role of breakage of covalent bonds (Si-O-Si, Si-O-Al, Al-O-Al), withdrawal of anions from the polycondensation reaction and their transition into a colloidal phase in presence of alkali metal cations [11].

Therefore, this problem necessitates a search for effective solutions in the field of controlling deformations in artificial stone of alkali-activated cements without deleterious effect on physical and mechanical properties when varying GBS content.

2. Literature review and problem statement

Results of present-day studies demonstrate inefficiency of known means used in controlling proper deformations in conventional cements by oxide [14] and hydrosulfoaluminate expansion [15].

At the same time, a possibility of solving the problem of high AASC shrinkage by the use of Na_2SO_4 salt electrolyte was shown in [16]. It is also known from [17] on the use (in AASC) of admixtures of cement bypass dust whose characteristic components are CaO, salts of alkali and alkaline-earth metals (KCl, NaCl, K_2SO_4, Na_2SO_4, $CaSO_4$, K_2CO_3, Na_2CO_3, etc.). Provisions of general mineralogy and cement chemistry provide explanation of the ability of mineral compounds to affect structure formation in cement systems. Ability of silicate and aluminate structures to change morphology with formation of solid solutions and crystalline structures is ensured. It was shown in the paper that such morphological changes can have an effect of reducing proper deformations in artificial stone [18]. However, the mechanism of action of such admixtures has not been amply studied and their use does not enable obtaining AAC with controlled shrinkage.

Another well-known way to control proper deformations in AAC by means of raising degree of crystallization of hydrate phases consists in modification with high-calcium admixtures, that is, with portland cement clinker [11] or lime [19].

In addition, cement shrinkage can be reduced by using surfactants as shrinkage reducing admixtures (SRA) and admixtures having a water-reducing effect [20]. The shrinkage reducing effect when using surfactants is explained by fall of surface tension of interstitial fluid. This makes it possible to reduce cement shrinkage deformation due to the falling pressure in capillaries and slowing down rate of moisture evaporation. Since most of surfactants are ineffective in a hydration medium of AAC, principles of their selection were proposed for such cements according to the criteria of variation of plastic strength [13], stability of molecular structure of admixtures having plasticizing [21] and other types of action [22] in a high alkaline medium. In this regard, it has been shown that maximum plasticizing effect is enabled by addition of sodium lignosulfonate [23], sodium gluconate [24], polyatomic alcohols and other acyclic low- and high-molecular compounds [13]. Additional effects of such compounds are known. For example, a decrease in AASC shrinkage in presence of polypropylene glycol (polyether) is due to redistribution of the pore space through raising number of pores with diameter of 0.1–1 μm in which capillary pressure is much lower than that in smaller capillaries [25].

The presented studies [14–25] show positive influence of mineral and organic admixtures on reduction of AAC shrinkage, however there is no explanation of the mechanism of their structure formation. This fact limits understanding ways of regulating proper deformations in artificial stone. This necessitates studies to identify effective ways of influencing the processes of structure formation in AAC with the provision of specified proper deformations.

Generalization of above results makes it possible to predict effectiveness of property regulation including regulation of proper deformations in AAC when varying content of GBS from 0 to 100 % of aluminosilicate component weight by a complex interference in the structure formation. It can be predicted whether complex modifying admixtures jointly influencing development of crystallization processes, formation of effective pore structure and morphology of hydration phases will be effective for this purpose. All of this determines urgency of using soluble compounds containing SO_4^{2-}, NO_3^-, F^-, Cl^- anions, etc. in combination with high-calcium compounds and effective surfactant types.

3. The aim and objectives of the study

The study objective is the analysis of patterns of variation of AAC proper deformation when varying content of GBS from 0 to 100 % by weight of the aluminosilicate component and development of effective solutions concerning regulation of such deformations.

To achieve this objective, the following tasks were set:

– to identify effective complex organo-mineral admixtures of the “mineral compound-surfactant” system for AAPC modification according to the complex influence on normal paste density (NPD) value, hardening time, strength and proper deformations;

– to determine features of structure formation in AAPC modified with complex organo-mineral admixtures;

– to carry out comparative analysis of effectiveness of complex organo-mineral admixtures of the “clinker–salt electrolyte–surfactant” system for AASC modification according to values of normal consistency of cement paste, setting time, strength, and proper deformations;

– to substantiate choice of the most effective complex admixture and study its effect on AASC structure formation;

– to propose a solution concerning regulation of proper deformations in AAC when varying content of GBS from 0 to 100 % of weight of aluminosilicate component.

4. Materials and methods used for studying effectiveness of admixtures for regulating AAC properties

4. 1. Raw materials used

Two types of AAC were used in the studies: type I (AASC) and type II (AAPC).

The following materials were used as aluminosilicate components for AASC and AAPC, respectively:

– GBS from PJSC Dneprovsky Integrated Iron&Steel Works named after Dzershinsky (Kamyanske, Ukraine) according to DSTU B V.2.7-302:2014, specific surface S_{sp}=4,500 cm^2/g (according to Blaine), basicity modulus M_b=1.11, content of the glass phase: 84.0 %;

– Portland cement clinker (hereinafter referred to as clinker) manufactured by Baltsem OJSC (Balakliya, Ukraine) with specific surface area of 4,500 cm^2/g: 66.15 % CaO; 22.61 % SiO_2; 5.29 % Al_2O_3; 3.93 % Fe_2O_3; 0.84 % MgO; 0.15 % Na_2O; 0.98 % K_2O; 0.50 % SO_3.

Sodium metasilicate (SM) ($Na_2SiO_3 \cdot 5H_2O$) in a dry powder form was used as alkaline component of AAC.

The following materials were used as components of complex organo-mineral admixtures:

– mineral compounds: Na_2SO_4 sodium sulfate (CAS No. 7757-82-6), $NaNO_3$ sodium nitrate (CAS No. 7631-99-4), Na_3PO_4 (CAS No. 7601-54-9), NaCl (CAS No. 7647-14-5), $Ca(NO_3)_2$ (CAS No. 13477-34-4), Ca $(OH)_2$ (CAS No. 1305-62-0), $CaSO_4 \cdot 0.5H_2O$ (according to DSTU B V.2.7-104:2000);

– surfactants of two types: sodium lignosulfonate (SLS) produced by Borrespers (Norway) according to CAS No. 8061-51-6 (pH≥8.5) and sodium gluconate (SG) according to CAS No. 527-07-1.

According to the complex effect of reducing water demand, slowing down the hardening period and raising strength of AAC, the most effective formulations of admixtures were determined and further used to regulate proper deformations of AAC.

The studied AACs were prepared by mixing dry components with water in a Hobart laboratory blade mixer. Content of SM in AAPC composition was 3 % (by Na_2O) or 10.26 % (by dry matter) of clinker weight. SM content in AASC was 3.91 (by Na_2O%) or 13.38 % (by dry matter) of slag weight which corresponded to principles of composition structure of alkali-activated cements of these types [12].

Standard quartz sand from Gusarivsky deposit (Ukraine) according to DSTU B V.2.7-189:2009 was used as fine aggregate in the study of strength development and proper deformations of AAC.

4. 2. The methods used in studying effectiveness of complex organo-mineral admixtures

Development of cement stone microstructure was studied by methods of physicochemical analysis: differential-thermal analysis (DTA) using derivatograph of R. Paulik, I. Paulik, L. Erday system, MOM Company (Budapest, Hungary), and probe analysis using REMMA 102 02 raster electron microscope-microanalyzer (SELMI OJSC, Sumy, Ukraine).

Normal consistency of cement paste and setting time of cements were determined according to DSTU B V.2.7-185:2009.

Water-reducing effect of complex admixtures was assessed by reduction of W/C values of solution mixtures (1:3) when spreading on a flow table (106–115 mm) according to DSTU B V.2.7-187:2009. Strength of the cured solution was also determined by this standard.

Proper deformations in AAC were determined on 40×40×160 mm specimens made of cement-sand mortar (1:3). After making specimens and hardening in molds for 1 day with surface covered, the specimens were cured for 7 days under normal conditions (t=20±2 °C, $R.H.$=95±5 %). The specimens were then stored at temperature t=20±2 °C and relative humidity $R.H.$=65 %. These conditions of specimen storage correspond to conventional conditions of mortar and concrete hardening. When calculating proper deformation, length of 1-day specimens was taken as initial value.

5. Results obtained in determining the effect of complex organo-mineral admixtures on proper deformations in AAC

5. 1. Effect of complex organo-mineral admixtures on properties of alkali-activated portland cement

AAPC of "clinker–SM" system (control composition) was characterized by normal consistency of cement paste value of 19.7 % and too short setting time: the initial setting 5 min and the end setting 7 min. Values of compressive strength of AAPC were 30.3 MPa on day 2, 37.3 MPa on day 7, and 43.5 MPa on day 28 at W/C=0.34.

Comparative analysis of AAPC properties in hydrate systems "clinker–SM", "clinker–SM–mineral compound", "clinker–SM–mineral compound–surfactant" was conducted.

Content of admixtures of mineral compounds was 50 % of alkaline component weight which corresponded to 2.96 % of clinker weight. Surfactants (SLS, SG) were introduced in amounts of 0.45 and 0.25 % of clinker weight, respectively.

It was found that by the complex effect on decrease in normal consistency of cement paste, setting time slowdown and hardening acceleration, effectiveness of mineral compounds decreased in the following order: $Ca(OH)_2 > CaSO_4 \cdot 0.5H_2O > NaNO_3 > Na_2SO_4 > Na_3PO_4 > Ca(NO_3)_2 > NaCl$.

The greatest effect of "clinker–SM" system on reduction of proper deformations of AAPC in presence of surfactants was observed when using salt electrolytes Na_2SO_4 and $NaNO_3$ (Fig. 1). In presence of Na_2SO_4, expansion of 0.062 mm/m was observed and with the use of $NaNO_3$, a virtually shrink-free system with shrinkage value of 0.017 mm/m was obtained.

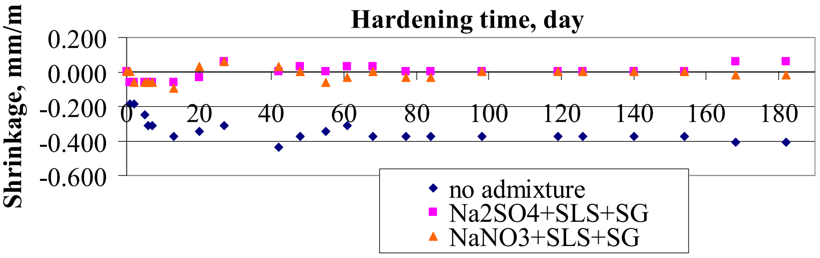


Fig. 1. Development of proper deformations in alkali-activated portland cement modified with complex admixtures

In addition, it was found that the complex admixture of "Na_2SO_4–SLS–SG" composition in relation to the control specimen provided a decrease in normal consistency of cement paste value from 19.7 to 17.0 %. In this case, extension of setting time: from 5 to 30 min for the beginning of hardening and from 7 to 35 min for the end of hardening was observed. There was a slight increase in compressive strength of modified AAPC relative to AAPC with no admixtures through reduction of the *W/C* value from 0.34 to 0.33: 34.6 MPa (2 days), 41.7 MPa (7 days) and 47.8 MPa (28 days).

Replacement of Na_2SO_4 with $NaNO_3$ in the composition of complex admixture determines additional lengthening of AAPC hardening time at normal consistency of cement paste=17.1 %: up to 37 min for the beginning and up to 44 min for the end. There was a much higher intensity of increase in compressive strength of solution through reduction of *W/C* from 0.34 to 0.29: 39.3 MPa (2 days), 48.7 MPa (7 days), 53.1 MPa (28 days).

Thus, presence of surfactants in composition of complex organo-mineral admixtures provides slowdown of hardening and increase in AAPC strength.

5. 2. Structure formation in alkali-activated portland cement modified with complex organo-mineral admixtures

Features of structure formation in AAPC modified with complex admixtures based on Na_2SO_4 and $NaNO_3$ were studied using differential-thermal analysis (DTA) (Fig. 2), electron microscopy (Fig. 3–5, *a*) and probe analysis (Fig. 3–5, *b*). Chemical and oxide compositions of new AAPC formations under study obtained by probe analysis with the help of REMMA 102-02 electron microscope-microanalyzer are given in Tables 1–3.

Formation of low-basicity calcium hydrosilicates of CSH(B) structure and xonotlite $6CaO{\cdot}6SiO_2{\cdot}H_2O$ (end effects at *t*=160 and 845 °C, that is recrystallization into wollastonite) was revealed in the products of hydration of AAPC without admixtures (Fig. 2). The presence of end effects at *t*=490 and 670 °C characterizes formation of a slightly crystallized hydrosilicate of $C_2SH(A)$ structure. In addition to hydrosilicates, formation of slightly crystallized calcium hydroaluminates of $CaO{\cdot}Al_2O_3{\cdot}10H_2O$ structure (exogenous effects at *t*=520 and 710 °C) was observed in the hydration products.

Analysis of electronic micrographs of cleavage surface of artificial AAPC stone of "clinker–SM" system makes it possible to identify globular formation of gel-like calcium hydrosilicates (Fig. 3, *a*) and calcium hydroaluminates with inclusions of Na^+ and K^+ ions in their structure (Table 1). Drop-like formations on the gel surface represent nuclei of the crystalline phase.

Microstructure of the AAPC stone modified with complex admixture "Na_2SO_4–SLS–SG" (Fig. 2) is represented mainly by the same new hydrate formations as the composition with no admixtures but with a greater degree of crystallization. Increased crystallization of calcium low-basicity hydrosilicates is indicated by displacement of the end effect of their recrystallization to the region of elevated temperatures (*t*=850 °C instead of 845 °C for the admixture system). Shift of the end effect which characterizes formation of calcium hydroaluminate ($CaO{\cdot}Al_2O_3{\cdot}10H_2O$) towards the elevated temperature (*t*=540 °C) and appearance of exo-effect at *t*=915 °C also characterize growth of microstructure crystallization.

Analysis of electron photomicrograph of the cleavage surface of AAPC stone modified with complex admixture "Na_2SO_4–SLS–SG" confirms presence of these new hydrate formations with a high degree of crystallization (Fig. 4, *a*). The results of probe analysis (Table 2) indicate additional formation of hexagonal lamellar crystalline structures of minamiite $(Na, Ca_{0.5})Al_3(SO_4)_2(OH)_6$ in the structure of artificial stone [26].

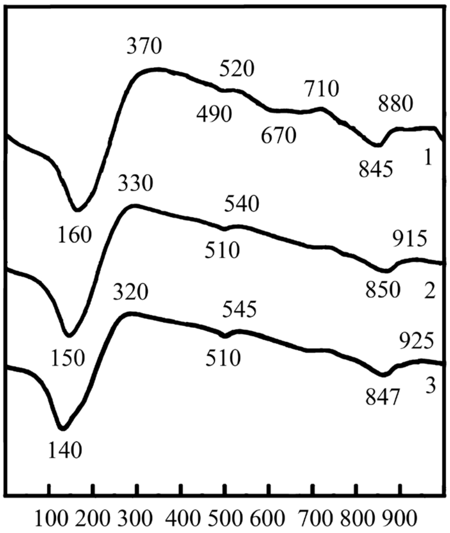
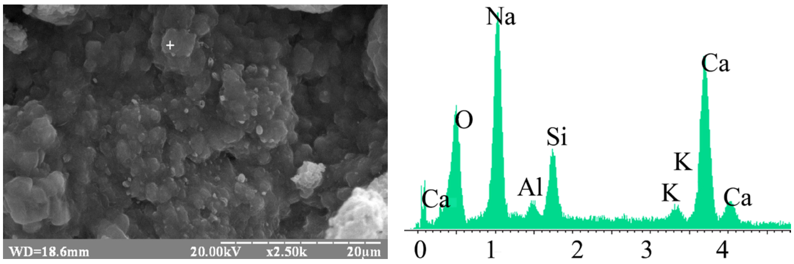
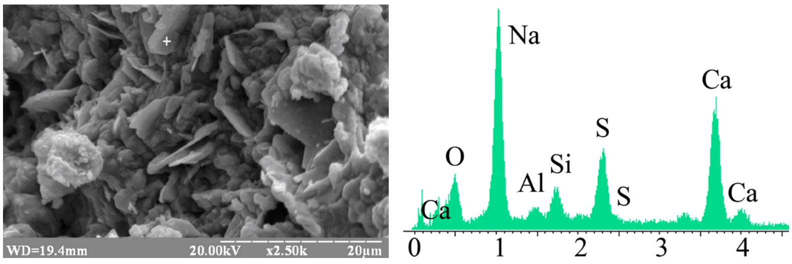


Fig. 2. Curves of differential-thermal analysis of AAPC (on day 28 of hardening): 1 – with no admixture; 2 – with complex admixture "Na_2SO_4–SLS–SG"; 3 – with complex admixture "$NaNO_3$–SLS–SG"



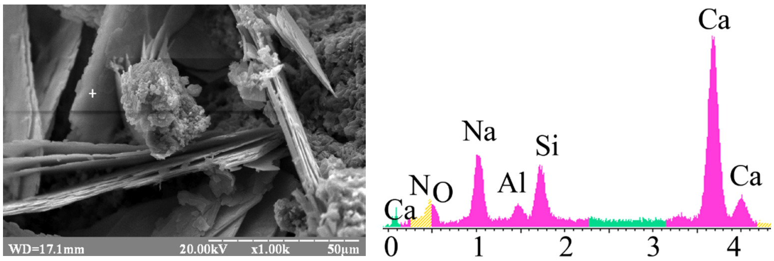
a *b*

Fig. 3. Characteristics of microstructure of alkali-activated portland cement after 28 days of hardening: *a* – electron photomicrograph of cleavage surface; *b* – probe analysis



a *b*

Fig. 4. Characteristics of microstructure of alkali-activated portland cement modified with complex admixture "Na_2SO_4–SLS–SG" after 28 days of hardening: *a* – electron photomicrograph of the cleavage surface; *b* – probe analysis



a *b*

Fig. 5. Characteristics of microstructure of alkali-activated portland cement modified with complex admixture “$NaNO_3$–SLS–SG” after 28 days of hardening: *a* – electron photomicrograph of the cleavage surface; *b* – probe analysis

Table 1

Chemical composition of new formations in AAPC without admixtures according to the results of probe analysis

Chemical composition, %					
O	Na	Al	Si	K	Ca
52.88	33.49	1.49	3.76	0.82	7.56

Oxide composition, %				
Na_2O	Al_2O_3	SiO_2	K_2O	CaO
60.61	4.97	14.33	1.71	18.38

Table 2

Chemical composition of new formations in the AAPC modified with complex admixture “Na_2SO_4–SLS–SG” according to the results of probe analysis

Chemical composition, %					
O	Na	Al	Si	S	Ca
37.95	41.39	2.22	3.38	6.09	8.97

Oxide composition, %				
Na_2O	Al_2O_3	SiO_2	SO_3	CaO
57.77	4.51	7.80	16.41	13.51

Table 3

Chemical composition of new formations of the AAPC modified with complex admixture “NaNO3–SLS–SG” according to the results of probe analysis

Chemical composition, %					
N	O	Na	Al	Si	Ca
6.77	46.85	22.38	2.30	5.24	16.46

Oxide composition, %				
N_2O	Na_2O	Al_2O_3	SiO_2	CaO
16.95	34.34	5.43	14.16	29.12

Unlike the system with Na_2SO_4, new layered lamellar formations with a distinct crystalline structure were observed along with calcium hydrosilicates and hydroaluminates during hardening of the AAPC modified with a complex admixture of "$NaNO_3$–SLS–SG" system (Fig. 5, *a*). These new formations can be attributed to calcium hydronitroaluminates, $3CaO\cdot Al_2O_3\cdot Ca(NO_3)_2\cdot 10H_2O$, (Table 3) [27] which is confirmed by presence of end effects in the DTA curves at t=140, 510 and 847 °C (Fig. 2). These new crystalline formations block the space between gel-like phases and may explain reduction of the cement stone shrinkage.

5. 3. Effect of complex organo-mineral admixtures on alkali-activated slag cement properties

Based on the studies, organo-mineral complex admixtures of the “salt electrolyte–surfactant” system based on Na_2SO_4 and $NaNO_3$ have been identified as the most effective for regulating proper deformations in AAPC. This has made it possible to introduce such systems together with clinker as modifying complex admixtures to regulate proper deformations in AASC of the GBS-SM system (control composition). Content of the complex admixture was 6 % of slag weight.

It has been found that AASC of control composition was characterized by following indicators: normal consistency of cement pastes 21.67 %, initial setting 45 min, end setting 60 min. Values of compressive strength of AASC at W/C=0.29 were 28.8 MPa on day 2, 40.0 MPa on day 7, and 50.3 MPa on day 28.

The use of organo-mineral complex admixture of “clinker–salt electrolyte–surfactant” system provided slowdown of AASC hardening as well as water-reducing effect. For example, complex admixture of “clinker–Na_2SO_4–SLS–SG” composition provided hardening beginning in 60 min and end in 75 min. Compressive strength of modified AASC has increased from 28.8 to 34.4 MPa at the age of 2 days, from 40.0 up to 45.3 MPa at the age of 7 days and from 50.3 to 56.9 MPa at the age of 28 days due to manifestation of water-reducing effect of the complex admixture (W/C was reduced from 0.29 to 0.26).

Replacement of Na_2SO_4 with $NaNO_3$ in the complex admixture makes it possible to obtain cement with initial setting 65 min and end setting 83 min. Also, strength of 31.9 MPa can be obtained at the age of 2 days, 43.4 MPa at the age of 7 days and 53.8 MPa at the age of 28 days.

The results of influence of organo-mineral admixtures of the “clinker–salt electrolyte–surfactant” system on proper deformations in AASC are shown in Fig. 6.

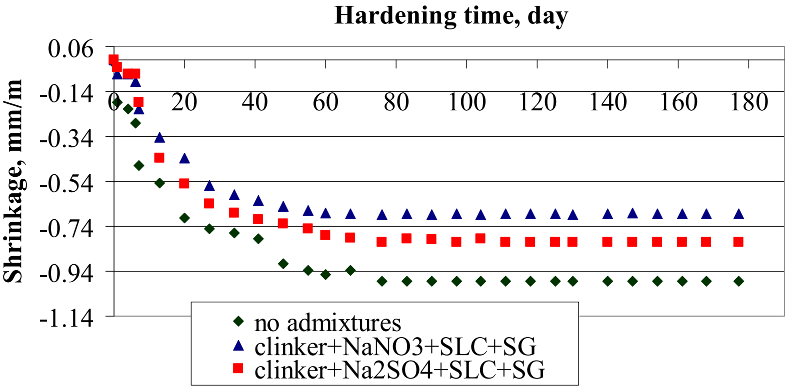


Fig. 6. Development of proper deformations in alkali-activated slag cement when using complex admixtures of “clinker–salt electrolyte–surfactant” system

The use of complex admixtures “clinker–Na_2SO_4–SLS–SG” and “clinker–$NaNO_3$–SLS–SG” enabled a reduction of AASC shrinkage from 0.984 to 0.810 and 0.683 mm/m, respectively.

5. 4. Structure formation in alkali-activated slag cement modified with a complex organo-mineral admixture

Influence of the most effective complex admixture of “$NaNO_3$–SLS–SG” composition on structure formation in AASC was studied using DTA (Fig. 7), electron microscopy (Fig. 8, *a*) and probe analysis (Fig. 8, *b*). Chemical and oxide compositions of new formations of the modified AASC obtained in probe analysis by means of REMMA 102-02 electron microscope-microanalyzer are given in Table 4.

According to the DTA results (Fig. 7), phase composition of modified AASC after hydration was represented mainly by calcium hydrosilicates CSH(B) of low basicity and gyrolyte $2CaO{\cdot}3SiO_2{\cdot}2H_2O$ (end effects at t=140–160 °C and 750–755 °C–>stepped dehydration, exo-effect at t=800–825 °C–>recrystallization to wollastonite). The end effect at t=590–610 °C indicated the presence of sodium hydroalumosilicate of gmelinite type $(Na_2Ca){\cdot}Al_2Si_4{\cdot}O_{12}{\cdot}6H_2O$ in the hydrate products.

Modification of AASC with complex admixture “clinker–$NaNO_3$–SLS-SG” provided an increased degree of crystallization of calcium hydrosilicates of low basicity as evidenced by the shift of exo-effect temperature from t=785 to 825 °C characteristic for recrystallization of above new formations to wollastonite.

New hydroalumosilicate formations additionally contain nitric oxide (Table 4) and form clusters in a form of spherulites and plates (Fig. 8).

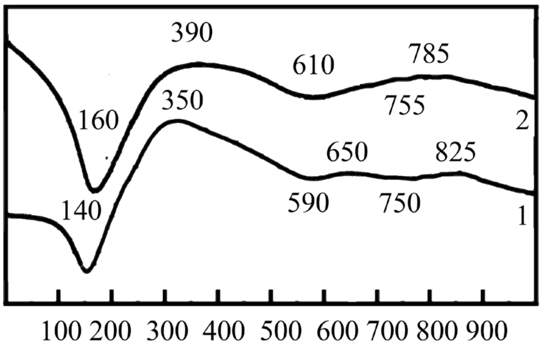
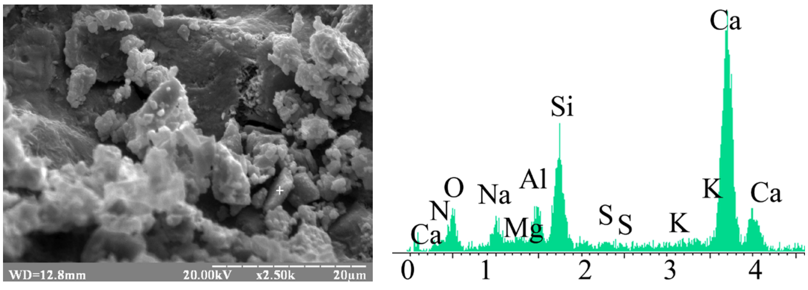


Fig. 7. Curves of differential thermal analysis (on day 28 of hardening) of alkali-activated slag cement:
1 – with no admixtures; 2 – with complex admixture “clinker-$NaNO_3$–SLS–SG”



a *b*

Fig. 8. Characteristics of microstructure of alkali-activated slag cement modified with complex admixture “clinker–$NaNO_3$–SLS-SG” after 28 days of strengthening: *a* – electron micrograph of the cleavage surface; *b* – probe analysis

Table 4

Chemical composition of specimens of alkali-activated slag cement modified with complex admixture “clinker–$NaNO_3$–SLS-SG” according to the results of probe analysis

Chemical composition, %							
N	O	Na	Mg	Al	Si	S	Ca
13.28	50.97	8.29	1.66	3.52	9.30	0.39	12.59

Oxide composition, %						
N_2O	Na_2O	MgO	Al_2O_3	SiO_2	SiO_3	CaO
30.10	12.47	3.20	7.83	23.85	1.20	21.36

Thus, microstructure of the modified AASC is characterized by higher density, uniformity, and consolidation of new hydrate formations with a high degree of crystallization.

6. Discussion of results obtained from studying the effect of complex organo-mineral admixtures on proper deformations in AAC

Ways were offered and regularities revealed for effective regulation of proper deformations in AAC at variation of GBS content from 0 to 100 %.

It was shown that the types of AAC that are diametrically opposite in content of slag (AAPC and AASC) are characterized by different kinetics of structure formation, phase composition of hydrate products and morphology of new formations. These differences determined different properties of these cements and required different approaches to regulate their proper deformations without adverse effect on their physical and mechanical properties.

For example, shrinkage of the “clinker–SM” system with SM content of 10.26 % of clinker weight (3.00 % Na_2O) was 0.406 mm/m (Fig. 1). In this case, AAPC is characterized by too short setting time: the initial setting 5 min and the end setting 7 min. Such short setting times lead to formation of imperfect initial structure of artificial stone. Composition of new hydrate formations of APS is represented mainly by gel-like hydrate formations resulting in a nucleus of crystalline phase on the gel surface.

Growth of GBS content in AAC composition from 0 to 100 % and, accordingly, alkaline component from 3.00 to 3.91 % for Na_2O determined satisfactory setting times AASC of the “GBS–SM” system: the initial setting 45 min and the end setting 60 min. In this case, growth of cement proper deformations was observed. For example, shrinkage of AASC of the control system was 0.984 mm/m (Fig. 6). Higher values of AASC shrinkage were found by higher content of gel-like formations in composition of the hydra-tion products in comparison with AAPC.

Complex organic-mineral admixtures based on the “salt electrolyte–surfactant” system have been proposed to regulate proper deformations of AAC. Positive effect of complex admixtures on reduction of shrinkage was determined by a decrease in water content (water-reducing effect) and an increase in the degree of crystallization of new formations (Fig. 2).

For example, when using a complex admixture based on $NaNO_3$ for modification of AAPC, a decrease in W/C from 0.34 to 0.29 led to an increase in strength of AAPC compared with the control composition: from 30.3 to 39.3 MPa (2 days), from 37.3 to 48.7 MPa (7 days), from 43.5 to 53.1 MPa (28 days).

By means of methods of physico-chemical analysis, the degree of crystallization of artificial stone of AAPC was raised when using complex admixtures based on Na_2SO_4 and $NaNO_3$ during formation of lamellar crystalline structures of minamite $(Na,Ca_{0.5})Al_3(SO_4)_2(OH)_6$ (Fig. 4, *a*) and calcium hydronitroaluminate $3CaO \cdot A1_2O_3 \cdot Ca(NO_3)_2 \cdot 10H_2O$ (Fig. 5, *a*), respectively. Expansion of AAPC to 0.062 mm/m when using admixture “Na_2SO_4–SLS–SG” and a slight shrinkage of 0.017 mm/m when using the admixture “$NaNO_3$–SLS–SG” (Fig. 1) was the combined effect of action of organo-mineral complex admixtures. In this case, modification of AAPC with complex admixtures based on Na_2SO_4 and $NaNO_3$ led to a longer the initial setting from 5 to 30 and 37 min, respectively, and to the end setting from 7 to 35 and 44 min, respectively.

The results obtained have allowed us to propose complex organo-mineral admixtures using clinker as expanding admixture for modification of AASC of the “GBS–SM” system with providing water-reducing effect and intensification of crystallization processes and, accordingly, reducing the gel phase content.

According to the study results, the greatest influence on reduction of AASC shrinkage was exerted by admixture of “clinker–$NaNO_3$–SLS–SG” composition. Reduction of shrinkage deformations was determined by reduction of W/C (from 0.29 to 0.26) and formation of globular formations of sodium hydroalumosilicates of gmelinite type $((Na_2Ca) \cdot Al_2Si_4 \cdot O_{12} \cdot 6H_2O)$ (Fig. 7) in the composition of hydrate products along with calcium hydrosilicates of low basicity. In this case, an increase in density, uniformity and consolidation of the artificial stone structure and reduction of content of the gel phase was observed. The use of a complex admixture has made it possible to reduce AASC shrinkage from 0.984 to 0.683 mm/m (Fig. 6) with a slight extension of hardening time: the initial setting from 45 to 60 and the end setting from 60 to 75 min. Reduction of W/C and intensification of crystallization processes through the use of complex admixtures have led to an increase in AASC strength compared to the control composition (without admixtures). For example, strength increased from 28.8 to 34.4 MPa, from 40.0 to 45.3 MPa and from 50.3 to 56.9 MPa on day 2, 7, and 28, respectively.

Hence, when GBS varied from 0 to 100 % (of weight of the aluminosilicate component), modification of AAC with organo-mineral complex admixtures of the developed compositions made it possible to reduce deformation shrinkage. Such changes are determined by influence of above admixtures on the degree of crystallization of new hydrate formations and their morphology while reducing water content in artificial stone. It should be noted that the use of complex admixtures of the salt electrolyte-surfactant system can significantly reduce AAPC shrinkage. Modification of AASC with admixtures of “clinker–salt electrolyte–surfactant” system also led to reduction of shrinkage deformation, but these variations were smaller compared to those of AAPC. This was determined by lower content of gel phase in the structure of artificial AAPC stone as well as formation in this case of new hydrate formations with a distinct crystalline structure (minamiite, calcium hydronitroaluminate). Instead, structure of AASC modified with complex admixture “clinker–$NaNO_3$–SLS–SG” was characterized by a high content of gel phase, even with growth of crystallization degree due to formation of gmelinite crystals. Thus, increase in GBS content in AAC makes it difficult to reduce shrinkage deformation in cement.

Thus, regularities of influence of complex organo-mineral admixtures on the processes of structure formation and AAC properties with GBS content from 0 to 100 % were revealed. Effective ways of regulating proper deformations of such cements by varying phase composition of new hydrate formations, their morphology and the degree of crystallization using the proposed complex admixtures were proposed. The obtained patterns can be used in development of materials for various functional purposes (concretes, mortars, dry building mixes) when optimizing content and composition of complex organo-mineral admixtures.

7. Conclusions

1. It was established that admixtures of “Na_2SO_4–SLS–SG” and “$NaNO_3$–SLS–SG” compositions are the most effective from the point of view of their influence on properties of AAPC of the “clinker–SM” system. It has been shown that modification of AAPC with a complex admixture of the “salt electrolyte–surfactant” system based on $NaNO_3$ reduces cement shrinkage from 0.406 to 0.017 mm/m. The use of an admixture based on Na_2SO_4 brought about expansion effect on AAPC measuring 0.062 mm/m. In addition, the use of a complex admixture based on Na_2SO_4 provided extension of the hardening period of unmodified AAPC: the initial setting from 5 to 30 min and the end setting from 3 to 35 min. Replacement of Na_2SO_4 with $NaNO_3$ in composition of a complex admixture provides an additional increase in the hardening time of AAPC: the initial setting – up to 37 min and the end setting – up to 44 min. Accelerated growth of AAPC strength by reducing the W/C ratio (water-reducing effect of surfactants) and increasing the degree of crystallization of new formations was also observed.

2. It was found that the effect of compensated shrinkage in AAPC when using complex admixtures was provided by raising the degree of crystallization of hydrosilicate components in the structure of artificial stone. In addition, formation of additional phases with a distinct crystalline structure was observed in hydrated cement systems. For example, formation of sulfate-containing sodium-calcium hydroaluminate and calcium hydronitroaluminate in composition of the products of AAPC hydration was observed when using complex admixtures based on Na_2SO_4 and $NaNO_3$, respectively. Additional crystalline phases created stresses in the interfacial space of new hydrate formations which reduced AAPC shrinkage.

3. It was shown that the use of complex “clinker–Na_2SO_4–SLS–SG” and “clinker–$NaNO_3$–SLS–SG” admixtures provided reduction of AASC shrinkage from 0.984 to 0.810 and 0.683 mm/m, respectively. In addition, a complex admixture based on Na_2SO_4 provided extension of the AASCs initial setting from 45 to 60 min and the end setting from 60 to 75 min. Replacement of Na_2SO_4 with $NaNO_3$ in composition of a complex admixture provided the cement with the initial setting 65 min and the end setting 83 min. The use of complex admixtures provided a water-reducing effect and intensifica-

tion of crystallization processes which caused an increase in strength characteristics of AASC. Complex admixture of "clinker–$NaNO_3$–SLS–SG" composition had the strongest effect on AASC properties.

4. Reduction of shrinkage deformation in AASC when using a complex admixture based on $NaNO_3$ was attained by increasing density, uniformity, and consolidation of hydrosilicate formations. Formation of hydroalumosilicate structures of different morphologies with inclusion of nitrate anions further contributed to the effect of compensated shrinkage.

5. Approaches to regulation of proper deformations of AAC were proposed and different efficiency of complex organo-mineral admixtures of the "clinker–salt electrolyte–surfactant" system depending on GBS content in the cement composition was shown. Increase in GBS content in AAC composition brought about a greater content of gel phase during hydration which required greater efficiency of the complex admixture to counteract shrinkage deformation in the AAC. In other words, an increase in GBS content in AAC has made it difficult to regulate proper deformations. For example, AAPC (0 % GBS) featured expansion (0.062 mm/m) when using an admixture based on Na_2SO_4 and a slight shrinkage (0.017 mm/m) when using an admixture based on $NaNO_3$. In this case, modification of AASC (100 % GBS) with an admixture of "clinker–$NaNO_3$–SLS–SG" composition determined reduction of shrinkage from 0.984 to 0.683 mm/m. Reduction of shrinkage deformations in AAC under influence of complex admixtures was determined in a general case by their water-reducing effect, intensification of crystallization processes and change of morphology and composition of hydrate phases in artificial stone.

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