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COMPARISON OF INFLUENCE OF SURFACTANTS ON THERMOKINETIC CHARACTERISTICS OF ALKALI-ACTIVATED SLAG CEMENT

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Increasing the durability of concrete and reinforced concrete structures according to the criterion of crack resistance is a relevant task of construction materials science. To solve this task, this paper proposes effective solutions for adjusting thermofinite characteristics of alkali-activated slag cement (ASC) by using surfactants of various chemical nature in order to control the thermally-stressed state of concrete based on it (ASC concrete).

The method of calorimetry was applied to show that the problematic issue is to adjust the structure formation of ASC by anion-active surface-active substances based on complex polyesters. This is predetermined by the instability of the molecular structure of surfactants in the hydration environment of ASC due to the destruction of complex ester bonds as a result of alkaline hydrolysis.

Thermokinetic analysis has demonstrated the effectiveness of using anion-active surfactants, which do not contain ester bonds, as regulators of crack resistance of ASC concrete. Simple polyesters and multi-atom alcohols provide the ability to adjust the duration of the induction period while ensuring the required completeness of ASC hydration within a time frame. The effectiveness of cation-active surface-active substances has been shown, which are characterized by the stability of the molecular structure in the hydration environment of ASC and an increased level of adsorbing capacity.

The decrease in the effectiveness of surface-active substances has been shown, in terms of the effect on the heat release of ASC, in the following series: alkaline salt of carboxylic acid>salt of the quaternary ammonium com pound>simple polyester>polyalcohol>complex polyester.

The reported results are important in view of the possibility of effective adjustment of ASC heat release by influencing the structure formation of surfactant with a certain molecular arrangement in order to predictably reduce crack formation in a thermally-stressed state and a corresponding increase in the durability of structures

Keywords: alkali-activated slag cement, surfactant, crack resistance, heat release of cement slurry, thermally-stressed state

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1. Introduction

Increasing the durability of building structures is a relevant global trend in modern materials science. Numerous studies on improving the durability of brick [1], steel [2], wooden [3], concrete [4], reinforced concrete [5] structures, etc. are a confirmation of this trend. Depending on the purpose and operating conditions of concrete and reinforced concrete structures, the properties of concrete, which are the most important in a particular case, are defined as criteria for assessing durability. These properties include frost resistance, resistance against penetration into the concrete of aggressive media (concrete density), resistance to atmospheric influences, crack resistance under thermal and mechanical loads, carbonation resistance, resistance against biological influences, etc. Crack resistance caused by the thermally-stressed state of concrete is an important criterion for assessing the durability of massive concrete and reinforced concrete structures. The thermally-stressed state caused by a temperature gradient between the nucleus and the surface zone of such structures can cause cracking [6]. In turn, the appearance of cracks can lead to a decrease in water resistance and frost resistance as criteria for durability [7]. In reinforced concrete structures, these phenomena can initiate corrosion of steel reinforcement [8].

One of the ways to control the thermally-stressed state and, accordingly, the crack resistance of concrete is the use of types of cement with low heat release during hydration [9]. In this context, the introduction of alkali-activated slag cement (ASC) in massive concrete and reinforced concrete structures is promising. In the ecological aspect, the advantages of ASC over Portland cement are predetermined by a decrease in CO_2 emission due to the use of by-products and production waste as ingredients [10]. It should be noted that ASC materials are characterized by increased corrosion resistance [11], sulfate resistance [12], and frost resistance [13], which can be considered as criteria for durability under different operating conditions. Another feature of ASC is low exoteria. This actualizes the use of ASC, including as the basis of concrete for massive structures of increased durability.

Thus, the issue related to ensuring the durability of massive concrete and reinforced concrete structures necessitates the search for effective solutions aimed to control the heat release by ASC to further handle the thermally-stressed state of concrete as a factor of crack resistance.

2. Literature review and problem statement

Known ways to reduce the heat release by regular Portland cement are the use of mineral admixtures and chemical additives, as well as their combinations [14]. Several works show the effectiveness of mineral additives as heat release regulators, for example, blast furnace granulated slag (FGS) [15]. The effectiveness of the flue ash additive is shown in [16] to reduce the heat release by concrete during the construction of a dam. Another paper demonstrates increasing the durability of massive concrete blocks by reducing heat release when replacing part of cement with the addition of micro silica [17]. The effectiveness of multicomponent Portland cement containing several mineral supplements, for example, FGS, zeolite, and limestone, has been determined. It has been shown that the combination of such additives in Portland cement provides an increase in a series of properties, including a decrease in exoteria during hydration [18]. However, since the alumosilicate component of mineral supplements is the basic ingredient in ASC, their use to adjust heat release cannot be considered.

An alternative way to control cement heat release is to use surface-active substances (SAS) as modifying additives. However, most SAS traditional for conventional clinker cement are ineffective in the hydration environment of ASC. The principles of informed choice of surface-active substances for various functional purposes are proposed. For example, [19] reports the criteria for SAS effectiveness with plasticizing effect in order to modify alkaline systems. The effectiveness of additives for adjusting the deformations of alkaline cement shrinkage obtained by combining SAS and strong acid salts is shown in [20]. According to the same principle of combining surface-active substances, salts-electrolytes, and mineral additives, multicomponent expansion additives [21] for alkaline systems were obtained.

Additives based on polycarboxylate and polyacrylate esters (complex polyesters) are high-molecular anion SAS, which are most effective in the Portland cement concretes and mortars due to the controlled change in both working properties and the heat of hydration [22]. However, the effectiveness of these additives is significantly reduced in ASC. First, this is explained by the destruction of the molecular structure in the hydration medium due to alkaline hydrolysis [19]. That predetermines the expediency of using SAS without complex ester bonds to modify ASC. Second, there is a decrease in the adsorbing capacity of anionic SAS by reducing the surface charge of mineral particles of cement with an increase in the content of the slag component [23]. This creates the prospect of using cation-active SAS to replace anion-active ones.

The above predetermines the expediency of modifying ASC with high-molecular non-ionogenic SAS represented by simple polyesters (polyethylene glycol $HO-[CH_2-CH_2-O]_n-H$ [24], polypropylene glycol $HO-[CH_2-CH(CH_3)-O]_n-H$ [25], etc.) due to the absence of complex-ester bonds. The interesting effects of such additives are not only plasticizing but also slowing down the process of structural formation of ASC at the initial stage of hydration, accompanied by a decrease in heat release [26]. However, simple polyesters, like non-ionogenic surface-active substances, are not characterized by sufficient adsorbing capacity. That predetermines the expediency of using such SAS along with ionogenic, which are adsorbed due to the presence of hydrophilic (polar) atomic groups on the surface of mineral particles of cement [27]. The properties of ionogenic and non-ionogenic SAS can be combined both as part of complex additives and in specially synthesized products with the combination of electrostatic and steric mechanisms of plasticization [28]. These effects lead to the prospect of using such complex additives to control the crack resistance of massive concrete and reinforced concrete structures made from highly mobile mixtures based on ASC [29].

It is known that multi-atom alcohols (polyalcohol, polyols) are ionogenic (anion-active) low molecular surface-active substances, which are characterized in alkaline (alkaline-activated) binding systems by the effects of plasticization, preservation of consistency over time, slowing down the hardening. The effectiveness of polyalcohols in ASC materials is due to the absence of complex ester bonds and depends on the number of hydroxyl groups in the alcohol molecule and the molecular weight of alcohol [19]. The effectiveness of using multi-atom alcohols as ASC modifiers is shown in work [30]. These properties make it possible to apply multi-atom alcohols to control the crack resistance of ASC concrete by reducing the heat release by ASC during hydration.

Anion-active low molecular SAS also include gluconic acid salt (sodium gluconate), which is known as an effective admixture to ASC according to the criteria of plasticization and slowing down the change in the consistency of cement paste [19]. However, that additive is characterized by a significant slowdown in the processes of early structural formation of ASC, which is accompanied not only by a decrease in the heat release during hydration but also a significant decrease in the strength of artificial stone [31]. This determines the limited effectiveness of such surface-active substance [32].

Among high molecular SAS with a positive charge of polar groups (anion-active), the effectiveness of additives based on sodium salts of lignosulfonate acids – sodium lignosulfonate (LST) [33] is known. LST is characterized by a plasticizing effect, as well as a slowing influence on the early structure formation of alkaline cement [34], which makes it possible to predict an increase in crack resistance due to a decrease in heat release. At the same time, the effectiveness of such a surface-active substance is due to the affinity of the cationic component of its polar groups with the cation of the alkaline component of cement [33]. The greatest efficiency of LST is achieved in joint use with hydrophobic surface-active substance based on polyorganohydridosiloxane [19]. Polyorganohydrosiloxanes are organosilicon polymers that are injected in order to intensify milled aluminosilicate components and preserve the properties of alkaline types of cement [35]. At the same time, polyorganohydridosiloxanes (HS) work according to the mechanism of a non-ionogenic surfactant, which partially blocks positively charged centers on the surface of cement particles and shows a weak plasticizing effect [19].

It should be noted that the slowing effect of LST on the development of ASC structure formation may be accompanied by a drop in strength, especially early. This limits the effectiveness of LST as a modifying additive and predetermines the expediency of using the "HS–LST–non-ionogenic surfactant" system when optimizing the composition.

The effectiveness of the use of cation-active SAS (whose molecules dissociate in an aqueous solution with the formation of a positively charged surface-active ion) as modifying additives in the presence of the "HS-LST" system has been shown in [36]. This predetermines an increase in the level of adsorption capacity of SAS at the solid and liquid phase interface while reducing positive, or increasing negative, values of the zeta-potential of cement particles surface (with an increase in the content of FGS). The above determines the feasibility of using a cation-active surfactant in combination with anionic SAS (HS and LST) to control the heat release by ASC.

Thus, the generalization of the above results allows us to predict the effectiveness of controlling the heat release by ASC by influencing the early structure formation using a SAS system to reduce crack formation in the thermally-stressed state and the corresponding increase in the durability of structures. It is the use of complex additives that makes it possible to enhance the individual impact of each surfactant on the structure formation of ASC towards reducing heat release. For our research, the method of calorimetric analysis was chosen, which makes it possible to sufficiently characterize the initial processes of structure formation from the point of their manufacturability, evolution, and the nature of the stressed-strained state of hardening systems [37]. Owing to the accepted criteria, the calorimetry method makes it possible, at the phenomenological level (comparative characteristic), to evaluate the effectiveness of additives of different chemical nature due to compatibility with cement [38].

3. The aim and objectives of the study

The purpose of this study is to determine the effect of the chemical nature of SAS on the thermokinetic characteristics of ASC during hydration. This will make it possible to control the crack resistance of ASC concrete in massive construction structures.

To accomplish the aim, the following tasks have been set:

– to make an informed choice of surface-active substances to control the heat release by ASC slurry;

– to evaluate with the help of thermokinetic criteria the influence of SAS on the structure formation of ASC;

– to determine with the help of thermokinetic analysis those surface-active substances that are effective in controlling the kinetics of heat release in massive concrete and reinforced concrete structures.

4. The study materials and methods

4. 1. Raw materials

FGS manufactured at Public corporation "MMK im. Illicha" (Mariupol, Ukraine) was used as an alumosilicate component of ASC (CaO – 47.30 %; SiO_2 – 39.00 %; Al_2O_3 – 5.90 %; Fe_2O_3 – 0.30 %; MgO – 5.82 %; SO_3 – 1.50 %; TiO_2 – 0.31 %) according to DSTU B V.2.7-302:2014; specific surface, S_{surf}=450 m^2/kg (by Blaine); the module of basicity, Mo=1.11; glass phase content, 84.0 %.

The following alkaline components of ASC were used:

– soda ash Na_2CO_3 (SA);

– pentahydrate sodium metasilicate ($Na_2SiO_3 \cdot 5H_2O$) (MS).

In our study, the following ASC were used as control compositions:

– based on SA (FGS – 96.20 %, soda ash – 3.80 % (dry substance) or 2.30 % (for Na_2O);

– based on MS (FGS – 95.20 %, sodium metasilicate – 4.80 % (dry substance) or 1.50 % for Na_2O).

As the basic ingredients of the complex additive for the modification of ASC properties, we used SAS in the form of HS additives (the liquid 136-41, according to CAS 63148-57-2) and LST additives (pH≥8.5, according to CAS 8061-51-6).

Aliphatic SAS of the following types were used as surface-active substances, which were added to the basic ingredients of the complex additive:

– JK-04PP made by JIANKAI (China);

– PEG-400 made by Dow Chemical (Germany);

– sorbitol in line with CAS 50-70-4;

– Mapetard SD 2000 made by Mapei (Italy);

– BC-50 in line with CAS 139-07-1.

To model the influence of the chemical nature of SAS (chemical structure) on the thermokinetic characteristics of cement systems, the additives were introduced in the following quantity, % by weight of FGS: HS – 0.06, LST – 1.0, aliphatic SAS of various chemical structure – 0.5.

4. 2. Methods for studying the effectiveness of modifying additives on the properties of alkali-activated slag cement

We prepared cement paste in a mixer of the Hobart type.

The heat of hydration of the cement paste modified by surface-active substance additives was determined using a modified semi-adiabatic method in accordance with the requirements set by DSTU B EN 196-9:2015 [39]. The initial temperature of the ingredients when mixing was (20±1) °C. The frequency of measurements was in the range from 15 s to 5 minutes. At the same time, the water-cement ratio (W/C=0.5) in cement paste was taken constant in terms of the mass of components according to the proposed procedure.

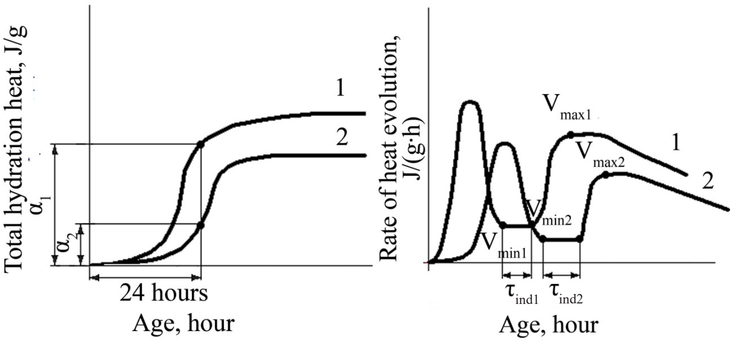
To assess the effect of SAS additives on the structure formation of alkaline types of cement, the following thermokinetic characteristics were adopted [40]:

– the duration of the induction period (τ_{ind}), which is determined as the time during which the rate of heat release, reduced after the first exothermic peak to the minimum value, remains unchanged (Fig. 1, *a*);

– the value of the second exothermic maximum heat release rate, which is defined as the difference between the maximum ($V_{\max}$) and the minimum ($V_{\min}$) values (Fig. 1, *a*);

– degree of hydration (α), which is determined by the value of the integrated heat release over 24 hours (Fig. 1, *b*).

The nature of thermokinetic curves makes it possible to estimate the progress of structural formation of cement systems according to their compliance with classical ideas [37]. The period from the first exothermic maximum, which corresponds to the end of dispersion of the dispersed phase, to the end of the induction period determines the duration of the coagulation structure. At the end of the induction period, the formation of a condensation-crystallization structure based on coagulation begins, accompanied by an increase in the rate of heat release and corresponds to the beginning of cement hardening. The value of the second exothermic maximum heat release rate (Fig. 1, *a*), as well as the completeness (degree) of hydration (Fig. 1, *b*), makes it possible to assess the influence of SAS on the activity in the formation of the initial condensation-crystallization structure.



a *b*

Fig. 1. Thermokinetic dependences of alkali-activated slag cement: *a* – total hydration hea; *b* – rate of heat evolution; 1 – control composition; 2 – modified cement

We estimated the effectiveness of the influence of SAS additives on the processes of structure formation of ASC with the help of known thermokinetic criteria [41]:

– the ratio of the duration of induction periods of modified and control compositions $k_\tau = \dfrac{\tau_{ind2}}{\tau_{ind1}}$ (Fig. 1, *a*);

– the ratio of values of the second exothermic maximum of modified and control compositions $k_v = \dfrac{V_{\max 2} - V_{\min 2}}{V_{\max 1} - V_{\min 1}}$ (Fig. 1, *a*);

– the ratio of degree of hydration of cement of modified and control compositions $k_\alpha = \dfrac{\alpha_2}{\alpha_1}$ (Fig. 1, *b*).

5. Results of the study on determining the influence of surfactants on the heat release by alkali-activated slag cement

5. 1. Substantiation of the choice of surfactants to control the heat release by alkali-activated slag cement

To control the thermokinetic properties, SAS of various chemical natures is proposed.

The anion-active surface-active substance “JK-04PP” based on polycarboxylates (complex polyester) was chosen. Such additives based on complex polyesters are the most effective for systems based on conventional Portland cement. However, in the highly alkaline environment of ASC, these additives undergo the destruction of the molecular structure due to the destruction of complex ester bonds in alkaline hydrolysis, as shown in work [19].

Other anion-active surface-active substances were used in the study as an alternative to additives based on complex polyesters:

– simple polyester – polyethylene glycol $C_{2n}H_{4n+2}O_{n+1}$ (PEG-400);

– hexahydric alcohol – sorbitol $C_6H_{14}O_6$;

– carboxylic acid salt – an additive based on sodium gluconate $NaC_6H_{11}O_7$ (*Mapetard SD 2000*).

The choice of these anion-active aliphatic SAS as effective regulators of heat release is due to their greater stability in the hydration environment of ASC due to the lack of complex ester bonds.

The salt of the quaternary ammonium compound in the form of alkyl benzyl dimethyl ammonium chloride “BC-50” was chosen in the role of a cation-active surface-active substance. FGS as the base of ASC predetermines an increase in the negative values of the zeta potential of the surface of its particles, which defines the effectiveness of the specified additive as a surfactant in a highly alkaline cement medium.

The selected surface-active substances were used in the study as part of a complex additive. As its basis, a carbocyclic anion-active surfactant in the form of LST and non-ionogenic SAS in the form of HS were used. The combination of such surface-active substances as part of a complex additive predetermines the combination of electrostatic and steric plasticization mechanisms, which increases efficiency as a regulator of thermokinetic characteristics.

5. 2. Estimating the influence of surfactants of different chemical nature on the structure formation of alkali-activated slag cement

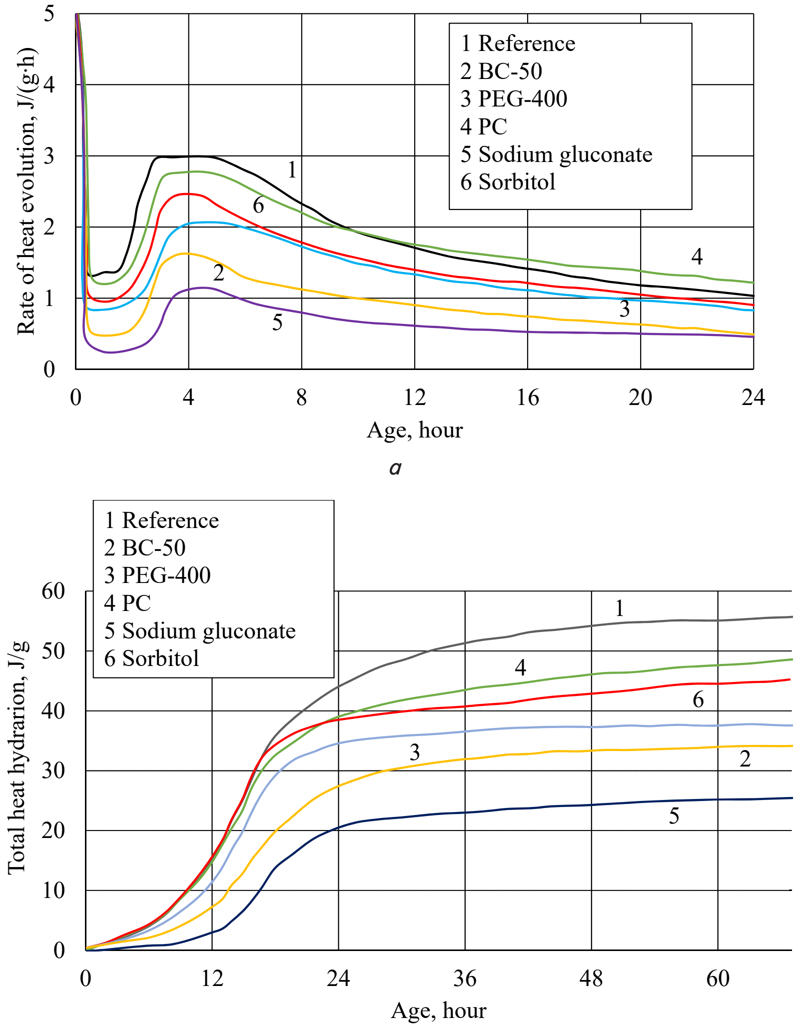
The thermokinetic analysis method was applied to study the influence of SAS of different chemical nature on structure formation towards reducing heat release in order to control the crack resistance of ASC concrete as a factor of durability.

Based on our results, curves of the rate and total hydration heat by ASC during hydration were constructed. In the control composition of ASC based on SA and based on MS, we observed, during 5...7 min, the wetting of the active centers of the dispersed phase; the formation of a coagulation structure begins. The rapid growth and subsequent fall of the heat release rate curve indicate the indicated development of structure formation at the phenomenological level [37]. The duration of the induction period, in this case, is 50 minutes (Fig. 2, *a*) and 35 min (Fig. 3, *a*), respectively. The formation of a condensation-crystallization structure is accompanied by an increase in the rate of heat release. When using SA, the value of the second exothermic maximum is 1.65 J/(g·h) (Fig. 2, *a*), degree of hydration – 46 J/g (Fig. 2, *b*). The thermokinetic criteria in the case of using MS: the value of the second exothermic maximum is 2 J/(g·h) (Fig. 3, *a*), the completeness of hydration – 117 J/g (Fig. 3, *b*). The second exothermic peak is mainly due to condensation of the embryos of low-base calcium hydro silicates [10].

There is a lack of compatibility of complex polycarboxylate esters with ASC. This is evidenced by the lack of influence of SAS on the extension of the period of existence of the coagulation structure: $k_\tau \approx 1$ for the ASC based on both SA (Fig. 2, *a*) and MS (Fig. 3, *a*). The slowing effect on the activity of the initial condensation-crystallization structure of cement when using complex polyesters is confirmed by the values of thermokinetic criteria. ASC based on SA is characterized by the values $k_v=0.88$ and $k_\alpha=0.83$ (Fig. 2, *b*); based on MS – $k_v=0.80$ and $k_\alpha=0.89$ (Fig. 3, *b*). Consequently, the effect of complex polyesters on the duration of the induction period, the value of the second exothermic maximum, and the degree of hydration is almost absent. The detected effects are explained by the instability of the molecular structure of SAS in the hydration environment of ASC [19].

The results of the thermal kinetic analysis reveal the absence of the possibility of adjusting the crack resistance of ASC concrete by modifying with SAS with complex ester bonds in the molecular structure.

We have investigated the influence of aliphatic anion-active surface-active substances without complex ester bonds (sodium gluconate, polyethylene glycol, multiatomic alcohol) on thermokinetic dependences in order to identify additives effective for controlling the heat release by ASC.



a

b

Fig. 2. Influence of additives of surfactants of various types on the thermokinetic characteristics of alkali-activated slag cement based on soda ash: *a* — rate of heat evolution; *b* — total hydration heat

The addition of alkaline salt of carboxylic acid (sodium gluconate) is effective for the modification of ASC and provides an increase in the period of existence of the coagulation structure. This is confirmed by an increase in the duration of the induction period from 50 minutes to 110 minutes (k_τ=2.2) when using SA (Fig. 2, *a*). When using MS, the induction period increases from 35 min to 95 min (k_τ=2.7) (Fig. 3, *a*). Other thermokinetic criteria indicate the slowing effect of this type of surface-active substance on the activity of the initial condensation-crystallization structure of ASC. Thus, the values of criteria based on SA are k_v=0.52 and k_α=0.48 (Fig. 2, *b*); based on MS – k_v=0.33 and k_α=0.60 (Fig. 3, *b*). These values of criteria indicate that sodium gluconate provides the greatest prolongation of the duration of the induction period and a decrease in the value of the second exothermic peak relative to the control composition. After the second exothermic maximum, we observe a decrease in the completeness of hydration which is the greatest of all the types of surface-active substances in question. Such an impact on the structure formation of ASC is accompanied by a significant increase in the crack resistance of concrete [42]; however, with a significant decrease in strength [30].

The additive of simple polyester is compatible with ASC, which is confirmed by the nature of the change in thermokinetic indicators. Thus, we registered the extension of the period of existence of the coagulation structure of ASC based on SA and MS as a result of modification using the PEG-400 additive, to 85 minutes (Fig. 2, *a*) and 60 minutes (Fig. 3, *a*), respectively. The surface-active substance has a slowing effect on the formation of the initial condensation-crystallization structure of cement: based on SA – k_v=0.73 and k_α=0.74 (Fig. 2, *b*); based on MS – k_v=0.73 and k_α=0.79 (Fig. 3, *b*). According to the criteria for prolongation of the duration of the induction period, reducing the value of the second exothermic maximum and the development (completeness) of hydration, the use of a surface-active substance as part of a complex additive is advisable for adjusting the crack resistance of ASC concrete.

Compatible with ASC is a surface-active substance in the form of *multi-atom alcohol*, the use of which prolongs the period of existence of the coagulation structure, the induction period changes from 50 min to 65 min (k_τ=1.30) when using SA (Fig. 2, *a*), and from 35 min to 44 min (k_τ=1.25) when using MS (Fig. 3, *a*). The surface-active substance has little impact on the slowdown of the initial condensation-crystallization structure of cement. Thus, the structure formation of ASC slurry is characterized by the following values of thermokinetic criteria: k_v=0.85, k_α=0.78 when using SA (Fig. 2, *b*), and k_v=0.80, k_α=0.85 (Fig. 3, *b*) when using MS. Changes in thermokinetic characteristics (extension of the induction period, reduction of the second exothermic maximum, and increase in degree of hydration values) indicate the possibility of controlling the crack resistance of ASC concrete by using a surface-active substance additive of this type.

The above values of the criteria k_τ, k_v, and k_α confirm the results on the stability of the molecular structure of surface-active substances without complex ester bonds in the hydration environment of ASC, obtained by the methods of physicochemical analysis [19]. Data on the effectiveness of the use of multi-atom alcohols as modifiers of ASC materials also complement the conclusions on the influence of SAS on the structure formation of ASC, obtained by the method of plastometry [30].

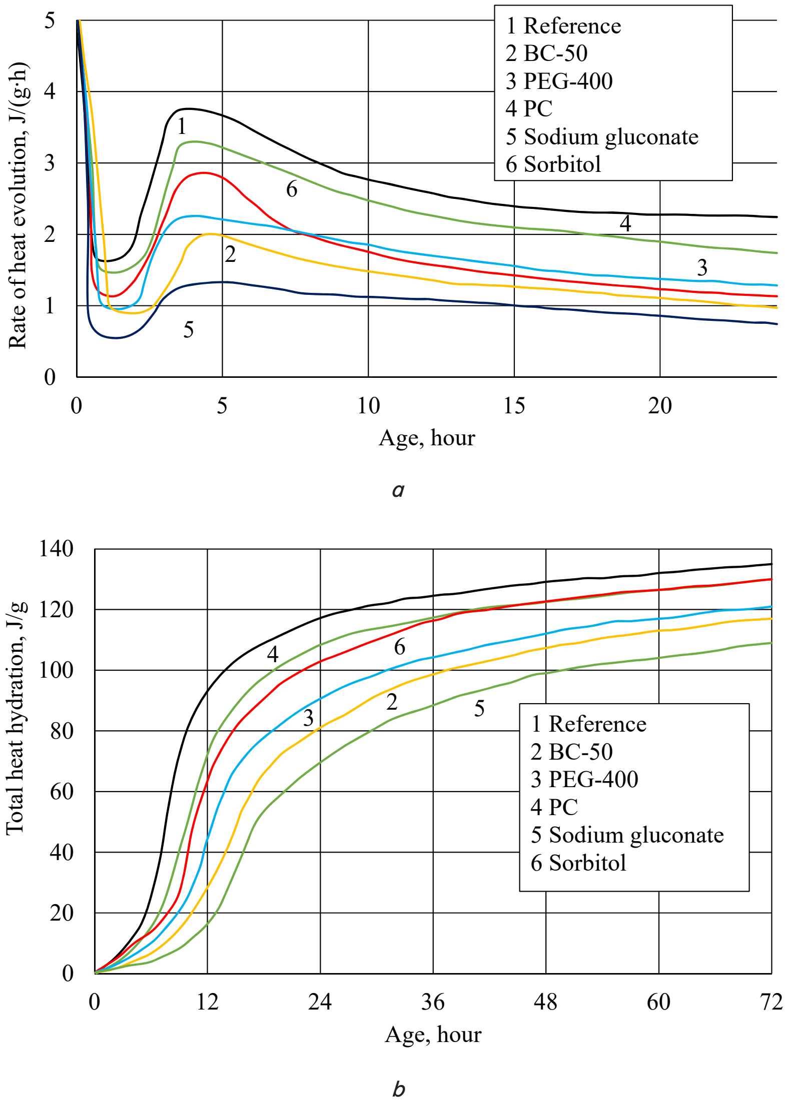


Fig. 3. Influence of additives of surfactants of different types on the thermokinetic characteristics of alkali-activated slag cement based on sodium metasilicate: *a* — heat release rate; *b* — completeness of heat release

Compatibility with ASC is also characteristic of the cation-active surfactant in the form of a salt of the quaternary ammonium compound. The surface-active substance of this type ensures prolongation of the period of existence of the coagulation structure. This is confirmed by an increase in the duration of the induction period to 105 minutes (k_τ=2.10) (Fig. 2, *a*) and to 70 minutes (k_τ=2.00) when using SA and MS (Fig. 3, *a*). The effect on the activity of the initial condensation-crystallization structure of ASC based on SA and MS is determined by the values of the criteria k_v=0.67 and k_α=0.59 (Fig. 2, *b*) and k_v=0.80 and k_α=0.68 (Fig. 3, *b*), respectively. Our results complement the data on the effectiveness of the use of cation-active SAS for ASC modification [19].

5. 3. Determining the effectiveness of surfactants for adjusting thermokinetic characteristics

Based on the results of thermal kinetic analysis, we determined the series of surface-active substances' efficiency in the composition of the complex additive in terms of the effect on the kinetics of the structure formation of ASC in order to control the thermally-strained state as a factor of crack resistance and, accordingly, the durability of ASC concrete. The main ingredients in the form of HS and LST are considered as the base for such complex additives.

The influence of SAS on the development of the coagulation structure is estimated by the duration of the induction period. The effect (positive) of stabilization of the development of the coagulation structure of ASC for additives is reduced in the following series: alkaline salt of carboxylic acid>salt of the quaternary ammonium compound>simple polyester>polyalcohol>polyester.

The influence of SAS on the development of condensation-crystallization structure is estimated by the value of the second exothermic maximum after the end of the induction period and the degree of hydration. The (negative) effect of the slowdown in the development of the condensation-crystallization structure for SAS additives is reduced in the following order: alkaline salt of carboxylic acid>salt of the quaternary ammonium compound>simple polyester>polyalcohol>polyester.

The resulting efficiency series make it possible to recommend SAS to adjust the crack resistance of ASC concrete. Patterns of changes in the efficiency of surface-active substances by their effect exerted on the heat release by ASC slurry confirm the earlier obtained data on the effect exerted on the initial plastic strength of ASC slurry [30], the strength properties, and the deformation of shrinkage of ASC concrete [34].

6. Discussion of results of studying the influence of surfactants on the heat release by alkali-activated slag cement

We have determined the series of surface-active substance efficiency by the impact on the heat release by ASC, as the base for massive concrete and reinforced concrete structures, while generalizing the efficiency series of additives based on the influence exerted on the kinetics of the structure formation of ASC. The SAS effectiveness decreases in the following series: alkaline salt of carboxylic acid>salt of the quaternary ammonium compound >simple polyester>polyalcohol>polyester.

According to the derived series of SAS effectiveness, the additives based on complex polyesters do not make it possible to control the structure-formation of ASC. The negative impact of complex polyesters on the development of both coagulation ($k_\tau\approx1.00$) and condensation-crystallization structures of ASC (k_v is within 0.80–0.88, k_α – within 0.83–0.89) (Curve 4, Fig. 2, 3) was registered. The inefficiency of complex polyesters is explained by the instability of the molecular structure of complex polyester in the hydration environment of ASC, as shown in work [19]. The destruction of the molecular structure of SAS predetermines the uncontrolled hardening of cement, and the resulting products of alkaline hydrolysis slow down the acquisition of strength. It is possible to predict greater destruction of the molecular structure of complex polyesters, observed in the MS environment compared to SA, which is due to the higher values of the pH of the hydration environment [43]. Another factor that determines the decrease in the effectiveness of SAS in the ASC medium is the nature of the alkaline component, that is, its anion component. This is due to the restriction of adsorption of hydrophilic groups of surface-active substances by ASC mineral particles due to “competition” not only with hydroxyl groups but also with anions of silicic acid SiO_3^{2-} [44]. With the valence of the SAS anion smaller than “–2”, its adsorption would be limited when using an alkaline component in the form of MS.

Complex additives containing aliphatic anion-active SAS (simple polyester, sodium gluconate, multiatom alcohol) have been proposed to control the heat release by ASC. The effectiveness of the selected additives is explained by the stability of these types of the molecular structure of SAS [19]. However, it is necessary, in this case, to take into consideration the peculiarities of the influence of each of these additives on the evolution of the coagulation and condensation-crystallization structures of ASC according to the derived efficiency series. Thus, the addition of sodium gluconate significantly slows down the processes of early structure formation (k_τ is within 2.2–2.7, k_v – within 0.33–0.52, k_α – within 0.48–0.60) (Curve 5, Fig. 2, 3). The above effect of the additive on the structure formation of ASC predetermines the low values of the strength of artificial stone [30]. The specified property limits the use of this type of SAS and requires content optimization, or use along with additives that increase the strength of concrete [34].

The complex additives containing simple polyesters and multi-atom alcohols are also characterized by a stable molecular structure in the hydration environment of ASC and may be recommended to control heat release. These additives provide a positive effect on the development of condensation-crystallization structure with a slowing effect on the evolution of the coagulation structure. The effect of additives is confirmed by the values of thermokinetic criteria (k_τ is within 1.25–1.71, k_v – within 0.73–0.88, k_α – within 0.74–0.79) (Curves 3, 6, Fig. 2, 3).

The derived efficiency series also predetermine the effectiveness of complex additives based on cation-active surface-active substances as regulators of ASC heat release. These SAS are characterized by a stable molecular structure in the hydration environment of ASC [19]. The effectiveness of cation-active surface-active substances is also caused by an increase in the adsorption level of these SAS, the charge of polar groups of which is opposite to the charge of mineral particles of ASC [36]. The analysis of the results indicates the effectiveness of cation-active SAS in view of the development of structure formation processes (k_τ is within 2.00–2.10, k_v – within 0.67–0.80, k_α – within 0.59–0.68) (Curve 2, Fig. 2, 3). This predetermines the advantages of using such SAS to adjust the thermally-strained state of ASC concrete in order to reduce crack resistance.

The results of studying the processes of early ASC structure formation, reported in this work, correlate with the data given in [38]. Unlike available research, a given work aims to determine the possibility to manage the structure formation of ASC according to the criteria of heat release by modifying SAS differentiated by chemical nature. The comparative characteristics of the effectiveness of surface-active substances of different chemical nature, determined by the calorimetric method, in terms of the influence on the processes of structure formation make it possible to recommend them as components of complex additives for controlling the crack resistance of ASC concrete in the thermally-stressed state. Solutions on the informed choice of the chemical nature of SAS to reduce the crack formation of concrete in the thermally-stressed state could increase the durability of massive concrete and reinforced concrete structures.

The peculiarity of the semi-adiabatic method of calorimetry used in this study is that the insulation of the heat meter allows heat loss from the sample. Alternative methods of thermokinetic analysis are adiabatic, isothermal, and liquid. The most relevant are the methods of isothermal and adiabatic calorimetry. The advantages of the semi-adiabatic method are relative simplicity and the possibility of application for large samples. The limitations of this method include forecasting the development of cement structure formation based on data on heat release during the short study period (2–3 days). Taking into consideration the above, the use of the method of semi-adiabatic calorimetry is advisable to obtain a comparative characteristic between the samples.

The prospects of calorimetric research methods refer to the possibility of applying in conjunction with other methods for the comparative assessment of the influence of surface-active substances on the structure formation of cement. Patterns of changes in heat release in conjunction with the patterns of changes in the plastic strength of cement paste, the time of hardening, and the strength of cement provide grounds for a reasonable choice of SAS for managing the processes of ASC structure formation and controlling the properties of ASC concrete.

7. Conclusions

1. We have shown the possibility of adjusting the thermokinetic characteristics of ASC by using SAS of a certain molecular structure. Effective in the role of regulators are the additives of anion-active surface-active substances, deprived of the complex ester bond, in the form of sodium simple polyesters and polyalcohols. The sodium salt of carboxylic acid is effective in joint use with additives that increase the strength of concrete. The effectiveness has been shown in ASC in terms of the influence exerted on the reduction of heat release by cation-active surface-active substances in the form of a salt of the quaternary ammonium compound. Controlling the ASC exothermia during hydration by the specified types of SAS in conjunction with LST and HS provides an opportunity for managing crack resistance in the thermally-stressed state and a corresponding increase in the durability of massive concrete and reinforced concrete structures.

2. The thermokinetic analysis has revealed the influence of the chemical nature of SAS on the processes of ASC structure formation. We have determined the thermokinetic characteristics at the following amounts of components of the

complex additive, % by weight of FGS: LST – 0.5, HS – 0.06, aliphatic SAS of various chemical structures – 0.5. Modification of ASC through the use of SAS based on complex polyesters determines the values of thermokinetic criteria $k_\tau \approx 1.00$, k_v – within 0.80–0.88, k_α – within 0.83–0.89. These values of the criteria indicate the loss of stabilizing influence exerted by SAS of this type on the development of coagulation structure with a negative impact on the evolution of condensation-crystallization structure. In contrast, the use of simple polyesters, polyalcohols, salts of the quaternary ammonium compounds ensures a positive effect both on the development of coagulation (k_τ is within 1.25–2.10) and condensation-crystallization structures (k_v is within 0.67–0.85, k_α– 0.59–0.8). The addition of sodium salt of carboxylic acid provides the greatest stabilization of the coagulation structure (k_τ is within 2.20–2.70) with a negative impact on the development of the condensation-crystallization structure (k_v is within 0.33–0.52, k_α – within 0.48–0.60).

3. The effectiveness of SAS as a component of the complex additive of the proposed composition in terms of the effect on the heat release by ASC, as the base for massive concrete and reinforced concrete structures, decreases in the following series: alkaline salt of carboxylic acid>salt of the quaternary ammonium compound>simple polyester>polyalcohol>polyester. The use of simple polyesters, polyalcohols, and salts of the quaternary ammonium compounds as additives would increase the durability of such structures by reducing crack formation caused by thermal processes and corresponding strains.

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