Alkali-activated Portland cement with adjustable proper deformations for anchoring application

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Abstract. The application of alkali-activated Portland cement (hereinafter AAPC) for anchoring grouts was investigated with obtaining of non-shrinking high performance cementing systems. The AAPC system “ordinary Portland cement clinker – sodium metasilicate” was modified by the complexes of mineral and organic compounds to ensure specified properties of anchoring grouts. It was revealed that the most effective multifunctional additives are represented by the system “salt-electrolyte – surfactant”. Alongside with slowing down of AAPC paste setting time, the effect of compensated shrinkage of AAPC mortar, i.e. expansion within 0.062 mm/m and slight shrinkage within 0.017 mm/m, was ensured when Na2SO4 and NaNO3 were used in the mentioned system respectively. The effect of compensated shrinkage is explained by greater crystallization of hydrosilicates and hydroaluminates, additional formation of sulfate-containing sodium-calcium hydroaluminate (for Na2SO4-based system) and crystalline calcium hydronitroaluminate (for NaNO3-based system). The advantages of the modified AAPC for anchoring application are indicated in the paper.

1. Introduction
The main tendency in cement industry is reduction of CO2 emission through application of composite cements with a lower content of ordinary portland cement clinker (hereinafter OPC clinker) due to application of additives and by-products. It was shown effectiveness of blast furnace slag, natural zeolite and limestone in eco-efficient composite cements with high early strength [1]. Substitution of clinker by zeolite ensures the increasing of strength, freeze/thaw resistance fracturing of concrete [2].

The actuality of alkali-activated cements (hereinafter AACs) in building materials is due to their conformity with modern tendencies for sustainable development of mankind in the part of efficient consumption of raw materials and energy resources, responsible attitude to ecology of environment, while ensuring the necessary performance properties [3, 4], including special ones [5, 6, 7]. AAPC differs in composition and properties among the known types of AACs [8]. The feasibility of an alkaline component in AAPC is based primarily on the idea of accelerated structure formation, especially at the early stages of hardening, and thus ensuring a high early strength of artificial stone. Application of soluble sodium silicates provides the highest activity of AAPC, which is caused by low-calcium hydrosilicates and alkaline as well as by alkaline earth hydrosilicates with a reduced
degree of crystallization at the early stages of structure formation during hydration [9]. Hence, AAPC is relevant in materials with an intensive strength set, particularly in anchoring grouts [10, 11].

The characteristic properties of anchoring grouts according to requirements [12] and experience [10, 11], in addition to strength, are mainly short setting time, high adhesion and ability to expand. It’s known that the AAPC is promising one for anchoring grouts [13]. AAPC grouts satisfy the mentioned requirements: workability retention time 20 min; consistency of 150 mm by Vicat cone; tensile strength in bending/compressive strength of mortar in 1 d and 28 d agreeably 5.2/22.3 MPa and 12.5/78.0 MPa; adhesion 1.2 MPa. However, the high content of gel and submicrocrystalline structures during hydration [14], as well as the lack of ettringite in hydration products through the features of the AAPC [15, 16] cause increasing AAPC grouts shrinkage. It’s well known the oxide as well as hydrosulphoaluminate types of extensions which control the proper deformations in traditional cements are ineffective for AACs [17, 18, 19].

2. Analysis of recent research and publications

The fundamentals of general mineralogy and chemistry of cement provide some explanations about possibility of salts-electrolytes to influence the structure formation of binding systems, namely about the isomorphism with replacing of silicate or aluminate anion, the ability to form solid solutions and additional crystalline formations, which affect the properties of artificial stone [20, 21]. Thus, it was shown acceleration of cement strength due to addition of CaCl₂ and CaNO₃ due to introduction into structure formation with synthesis of calcium hydrochloraluminate and calcium hydronitroalyuminate [22]. Decreasing of AAC shrinkage was also confirmed by application of Na₂SO₄ [23] as well as bypass cement kiln dust which contains CaO and salts, i.e. KCl, NaCl, K₂SO₄, Na₂SO₄, CaSO₄, K₂CO₃, Na₂CO₃ [24].

In addition, the control of AACs shrinkage deformations can be also accomplished by surfactants. In this case the positive effect is due to redistribution of porous space and higher volume of pores with diameter of 0.1 to 1 μm, the capillary pressure in which is much smaller than that of capillaries with less size [25, 26]. To date, the effective types of surfactants have been identified as modifying admixtures for concretes and mortars based on traditional portland cements [27, 28]. However, most of these surfactants are ineffective for AACs and therefore the principles for their choice were proposed [13, 29, 30]. Thus, the maximum plasticization effect can be provided by sodium lignosulfonate [31], sodium gluconate [32], polyols as well as other acyclic low and high molecular compounds [29].

The above results allows predicting the effective manage AAPC anchoring grouts proper deformations by interference in structure using complex additives (further, CAs) co-acting on crystallization processes, porous structure and morphology of hydrated phases. This causes the relevance of investigations aimed on creation of CAs containing soluble compounds with anions (SO₄²⁻, NO₃⁻, F⁻, Cl⁻, SiF₆²⁻, PO₄³⁻ etc.) together with effective types of surfactants. The effect of CAs on reduction of AAC shrinkage was shown [33, 34].

3. Purpose and Tasks

The aim was the problem to control of proper deformations of anchoring mortars based on AAPC by CA’s in the system of “mineral compound – surfactant”.

4. Raw Materials and Methods

OPC clinker characterized by specific surface= 450 m²/kg (by Blaine) was used as AAPC 100% aluminosilicate component. The chemical composition was, % by mass: CaO – 66.15, SiO₂ – 22.61, Al₂O₃ – 5.29, Fe₂O₃ – 3.93, MgO – 0.84, Na₂O – 0.15; K₂O – 0.98; SO₃ – 0.50.

AAPC alkaline component was presented by sodium silicate pentahydrate Na₂SiO₃·5H₂O (SSP). CAs components were presented by:
- the mineral compounds: Na$_2$SO$_4$ (CAS 7757-82-6), NaNO$_3$ (CAS 7631-99-4), Na$_2$PO$_4$ (CAS 7601-54-9), NaCl (CAS 7647-14-5), Ca(NO$_3$)$_2$ (CAS 13477-34-4), Ca(OH)$_2$ (CAS 1305-62-0), CaSO$_4$·0.5H$_2$O (according to the national standard of Ukraine DSTU B V.2.7-104: 2000);
- the surfactants of two types, i.e. sodium lignosulphonate (further, LST) production “Borrespers” (Norway) under CAS No. 8061-51-6 (pH ≥ 8.5 in) and sodium gluconate (GL) under CAS No. 527-07-1.

The standard quartz sand in accordance with the national standard of Ukraine DSTU B V.2.7-189:2009 was used as a fine aggregate.

The total effect on water reduction, slowing down setting time and increasing strength of AAPC was accepted for determination the most effective CAs formulations, which were further used to reduce AAPC proper deformations.

The AAPCs were prepared by dry mixing of components with further adding of water for hydration.

The AAPC microstructure was researched by differential-thermal analysis (DTA), electronic microscopy and probe analysis.

Normal consistency and setting time of cement pastes were determined according to the national standard of Ukraine DSTU B V.2.7-185:2009, compressive strength of cements – as prescribed by DSTU B V.2.7-187:2009.

The proper deformations were determined on specimens 40×40×160 mm of cement-sand mortar (1:3). After hardening in forms with an insulated surface for 1 d, the samples were stored for 7 d under normal conditions (t= 20 ± 2 °C, R.H. = 95 ± 5%). Then the samples were stored over saturated solution of ammonium nitrate (NH$_4$NO$_3$) under t= 20 ± 2 °C and humidity= 65% till the control age. The length of samples after 1 d was taken as the initial one (zero) for calculations.

5. Experimental Process
The comparative analysis of AAPC systems “OPC clinker – SSP” (the reference one) and “OPC clinker – mineral compound – SSP”, “OPC clinker – SSP – mineral compound” was carried out after hydration. The content of SSP was 3% (by Na$_2$O) or 10.26% (by dry matter) of OPC clinker. The content of the mineral compounds was 50% by weight of SSP, i.e. 2.96% of OPC clinker. The surfactants (LST and GL) were added in amounts of 0.45% and 0.25% by weight of OPC clinker respectively.

It was revealed, that effectiveness of mineral compounds determined by their influence on normal consistency of AAPC pastes, deceleration of setting time and acceleration of strength of the mentioned systems goes down in the row: Ca(OH)$_2$ > CaSO$_4$·0.5H$_2$O > NaNO$_3$ > Na$_2$SO$_4$ > Na$_2$PO$_4$ > Ca(NO$_3$)$_2$ > NaCl.

It was shown that the greatest effect on reduction of proper deformations was determined for the systems with mineral compounds which belong to salts-electrolytes Na$_2$SO$_4$ and NaNO$_3$. The expansion within +0.062 mm/m in presence of Na$_2$SO$_4$ was observed, while application of NaN$_3$ caused creation of practically unshrinkable AAPC system with value -0.017 mm/m (Figure 1).

It was revealed that CA presented by the system “Na$_2$SO$_4$ – LST – GL” ensured obtaining of AAPC, characterized by initial setting time of 30 min, final setting time of 35 min. Tensile strength in bending/compressive strength of the AAPC mortar corresponds of 5.3/25.3 MPa (1 d), 6.7/34.6 MPa (2 d), 7.5/41.7 MPa (7 d) and 9.2/47.8 MPa (28 d).

The replacement of Na$_2$SO$_4$ by NaNO$_3$ ensures prolongation of initial setting up to 37 min and final setting time within 44 min while 1 d tensile strength in bending/compressive strength of AAPC mortar was 5.5/27.2 MPa (1 d), 2 d – 6.9/39.3 MPa (2 d), 7.9/48.7 MPa (7 d) and 9.7/53.1 MPa (28 d).

The features of AAPC structure modified by CAs based on Na$_2$SO$_4$ with NaNO$_3$ were investigated by DTA (Figure 2) and electronic microscopy (Figures 3a, 4a, 5a) as well as by probe analysis (Figures 3b, 4b, 5b).

According to DTA, the phase composition of hydrated AAPC without CA (Figure 2) is represented low-calcium hydroxosilicates CSH(B) (endothermic effects at t= 160 and 845 °C are determined by
recrystallization in wollastonite). Endothermic effects at $t=490$ and $670 \, ^\circ C$ characterize the formation of slightly crystallized calcium hydrosilicates $C_2SH$ (A). Slightly crystallized calcium hydroaluminates $\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 10\text{H}_2\text{O}$ (exothermic effects at $t=520$ and $710 \, ^\circ C$) are formed in hydration products besides hydrosylicates.

![Figure 1](https://example.com/image1.png)

**Figure 1.** The proper deformations of AAPC in the system “OPC clinker – SSP – salt-electrolyte – surfactant”.

According to electron microscopy, globular formations of gel-like calcium hydrosilicates (Figure 3 a) and calcium hydroaluminates with involved Na$^+$ and K$^+$ ions (Figure 3 b) are identified in reference AAPC. Drop-like formations on gel surface are “germs” of crystal phase.

![Figure 2](https://example.com/image2.png)

**Figure 2.** DTA curves of 28 d AAPC: 1 – the reference; 2 – with CA system “$\text{Na}_2\text{SO}_4 \cdot 1\text{LST} \cdot 1\text{GL}$”; 3 – with CA system “$\text{NaNO}_3 \cdot 1\text{LST} \cdot 1\text{GL}$.”
Structure of AAPC, modified with CA in the system “Na$_2$SO$_4$ – LST – GL”, is represented by hydrates with a higher degree of crystallization in comparison with the reference AAPC (Figure 2). Displacement of exothermic effect from $t = 845$ to $850 \, ^\circ$C is evidence of higher crystallinity of low-calcium hydrosilicates CSH(B). Displacement of endothermic effect in the direction of higher temperature ($t = 540 \, ^\circ$C) as well as exothermic effect at $t = 915 \, ^\circ$C are evidence of calcium hydroaluminate (CaO$\cdot$Al$_2$O$_3$$\cdot$10H$_2$O) with a higher degree of crystallization.

![Figure 3](image)

**Figure 3.** Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC without CA.

![Figure 4](image)

**Figure 4.** Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC modified with CA system “Na$_2$SO$_4$ – LST – GL”.

![Figure 5](image)

**Figure 5.** Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC modified with CA system “NaNO$_3$ – LST – GL”.

The microstructures of AAPC in presence of CA based on Na$_2$SO$_4$ and NaNO$_3$ were investigated (Figure 4, 5). In case of Na$_2$SO$_4$ the data indicate the hexagonal lamellar crystalline structures of minamiite ($(Na,Ca_{0.5})Al_3(SO_4)_2(OH)_6$) [35, 36] along with hydrosilicates and hydroaluminates with a
higher degree of crystallization. In the case of NaNO₃ the layered lamellar crystalline formations of calcium hydronitroaluminate 3CaO·Al₂O₃·Ca(NO₃)₂·10H₂O (Figure 5) [21] were observed additionally as well. Such crystal formations definite the low shrinkage of AAPC modified with CA through covering the space between gel-structure phases.

The properties of AAPC anchoring grouts modified by CA systems “Na₂SO₄ – LST – GL” and “NaNO₃ – LST – GL” are in compliance with the mandatory basic requirements [11] while providing satisfactory proper deformations (table 1).

Table 1. Properties of the anchoring grouts based on AAPC, modified by CA system “salt-electrolyte – surfactants”.

| Property                              | The value for CA |
|---------------------------------------|------------------|
|                                       | based on Na₂SO₄ | based on NaNO₃ |
| Workability time, min                 | 25               | 30             |
| Consistency of mortar by Vicat cone, mm| 200              | 210            |
| Compressive strength, MPa:           |                  |                |
| – 1 d                                 | 24.8             | 27.3           |
| – 28 d                                | 82.5             | 85.3           |
| Tensile strength in bending, MPa:     |                  |                |
| – 1 d                                 | 5.7              | 6.1            |
| – 28 d                                | 12.9             | 13.5           |
| Adhesion to the concrete base, MPa    | 1.35             | 1.40           |
| Proper deformations, mm/m             | +0.035           | -0.027         |

6. Conclusion
The possibility of AAPC with regulated proper deformations for anchoring application was proved. Compensated shrinkage of AAPC can be provided by CAs system “salt-electrolyte – surfactants” while ensuring effective structure of artificial stone. CA based on Na₂SO₄ provides initial setting time 30 min, final setting time 35 min and expansion within 0.062 mm/m. AAPC modified by CA based on NaNO₃ characterized by initial setting time 37 min, final setting time 44 min and slight shrinkage within 0.017 mm/m. The effect of AAPC compensated shrinkage is explained by greater crystallization of hydrosilicates and hydroaluminates, additional formation of sulfate-containing sodium-calcium hydroaluminate (for Na₂SO₄-based system) and crystalline calcium hydronitroaluminate (for NaNO₃-based system). Anchoring grouts based on AAPC modified by CAs are characterized by manage-able proper deformation that determines perspective improvement of such materials.

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