

The efficiency of plasticizing surfactants in alkali-activated cement mortars and concretes

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Abstract. Functionality of mortar and concrete mixes is regulated by surfactants, which act as plasticizers. The molecular structure of these admixtures can be changed during hydration of alkali-activated cements (AAC). The objective was to determine the chemical nature of plasticizers effective for property modification of mortars and concretes based on AACs with changing content of granulated blast furnace slag from 0 to 100 %. The admixtures without ester links become more effective than polyesters when content of alkaline component increase. The admixtures effective in high alkaline medium were used in dry mixes for anchoring (consistency of mortar 150 mm by Vicat cone; 1 d tensile strength in bending / compressive strength of mortar 6.6 /30.6 MPa) and in ready-mixed concretes (consistency class changed from S1 to S3, S4 with consistency safety during 60 min; 3 d compressive strength of modified concrete was not less than the reference one without admixtures).

1 Introduction

Application of alkali-activated cements (AAC) allows to provide high quality, functional and durable concretes in the view of efficient use of raw materials and energy. Priority in development of AACs belongs to V.D. Glukhovskiy [1, 2]. His scientific school governed by P.V. Krivenko proposed principles of AAC's compositions [3, 4], with involvement of by-products and industrial wastes as well [5, 6]. The mentioned principles underlay the National standard of Ukraine DSTU B V.2.7-181:2009 [7] for practical application. There are five types of AACs depending on composition (% mass of aluminosilicate components): I – granulated blast-furnace slag (GBFS) (90-100), II – portland cement clinker (100), III – fuel fly-ash or basalt (36-80), IV – GBFS (36-89), V – GBFS and fuel fly-ash in total (90-95). Thus the basic factor of AAC composition can be considered as part of GBFS that can change from 0 % (type II) to 100 % (type I) in aluminosilicate component of cement. Compounds of alkaline metals are considered as AAC structurization components, which contents depend on AAC type. Sodium lignosulphonate (LST) is indispensable component of AAC based on GBFS for ensuring of satisfactory setting time and strength of the cements [7, 8].

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It is necessary in chemical admixtures application to obtain modern concretes and mortars. However modification of AAC by admixtures has certain features connected with risk of their molecular structure degradation in hydration medium of AAC due to alkaline hydrolysis (saponification) [9, 10, 11]. The emergence and speed of this process are determined first of all by AAC's composition including nature (group) of alkaline component [12]. For one's turn the efficiency of surfactants as admixtures is caused by their surface activity, depends on molecular mass and adsorption. Compatibility of AACs with aliphatic organic compounds (polyols, polyesters, ethoxylated fat alcohols, salts of carbon acids etc.) as surfactants with plasticizing effect was demonstrated [13, 14, 15]. Surfactants can be used to ensure low water consumption with decrease in the surface tension of porous fluid. It is known that the latter circumstance facilitates migration of porous fluid, respectively, reducing the capillary stress that causes shrinkage [16]. In turn, shrinkage is considered as one of the criteria for autogenous self-healing of cementitious materials [17]. Control methods for shrinkage of mortars by changing of AAC composition were considered [18]. To ensure the effective influence of plasticizers on fresh and hardened concretes and mortars based on AACs, the investigations in effective surfactant's nature are reasonable.

The purpose of the paper was to determine the substantiate effectiveness of different chemical types of plasticizers in concretes and mortars while AAC's composition undergoing changes.

2 Experimental program

2.1 Raw Materials

Aluminosilicate components of AACs (% by mass): portland cement clinker (CaO – 66.15; SiO₂ – 22.61; Al₂O₃ – 5.29; Fe₂O₃ – 3.93; MgO – 0.84; Na₂O – 0.15; K₂O – 0.98; SO₃ – 0.50) and GBFS (CaO – 47.30; SiO₂ – 39.00; Al₂O₃ – 5.90; Fe₂O₃ – 0.30; MgO – 5.82; MnO – 0.50; SO₃ – 1.50).

Alkaline components of AACs: sodium silicate pentahydrate Na₂SiO₃·5H₂O (SSP) and sodium carbonate ash Na₂CO₃ (SC).

Calcium sulphate (CS) in modification of hemihydrate CaSO₄·0.5H₂O was used as setting retarder, density 2.7 g/cm³.

Plasticizers: «JK-04PP» based on polycarboxylate esters (PC), «JIANKAI» (Chine); sodium lignosulphonate (LST), «Borrespers» (Norway); «Melflux PP100F» based on modified polyethylene glycol (PEG-M), «SKW Polymers» (Germany); PEG-400 based on polyethylene glycol (PEG), «Dow Chemical» (Germany); «Triameen Y12D» based on acyclic polyamine (APM), «AkzoNobel» (Netherlands).

2.2 Experimental Process

The research was realized in two stages.

The first stage. Stability of plasticizers' molecular structure in hydrated medium of AAC with different content of GBFS was investigated by means of infrared spectroscopy (IR) by Specord 75 IR (Germany).

Five compositions of AAC were used:

– № 1 (clinker – 97.6 %, SSP – 2.4 % (0.7 % on Na₂O)) – AAC type II (alkali-activated portland cement, AAPC);

– № 2 (clinker – 67.0 %, GBFS – 30.1 %, SC – 2.9 % (1.7 % by Na_2O)) and № 3 (clinker – 66.7 %, GBFS – 30.0 %, SSP – 3.3 % (1.0 % by Na_2O)) – AAP type IV (alkali-activated slag portland cement, AASPC);

– № 4 (GBFS – 95.2 %, SC – 4.8 % (2.8 % by Na_2O)) and № 5 (GBFS – 94.3 %, SSP – 5.7 % (1.7 % by Na_2O)) – AC type I (alkali-activated slag cement, AASC);

AACs with specific surface 450 m^2/kg (by Blaine) were produced by mixing the components in “HOBART” mixer. The cements were modified by admixture based on ethylhydroxysiloxane polymer (0.04 %) for intensification of grinding and to prevent absorption of water from air as well as for maintaining of AACs performances.

The specimens for IR tests were obtained from cement pastes with one of the mentioned plasticizers (10 % AAC mass) at water-to-cement ratio = 0.4. After 7 d hardening at normal conditions ($t = 20 \pm 2$ °C, $\text{RH} = 95 \pm 5$ %) the specimens were dried at $t = 40$ °C to constant mass and grinded for full passing through sieve 0.08 mm.

The second stage. Dry mixes for anchoring and ready-mixed concretes based on AACs were modified by admixtures most effective in high alkaline medium (see *first stage*).

Slump of fresh concrete mix was determined according to EN 12350-2:1999, compressive strength - EN 12390-3:2001, consistency (flow) of fresh mortar by Vicat cone - EN 196-3:2007, tensile strength in bending and compressive strength of mortars - EN 12190:1999 and EN 196-1:2007, mortar adhesion - EN 1542:1999.

3 Results and discussion

The first stage. Changes of surfactants' molecular structure in AAC medium are shown in fig. 1, 2, 3.

Hardened AAC was characterized by the follow phases (curves 1 - 5, fig. 1, 2, 3): anhydrous calcium silicates (450, 520, 870-880 cm^{-1}), hydrated calcium silicates (920-980, 3400-3450 cm^{-1}), chemically combined and adsorbed water of hydrated calcium silicates (3400-3450 cm^{-1}), molecular water (1620-1650 cm^{-1}), calcium hydroxide (3620-3660 cm^{-1}).

PC admixture was defined by the effect at 1730 cm^{-1} (C=O, ester group) and 1100 cm^{-1} (C-O-C, ether group) (fig. 1a). The admixture undergoes changes in molecular structure due alkaline hydrolysis of ester groups with formation of carboxylate acids and corresponding ethers [19]. The bonds at 1415 cm^{-1} and 1520-1560 cm^{-1} (COO-, carboxylate group) confirm the molecular structure degradation because of alkaline hydrolysis. However hydrolysis was partial that is evidence by effect at 1730 cm^{-1} (curves 1 - 5). Higher destruction of PC admixture took place due to increasing content of alkaline component (by Na_2O) from 0.7 % (curve 1) to 1.7 % (curve 5) that was prescribed by increasing volume of GBFS in AAC. This effect can be confirmed by intensity of bonds at 1415 cm^{-1} , 1520 - 1560 cm^{-1} and decreasing effects at 1730 cm^{-1} and 1100 cm^{-1} .

Thus molecular structure of PC admixture is unstable in alkaline medium. The main chain with carboxylate groups adsorbs on surface of cement particles. Side chains tear from main chain due to hydrolysis of ether bond. Agreeably plasticizing effect of PC admixture due to steric effect of side chains in AAC's medium is significantly less due to increasing of alkaline component content (by Na_2O) from 0.7 % (AAC type II) to 1.7 % (AAC type IV). SSP caused higher degradation of PC admixture than SC, that was fixed for AAC with 1.7 % of alkaline component (by Na_2O) for compositions № 5 (curve 5) and № 2 (curve 2) respectively.

The mentioned effect can be explained by higher pH value of SSP in comparison of SC in the medium, i.e. 12.6 and 11.3 agreeably. Hence stability of PC admixture's molecular structure in hydration medium of AACs depends on the content and nature of alkaline component.

LST admixture unlike to PC admixture characterizes by stable molecular structure in AAC medium. Stability of molecular structure was confirmed by the corresponding effects on all IR curves (fig. 1 b): 620, 650, 780 cm^{-1} (CH_2 bonds); 660, 1200 cm^{-1} (SO_3 groups); 1020 cm^{-1} (OH^- groups); 1100 cm^{-1} (OH alcohol groups); 1360 cm^{-1} (CH_3 bonds); 1430, 1500, 1590 cm^{-1} (substituted aromatic ring of lignin); 1630 cm^{-1} ($\text{C}=\text{C}$ bonds in benzol ring, $\text{C}=\text{O}$ carbonyl groups and COOH groups); 1710 cm^{-1} ($\text{C}=\text{O}$ group of aromatic acids and COOH groups); 2910 cm^{-1} (CH_2 bonds); 3380, 3450 cm^{-1} (O-H bonds in hydroxyl, phenol, alcohol and carboxyl groups). The results concerning molecular stability of LST admixture in AAC medium correlate with well known results [20].

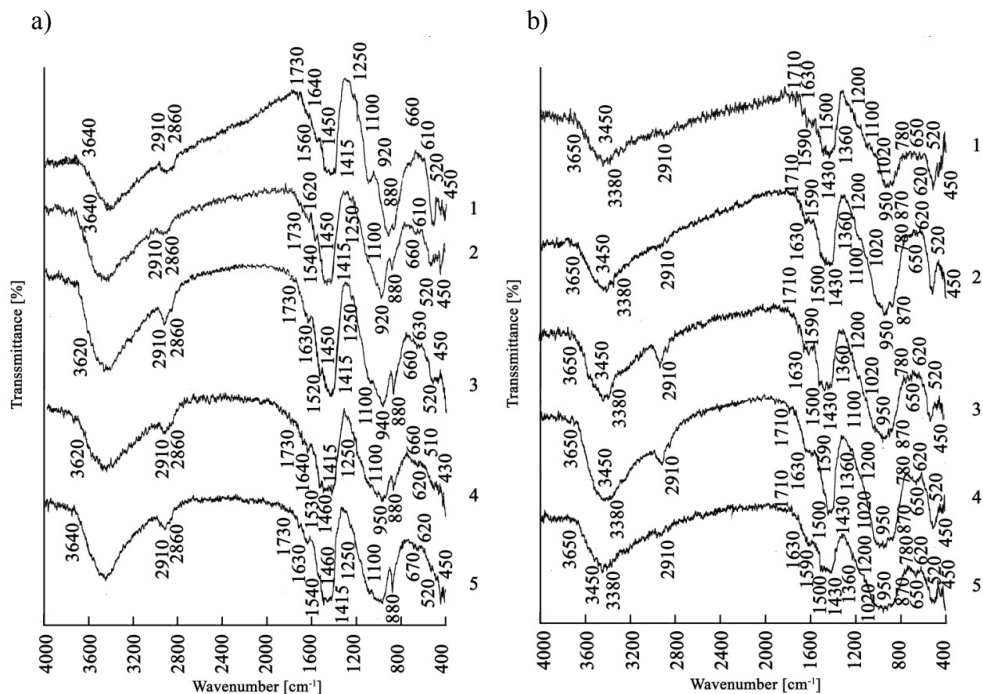


Fig.1. IR spectra of PC (a) and LST (b) in hydration medium of AAC's compositions: 1 – №1; 2 – №2; 3 – №3; 4 – №4; 5 – №5.

PEG admixtures can be also characterized by stable molecular structure in AAC's medium. Characteristic effects (fig. 2 a) are: 710, 2920 cm^{-1} (CH_2 bonds), 1100 cm^{-1} (C-O-C ether group) and 3620 cm^{-1} (OH^- group). PEG is nonionic surfactant without dispersible effect. However, this organic substance acts as dispersant after attaching to carboxyl groups ($-\text{COOH}$) of superplasticizer molecules [21]. Such method for increasing adsorption was realized in admixture based on modified polyethylene glycol (PEG-M). Melflux PP100F is copolymer of PEG and acrylic acid, ensure much higher plasticizing effect but is unstable in high alkaline medium. This type of admixture undergoes insignificant changes in medium of AAC type II (fig.2 b, curve 1) only when the content of alkaline component in AAC is low. Effects at 1720 cm^{-1} ($\text{C}=\text{O}$, ester groups) confirms such fact. And the presence of effects at 1415 cm^{-1} and 1520 cm^{-1} (COO^- , carboxylate group) confirms partial hydrolysis of the admixtures. Increasing content of alkaline component (by Na_2O) from 0.7 % (curve 1) to 1.7 % (curve 5) ensures lack in stability of molecule structure, that can be confirmed by decreasing effect at 1720 cm^{-1} (ether group) with increasing at 1415 cm^{-1} and 1520 cm^{-1} . Destruction of the admixture in presence of SSP is higher in comparison with SC in AAC.

Dodecyl dipropylene triamine (acyclic polyamine, APM) acts as cationic surfactant regarding to AAC and is characterized by stability in high alkaline medium. The effects at 1230 cm^{-1} (C–N bonds, aliphatic amines), 1450 , 2860 , 2920 cm^{-1} (CH_2 , CH_3), 1490 cm^{-1} (C–H, aromatic amines), 1620 cm^{-1} (N–H bond, primary amines), 3320 and 3430 cm^{-1} (two bonds N–H, primary amines) are present on all curves.

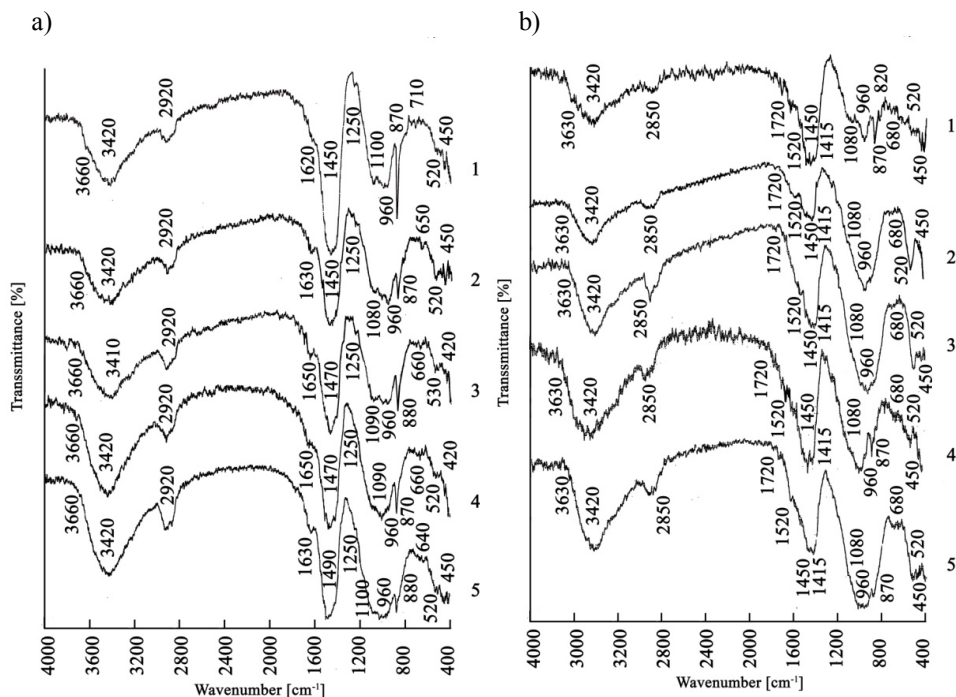


Fig.2. IR spectra of PEG (a) and PEG-M (b) in hydration medium of AAC's compositions: 1 – №1; 2 – №2; 3 – №3; 4 – №4; 5 – №5.

Thus LST, PEG and APM are admixtures with stable molecular structure in AAC medium in all range of alkaline component content's changing. PC and PEG-M admixtures are effective at low content of alkaline component i.e. 0.7 % by Na_2O (AAC type II). Increasing of pH figure that is caused by content and nature of alkaline component ensure significant decreasing in effectiveness of admixtures with ester bands as a result of alkaline hydrolysis.

Second stage. Compositions of dry mixes for anchoring and ready-mixed concretes based on AAC were developed on the grounds of obtained regularities.

AAC type II in system «clinker – SSP – CS» was used in mortar for anchoring. AAC types I and IV in system «clinker – GBFS – alkaline component (SSP, SC) – CS» were used for ready-mixed concretes. LST admixture, 0.8 % mass of aluminosilicate components, was used as necessary component in AAC types I and IV.

CS was used as setting retarder and to increase strength of AAC. The effectiveness of this additive in AAC was already demonstrated [8, 22]. CS was added above 100 % of aluminosilicate component mass: 9.0 % and 6.5 % for AAC type II and AAC type IV agreeable.

PEG-M admixture (Melflux PP100F) was used as water-reducing admixture in mortar for anchoring based on AAC type II. Consistency of mortar was 150 mm. The values of tensile strength in bending / compressive strength of mortars 6.6 / 30.6 MPa in 1 d and adhesion 1.1 MPa were obtained.

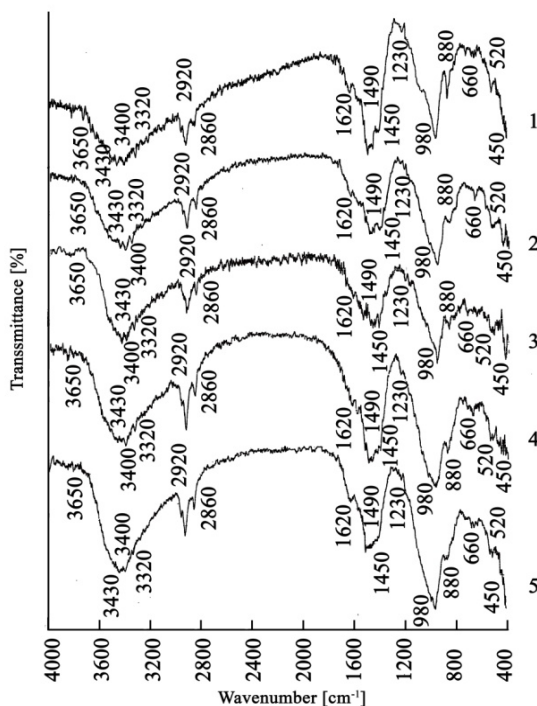


Fig.3. IR spectra of APM in hydration medium of AAC's compositions: 1 – №1; 2 – №2; 3 – №3; 4 – №4; 5 – №5.

4 Conclusions

It was shown that PC and PEG-M admixtures with ester bonds undergo of molecular structure degradation as a result of alkaline hydrolysis at increasing pH values that is caused by content of alkaline component depending on GBFS content and on the nature of alkaline component. LST, PEG and APM admixtures are characterized by stability of molecule regardless of alkaline component content. Effectiveness of admixtures without ester bonds (LST, PEG and APM) is higher at increasing of alkaline component's content agreeably to increasing of GBFS content in AAC type I and IV.

Practicability in application of admixtures according to AAC type was confirmed by properties of mortars and concretes. Thus mortar for anchoring, based on AAC type II modified with PEG-M admixture, was characterized by appropriated consistency (150 mm) and tensile 1 d strength in bending / compressive strength 6.6 /30.6 MPa and adhesion 1.1 MPa. PEG and APM admixtures in presence of LST define changing in consistency of fresh concrete from S1 to S3, S4 and its safety during 60 min; compressive strength of modified concrete was provided at the level of non-modified analog.

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