1. Introduction

Classification of chemical admixtures according to the main technological effect makes it possible to conclude that the most common type of regulators are regulators of rheological properties of mortar and concrete mixtures [1, 2], primarily plasticizers and superplasticizers (SP). Admixtures of these types are effective for cements based on Portland cement clinker (PCC) for which they were developed [3, 4]. At the same time, provision of effective plasticization for alkaline cements causes great complexity because of structural changes in chemical admixtures and adsorption [5]. Additional ambiguity in assessment of the admixture effect is associated with a wide range of alkaline cement compositions which are regulated by national standard of Ukraine for their five types [6]. For example, content of PCC can vary from 0 to 100 % and content of alkaline components of diverse types is 1.5 to 12.0 % depending on cement composition (type). Meanwhile, expansion of the application domain of alkaline cements for special concretes causes the need of regulation of rheological properties of the concrete mixture and early concrete structure formation.

2. Literature review and problem statement

Authors of article [7] have shown that effectiveness of influence of plasticizers on rheological parameters of alkaline cement paste depends both on the type and dosage of such admixtures and the composition of cement itself. Authors of the study [8] associate reduction of effectiveness of traditional types of plasticizers in systems featuring high ionic strength with a rivalry in adsorption of anions of such systems and functional groups of admixtures. The procedures used for the study of interaction in the “cement-plasticizer” system apply diverse approaches [9]. However, effectiveness of polymer effects resulting from adsorption can be regulated by changing chemical nature of admixtures: molecular weight, the charge of monomers in the molecular structure, the number of monomers in the main and side chains [10].
The paper [11] indicates necessity of modifying molecular structure of plasticizers taking into account changes in the mechanism of adsorption of such admixtures in an alkaline medium and in their manifestation of dispersing functions in dispersions of alkaline cements. Authors of [10] have noted advantages peculiar to molecular structure of polycarboxylate ethers with side chains and no hydrophilic groups. Moreover, the side chains of such polymers are practically incapable for adsorption, but create a steric hindrance between the adsorbed layers [12].

It was shown in [13] that when using alkaline cement, effectiveness of influence of another type of oxygen-containing organic compounds of fatty series, namely polyatomic alcohols (polyls) on consistency of concrete mixture and strength of concrete depends on the number of hydroxyl groups in alcohol molecules and molecular weight. This is confirmed by the results of studies of the disperse-coagulation structure of alkaline cement paste in terms of plastic strength [14]. Variability of cement formulation at which effectiveness of surface-active substances (SAS) is ensured was shown in [11]. At the same time, there is no systematization of SAS from the point of view of selective action with an account for alkaline cement composition hence determining the nature of processes taking place at an early stage of cement stone structure formation was not disclosed.

It can be concluded that the changes in the structure of plasticizing admixtures which are most effective for clinker cements require a search for organic compounds, which can influence initial structure formation in alkaline cements. At the same time, analysis of the current problem state shows that there is no systematization of SAS from the point of view of selective action with an account for cement composition and the nature of processes taking place at an early stage of cement stone structure formation was not revealed.

3. The aim and objectives of the study

The study goal was to experimentally substantiate effectiveness of SAS in the capacity of plasticizers proceeding from assessment of rheological properties of the alkaline cement paste. As a result, this will make it possible to systematize such admixtures for their application taking into consideration cement composition.

To achieve this goal, it was necessary to solve the following tasks:
- make a reasonable choice of a SAS molecular structure for plasticization of alkaline cements;
- conduct a comparative evaluation of SAS as plasticizing admixtures for modification of alkaline cements when composition changes;
- make a conclusion on advisability of practical use of SAS as chemical admixtures for modification of mortars and concretes based on alkaline cements.

4. Materials and methods used in studying SAS effectiveness proceeding from assessment of rheological properties of the alkaline cement paste

4.1. Raw materials

SAS of the following groups (types) were used for the plasticization of alkaline cements:

1) polyatomic alcohols (polyls), i.e. organic substances containing more than one functional hydroxyl group (–OH) and having the general formula \( \text{C}_n\text{H}_{2n+2}\text{O} \);  
2) polyethers (the products of hydroxyethylation of polyls) i.e. the substances with the general structural formula \((\text{OH}–[\text{R}–\text{O}–\text{CH}_2\text{CH}_2\text{O}]_n\text{H})\);  
3) hydroxyethylated fatty alcohols (products of hydroxyethylation of higher fatty alcohols), i.e. polyhydroxyethylene ethers of alcohols with the general structural formula \((\text{R}–\text{O}–[\text{CH}_2\text{O}]_n\text{H})\);  
4) carboxylic acids, i.e. organic compounds containing one or more functional carboxylic (–COOH) and hydroxyl groups;  
5) salts resulted from the reaction of alkali metal hydroxides with organic acids; carboxylic acids containing a carboxylic group (–COOH) and sulfonic acids containing a sulfonate group (–SO\(_3\)H).

The listed organic compounds belong to the class of acyclic (aliphatic) compounds or to fatty compounds that are either involved in the preparation of plasticizers or are such. Therefore, effectiveness of combining such products for work in an alkaline environment could be assumed.

Among the types of organic compounds under consideration, non-ionic surfactants include products with an extended polar group obtained by hydroxyethylation. In turn, ionic SAS can be referred to both acyclic and carboxylic compounds and can contain polar groups. For example, a lignosulphonate (LST) type admixture which is a compound of a diphylic character with a (–SO\(_3\)Na) functional group can act as such anionic SAS.

As a slag component of alkaline cements, a ground granulated blast furnace slag (GBFS) with a glass phase content of 54.5 %, real density of \( \gamma = 2.88 \text{g/cm}^3 \), activity modulus \( a = 0.15 \) and basicity modulus \( b = 0.15 \) was used. As a component of alkaline cements, PCC was also used with the following chemical composition: 21.3 % SiO\(_2\); 5.9 % Al\(_2\)O\(_3\); 4.6 % Fe\(_2\)O\(_3\); 1.2 % MgO; 64.9 % CaO; 0.31 % K\(_2\)O; 0.86 % SO\(_3\). Technical soda ash (Na\(_2\)CO\(_3\)) and five-water sodium metasilicate (Na\(_2\)SiO\(_3\).5H\(_2\)O) were used as alkaline components of cements.

Cements were prepared by mixing ingredients in a Hobart type blade mixer used in cement tests in accordance with EN 196-1. Dispersity of cements was characterized by a specific surface of 450 m\(^2\)/kg (according to Blaine).

Three types of alkaline cements were considered (Table 1) with GBFS content of 0 % to 100 % slag alkaline cement (type I), alkaline Portland cement (type II) and slag alkaline Portland cement (type IV).

Thus, the content of GBFS was the main factor of variation of the alkaline cement composition hence determining consumption of the alkaline component of diverse natures (Table 2).

The following SAS of the described types were used as modifying chemical admixtures:

1) glycerol (triatomic polyol) and ethylene glycol (diatomic polyol);  
2) polyethylene glycol (polyether);  
3) syntanol and OS-25 preparation (Barva Fine Organic Synthesis Plant JSC, Ukraine), the surfactants based on polyhydroxyethylene glycol ethers of synthetic primary higher fatty alcohols;  
4) salicylic acid (C\(_5\)H\(_3\)(OH)COOH);  
5) admixture based on sodium gluconate: Mapetard SD 2000, Mapei, Italy;  
6) sodium lignosulfonate: LST, Borrespers, Norway.
Table 1

| Cement composition No. | Cement type | GBFS | PCC | Alkaline component | Content, % |
|------------------------|------------|------|-----|-------------------|------------|
| 1                      | II         | 0.0  | 100.0 | –                 | 2.5        |
| 2                      | IV         | 50.0 | 50.0 | 2.5               | 1.5        |
| 2a                     | IV         | 50.0 | 50.0 | 2.5               | 1.5        |
| 3                      | IV         | 50.0 | 50.0 | –                 | 3.0        |
| 4                      | IV         | 69.0 | 31.0 | 3.0               | 1.8        |
| 5                      | IV         | 69.0 | 31.0 | –                 | 3.5        |
| 6                      | IV         | 88.0 | 12.0 | 3.5               | 2.0        |
| 7                      | I          | 100.0| –    | 4.0               | 2.3        |
| 8                      | I          | 100.0| –    | –                 | 5.0        |
| 9                      | I          | 100.0| –    | 4.5               | 2.6        |

Note: Formulations Nos. 2–8 contained sodium lignosulfonate (1 % of cement weight); compositions Nos. 1 and No. 2a contained 9.0 % and 6.5 % CaSO₄·0.5H₂O, respectively.

Table 2

| Cement composition No. (as in Table 1) | Normal consistency, % | Initial setting, hr/min | Compressive strength, MPa, after the setting period, days |
|---------------------------------------|-----------------------|-------------------------|----------------------------------------------------------|
|                                       |                       |                         | 2 | 7 | 28 |
| 1                                     | 26.0                  | 0.30                    | 32.0 | 39.0 | 49.0 |
| 2                                     | 23.0                  | 0.45                    | 21.4 | 30.6 | 39.4 |
| 2a                                    | 24.0                  | 1:10                    | 21.7 | 38.5 | 48.6 |
| 3                                     | 22.0                  | 0.59                    | 23.5 | 34.0 | 41.4 |
| 4                                     | 24.0                  | 0.55                    | 15.1 | 31.3 | 40.2 |
| 5                                     | 23.5                  | 1:08                    | 18.9 | 32.6 | 41.9 |
| 6                                     | 24.5                  | 1:00                    | 6.9  | 26.3 | 38.9 |
| 7                                     | 23.4                  | 0.50                    | 7.2  | 26.9 | 39.5 |
| 8                                     | 23.6                  | 0.55                    | 11.6 | 28.5 | 40.2 |
| 9                                     | 24.9                  | 0.20                    | 10.2 | 24.5 | 40.1 |

Besides, traditional for Portland cement products based on polycarboxylic and polycarboxylate esters (PA and PC types) such as Dynamon SR 2, Vinavil Flux, Mapei, Italy, Stachement 2572, Stachema, Czech Republic and JK-04PP, JANKAI, China, were used. Sodium lignosulfonate was used as a component of the complex admixture (CA) for cements of compositions No. 2...8.

The admixtures were introduced with mixing water in a form of solution, paste (synthanol) and powder (OS-25, LST, JK-04PP, Vinavil Flux).

4.2. Methods for determining the rheological properties of cement testing

Rheological properties of the cement paste were evaluated proceeding from the change in the plastic strength $P_m$ ($10^{-3}$ Pa–1 mPa), which was determined by the formula:

$$P_m = kFh,$$

(1)

where $k$ is a constant depending on the angle at the cone vertex; $F$ is force (load) acting on the cone, $N$; $h$ is the depth of the cone immersion in the cement paste, m.

The plasticizing effect of the admixtures was determined from the initial values of the plastic strength ($P_m$) of the cement paste. At the same time, water content in the cement paste was assumed constant and maintained normal consistency of the paste without admixtures (Table 2).

Preservation of consistency (intensity of structure formation) depending on the nature of the admixtures used was evaluated from the $P_m$ variation with time. Correspondence of the cement paste consistency to normal consistency was ensured by reduction of water consumption when introducing admixtures.

5. Results of studies and discussion of the effects of admixtures on rheology of cement paste

Effectiveness of admixtures action was assessed according to the following criteria: nature of the main active substance of SAS (it was assumed to be the main factor affecting the initial value of plastic strength), duration of the induction period and the $P_m$ value growth rate upon termination of this period.

Analysis of the results is expedient from the position of one of the defining principles of the alkaline cement theory, namely the role of composition in achieving effectiveness of the SAS use, which is predetermined by the choice of cement compositions according to Table 1.

Polymers are advisable for plasticization of the alkaline cement that does not contain GBFS. The plasticizing effect is characterized by a decrease in the initial $P_m$ value from 50 to 10 mPa for PC type admixtures and to 15 mPa for PA type admixtures. Preservation of the plasticizing effect up to 1 hour is due to the gradual dissolution of the relatively low sodium metasilicate content (0.7 % Na₂O) in the alkaline cement composition.

It has been established that polymers exerted a material influence on the cement paste structure formation (Fig. 1, a, b) only to a certain limit of the alkaline component content (GBFS respectively). For example, at 50 % GBFS in the presence of soda ash (1.5 % respective to Na₂O), a decrease in the initial values of $P_m$ from 50 mPa (control composition) to 10–11 mPa was recorded. With an increase in concentration of alkaline component respective to Na₂O to 1.8 % for soda ash and up to 1.0 % for sodium metasilicate (with a GBFS content of 69 %), the initial $P_m$ value increased and was as high as 13-18 mPa. At 88 % GBFS content and growth of the Na₂O content up to 2.3–2.6 % for soda ash and up to 1.5 % for sodium metasilicate, the initial value was $P_m=16–20$ mPa. In addition, formation of the cement paste structure was intensified.

Such admixtures make it possible to extend the induction period of structure formation up to 2 hours with a subsequent intensive growth of the $P_m$ values; this period increased to 2.5 hours with the use of sodium metasilicate.

At a maximum GBFS content (100 %) and corresponding growth of the alkaline component in the cement, initial values of $P_m$ increased to 18–24 mPa (Fig. 1, a, b) and duration of the induction period was reduced to 0.5–1.0 h depending on the kind of anionic part of the alkaline component. Thus, destructive effect of highly alkaline media on SAS based on esters (polymers) associated with hydrolysis has been confirmed.

Polymers, in contrast to the admixtures based on polyes-

...ters in alkaline cement with clinker content of 100 % (com-
position No. 1), do not possess a plasticizing effect which is confirmed by growth of $P_m$ values from 50 to 55 mPa for glycerin (Fig. 2, a) and up to 60 mPa for ethylene glycol (Fig. 2, b).

Fig. 1. The effect of polyester admixtures on the initial plastic strength of cement paste: a – polyacrylate; b – polycarboxylate

The expediency of using admixtures in the form of polyols in CA compositions generally gets higher with an increase in alkaline component in a cement composition. Thus, for systems containing 50 % GBFS and correspondingly 2.5 % soda ash (1.5 % respective to Na$_2$O), application of organic compounds of this type was not yet effective enough in terms of the plasticization effect. The same applies to the influence of polyols on preservation of the cement paste consistency. The use of a semi-aquatic gypsum additive as a setting regulator or replacement of soda ash with sodium metasilicate in the cement composition did not significantly reduce the initial values of $P_m$ or positively affect kinetics of the cement paste structure formation. However, already with a slight increase in the GBFS to 69–88 % and a corresponding increase in component (respective to Na$_2$O) to 1.8–2.0 % for soda and up to 1.0 % for sodium metasilicate, effectiveness of action of polyols in the CA composition increased. This was accompanied by a decrease in the initial values of $P_m$ to 30–32 mPa (i. e., by 36–40 %) and an increase in duration of the induction period to 0.5 h. With an increase in the GBFS content to 100 %, the initial $P_m$ values decreased even more significantly, up to 23 mPa (by 46 %) and duration of the induction period increased to 1 h.

It should be noted that, polyols introduced in the paste of alkaline cement, type I, exhibited a plasticizing effect with no participation of LST which appeared to be higher than that of the latter. With an increase in the number of hydroxyl groups in the polyol molecule and a corresponding increase in its molecular weight, a higher plasticizing effect was obtained which manifested itself by a decrease in the initial $P_m$ values. However, the use of polyols and addition of LST in the complex makes it possible to increase plasticization which was confirmed by a decrease in the $P_m$ values.

Sodium lignosulfonate in type II alkaline cements (composition I) was characterized by a sufficiently high plasticizing effect with a decrease in the initial plastic strength of the cement paste from 50 to 15 mPa. Duration of the induction period was about 1 hour followed by an intensive structure formation.

Polyethers and hydroxyethylated fatty alcohols are characterized by a plasticizing effect in the systems based on alkaline Portland cement. This was evidenced by a 30 % (Fig. 3, a) and a 10 % (Fig. 3, b) decrease in the initial plastic strength of the cement paste, respectively.

Fig. 2. The effect of polyalcohol admixtures on variation of the initial plastic strength of cement paste: a – glycerin; b – ethylene glycol

As opposed to polyesters, effectiveness of polyethers increased with the GBFS content. Polyethers act analogously to polyols. Thus, at 50 % GBFS in the presence of soda ash in the cement composition, introduction of polyethylene glycol precluded effective change of the cement paste consistency or prolongation of the induction period of the structure for-
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Effectiveness of the polyethylene glycol admixture increased with an increase in the GBFS content to 69 %. Thus, initial $P_m$ values decreased from 50 mPa for the control composition to 32–35 mPa (Fig. 3, a). In this case, the induction period of structure formation was extended to 40 min. When the GBFS content increased to 88 %, the plasticizing effect of the SAS increased, which was indicated by a decrease in the initial plastic strength to 22–4 mPa (by 52–56 %). At the presence of soda ash, this admixture in the CA composition exhibited the greatest plasticizing effect: the initial $P_m$ reached 5 mPa. In this case, the induction period was extended to 2–2.5 hours followed by an intensive increase in the $P_m$ values. When an additional semi-aqueous gypsum was introduced or soda ash was replaced with sodium metasilicate, the induction period could extend to 3 hours.

Thus, the molecular structure of polyethers is more resistant to the action of highly alkaline media including soluble sodium silicates in comparison with polyesters.

Effectiveness of modification of alkaline cements with SAS in the form of hydroxyethylated fatty alcohols in CA also increases in proportion to the content of slag and alkaline components. In general, smaller initial plastic strength of the cement paste makes it possible to extend the induction period. When soda ash is replaced with sodium metasilicate, the admixture effectiveness increases. Modification of alkaline cement with admixtures of this type is effective from the point of view of regulation over a wide range of the induction period duration with a subsequent intensive growth of plastic strength. Even with a minimum consumption of the admixture (0.5 %), the induction period increased to 1–2 hours.

**Carbonic acid** in the CA composition is only effective at a high content of alkaline component. Thus, addition of salicylic acid at an 88 % GBFS content reduces initial $P_m$ value by 50–52 % compared to the control composition (Fig. 5, a).

In this case, duration of the induction period increased to 1.5 h. The increase in content of the alkaline component at a 100 % GBFS content in the cement composition did not exert adverse influence on the admixtures effectiveness.

Sodium salt of carboxylic acid has the greatest effect on the decrease in the initial $P_m$ value and slowing down structure formation in alkaline cements.

The plasticizing effect of adding sodium gluconate in alkaline cements of type II with a maximum (100 %) clinker content (composition No. 1) was confirmed by a decrease in the initial $P_m$ values from 50 to 25 mPa (Fig. 5, b). Besides, the lowest intensity of structure formation of the cement paste was observed. If cement contained 50 % GBFS in the presence of soda ash, this admixture in the CA composition exhibited the greatest plasticizing effect: the initial $P_m$ reached 5 mPa. In this case, the induction period was extended to 2–2.5 hours followed by an intensive increase in the $P_m$ values. When an additional semi-aqueous gypsum was introduced or soda ash was replaced with sodium metasilicate, the induction period could extend to 3 hours.

6. Discussion of the results obtained in the study of effectiveness of SAS as plasticizers

The change in effectiveness of surfactants as plasticizing admixtures reflects general patterns characteristic of the groups (types) of organic substances to which they belong. The obtained regularities extend to cement systems of the wide range of compositions considered. This gives grounds for making practical conclusions about advisability of using such admixtures for the purpose of plasticizing mortar and concrete mixtures based on alkaline cements. In addition, duration of the induction period can be used to judge on the ability of a concrete and mortar mixture to maintain consistency over time.

According to the set of efficiency criteria, admixtures based on sodium lignosulfonate, alkali salt of carboxylic

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**Fig. 4.** Change of the cement paste plastic strength with addition of polyether in time: a — type IV cement (composition 2 in Table 1); b — type I cement (composition 7 in Table 1)

**Fig. 5.** Effect of admixtures of carboxylic acid and sodium salt of carboxylic acid on initial plastic strength of the cement paste: a — salicylic acid; b — sodium gluconate
Acid, polyesters and polyethers are the most promising for controlling structure formation of the type II cements.

The SAS based on polyethers are effective for modification of alkaline cements only up to some limit of slag content and accordingly the content of the alkaline component. When the alkaline component is introduced in a dry form ("cement" technology), its negative effect on the structure of admixtures of PA and PC types shows up only when the cement composition passes from type IV (alkaline slag Portland cement) to type I (slag cement). This is manifested by reduction of the plasticization effect and loss of consistency. In the case of introduction of alkaline component in a form of solution ("concrete" technology), the decrease in effectiveness of these admixtures manifests itself more intensively even with a smaller slag content in the cement.

The alkaline salt of carboxylic acid exhibits a relatively high plasticizing effect, but it adversely affects strength of artificial stone regardless of composition of the alkaline cement.

According to the adopted set of efficiency criteria, admixtures of polyethers, hydroxyethlated fatty alcohols and polyalcohols are the most promising SAS for controlling structure formation of alkaline cements with a maximum slag content (up to 100 %).

7. Conclusions

1. The molecular structure of organic compounds belonging to the class of acyclic (aliphatic) or fatty compounds provides the effect of plasticization of alkaline cements. Stability of the molecular structure of such SAS in an alkaline medium is determined by the absence of bonds characteristic of esters being the main active substances of the most efficient modern plasticizing admixtures for clinker cements.

2. The obtained rheological characteristics of the paste of alkaline cements modified with chemical admixtures has allowed comparative estimation of effectiveness of SAS in such systems.

According to the initial values of plastic strength of the cement paste, the plasticizing effect of SAS decreases in the following order:

- for type II cement (100 % PCC and less than 1.0 % Na₂O): polyester>Na₂sulfonate>alkaline salt of carboxylic acid>polyether>hydroxyethlated fatty alcohol>
- for type IV cement (50 to 69 % GBFS and 1.0 to 1.5 % Na₂O): alkaline salt of carboxylic acid>polyester>polyol;
- for type I cement (88 to 100 % GBFS and more than 1.5 % Na₂O): alkaline salt of carboxylic acid>polyester>hydroxyethlated fatty alcohol>carboxylic acid>

Concerning preservation of the cement paste consistency, the SAS effect decreases in the following order:

- for type II cement: alkaline salt of carboxylic acid>polyester>Na₂sulfonate>hydroxyethlated fatty alcohol>polyether>polyol;
- for type IV cement: alkaline salt of carboxylic acid>polyester>polyether>polyol;
- for type I cement: alkaline salt of carboxylic acid>hydroxyethlated fatty alcohol>polyether>carboxylic acid>polyol>polyester.

Concerning retardation of setting or hardening estimated by the rate of plastic strength of the cement paste, the SAS action is reduced in the following order:

- for type II cement: alkaline salt of carboxylic acid>polyester>hydroxyethlated fatty alcohol>polyol>Na₂sulfonate>polyether;
- for type IV cement: alkaline salt of carboxylic acid>polyether>polyol;
- for type I cement: alkaline salt of carboxylic acid>carboxylic acid>hydroxyethlated fatty alcohol>polyether>polyol>polyester.

3. The revealed regularities can be used in the future practice for development of commercial products based on the organic compounds considered hereinafore in a form of plasticizing admixtures for concretes and mortars.

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EXAMINING THE EFFECT OF ELECTROSYNTHESIS CONDITIONS ON THE Ni–P ALLOY COMPOSITION

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1. Introduction

Alloys are widely used in different sectors of modern industry. Improved physical and mechanical characteristics provide durability and reliability during operation of alloys. Certain alloys possess catalytic and magnetic properties. Properties of alloys are determined by the nature of components and qualitative composition. Alloys of the iron group are characterized by the most varied palette of useful exploitation properties. At various combinations of components such alloys possess high hardness, heat resistance, magnetic, catalytic, anticorrosion properties.

One of the most regulated methods of obtaining alloys with predicted properties is the electrosynthesis. Depending on the requirements to qualitative and quantitative composition of the alloy, the electrolysis is performed from specially selected electrolytes. The content of components in the alloy depends also on the parameters of conducting