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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 CaCl_2 and CaNO_3 due to introduction into structure formation with synthesis of calcium hydrochloraluminat and calcium hydronitroaluminat [22]. Decreasing of AAC shrinkage was also confirmed by application of Na_2SO_4 [23] as well as by-pass cement kiln dust which contains CaO and salts, i.e. KCl , NaCl , K_2SO_4 , Na_2SO_4 , CaSO_4 , K_2CO_3 , Na_2CO_3 [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 (SO_4^{-2} , NO_3^- , F^- , Cl^- , SiF_6^{-2} , PO_4^{-3} 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 m^2/kg (by Blaine) was used as AAPC 100% aluminosilicate component. The chemical composition was, % by mass: CaO – 66.15, SiO_2 – 22.61, Al_2O_3 – 5.29, Fe_2O_3 – 3.93, MgO – 0.84, Na_2O – 0.15; K_2O – 0.98; SO_3 – 0.50.

AAPC alkaline component was presented by sodium silicate pentahydrate $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ (SSP).

CAs components were presented by:

- the mineral compounds: Na_2SO_4 (CAS 7757-82-6), NaNO_3 (CAS 7631-99-4), Na_3PO_4 (CAS 7601-54-9), NaCl (CAS 7647-14-5), $\text{Ca}(\text{NO}_3)_2$ (CAS 13477-34-4), $\text{Ca}(\text{OH})_2$ (CAS 1305-62-0), $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ (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 ($\text{pH} \geq 8.5$ 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 $40 \times 40 \times 160$ 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 ($t = 20 \pm 2$ °C, R.H. = $95 \pm 5\%$). Then the samples were stored over saturated solution of ammonium nitrate (NH_4NO_3) under $t = 20 \pm 2$ °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_2O) 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: $\text{Ca}(\text{OH})_2 > \text{CaSO}_4 \cdot 0.5\text{H}_2\text{O} > \text{NaNO}_3 > \text{Na}_2\text{SO}_4 > \text{Na}_3\text{PO}_4 > \text{Ca}(\text{NO}_3)_2 > \text{NaCl}$.

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_2SO_4 and NaNO_3 . The expansion within +0,062 mm/m in presence of Na_2SO_4 was observed, while application of NaNO_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_2SO_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_2SO_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_2SO_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 hydrosilicates CSH(B) (endothermic effects at $t = 160$ and 845 °C are determined by

recrystallization in wollastonite). Endothermic effects at $t = 490$ and 670 °C characterize the formation of slightly crystallized calcium hydrosilicates C_2SH (A). Slightly crystallized calcium hydroaluminates $CaO \cdot Al_2O_3 \cdot 10H_2O$ (exothermic effects at $t = 520$ and 710 °C) are formed in hydration products besides hydrosilicates.

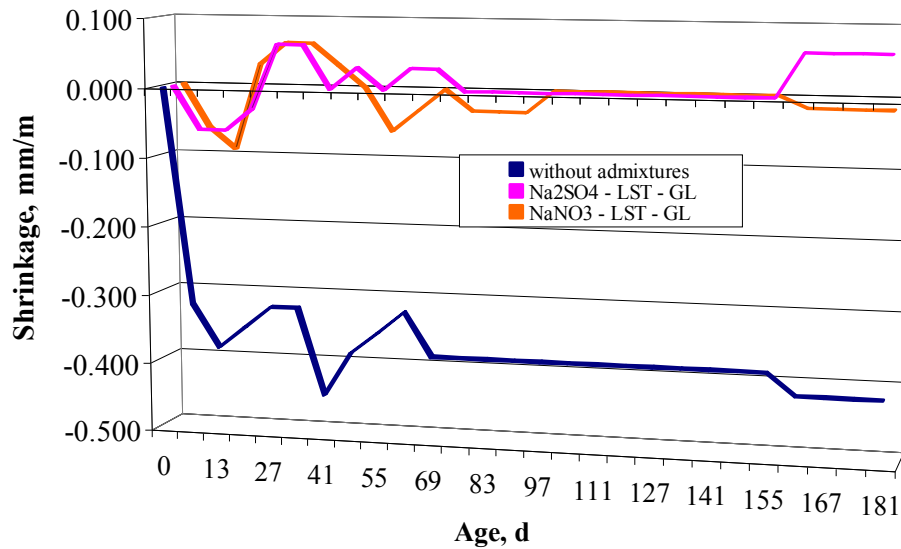


Figure 1. The proper deformations of AAPC in the system “OPC clinker – SSP – salt-electrolyte – surfactant”.

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.

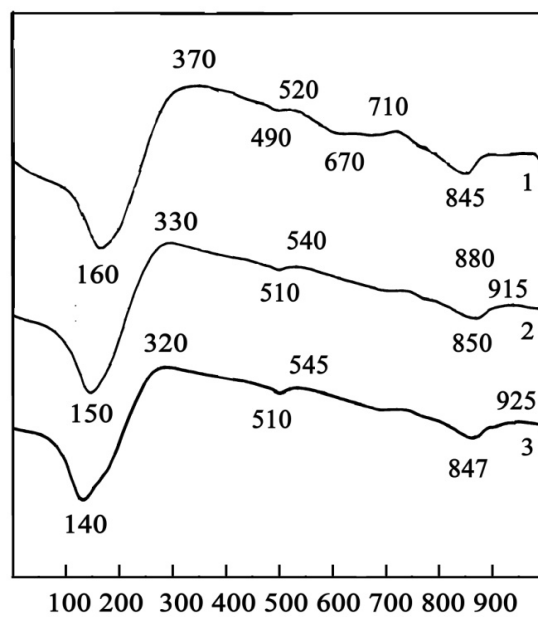


Figure 2. DTA curves of 28 d AAPC: 1 – the reference; 2 – with CA system “ $Na_2SO_4 - LST - GL$ ”; 3 – with CA system “ $NaNO_3 - LST - GL$ ”.

Structure of AAPC, modified with CA in the system “ $\text{Na}_2\text{SO}_4 - \text{LST} - \text{GL}$ ”, 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°C is evidence of higher crystallinity of low-calcium hydrosilicates CSH(B). Displacement of endothermic effect in the direction of higher temperature ($t = 540^\circ\text{C}$) as well as exothermic effect at $t = 915^\circ\text{C}$ are evidence of calcium hydroaluminate ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 10\text{H}_2\text{O}$) with a higher degree of crystallization.

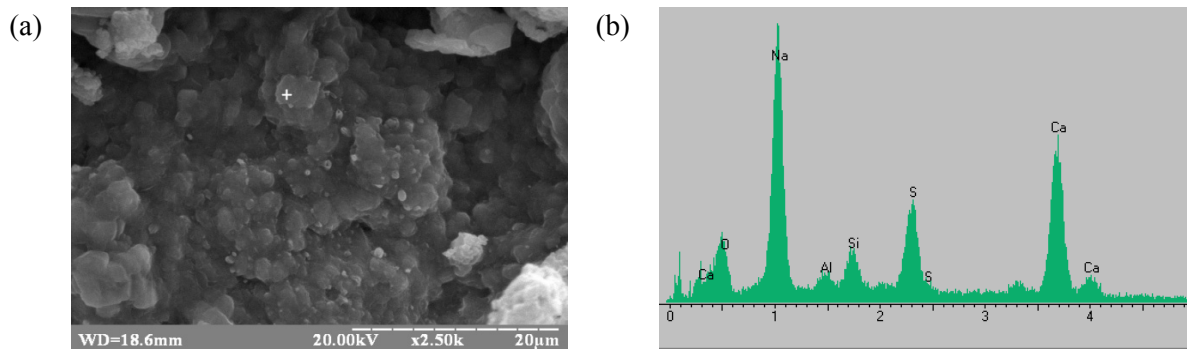


Figure 3. Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC without CA.

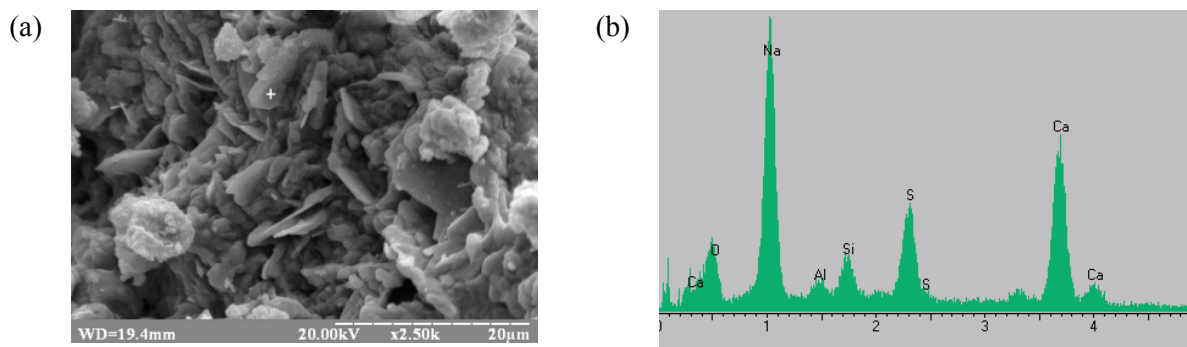


Figure 4. Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC modified with CA system “ $\text{Na}_2\text{SO}_4 - \text{LST} - \text{GL}$ ”.

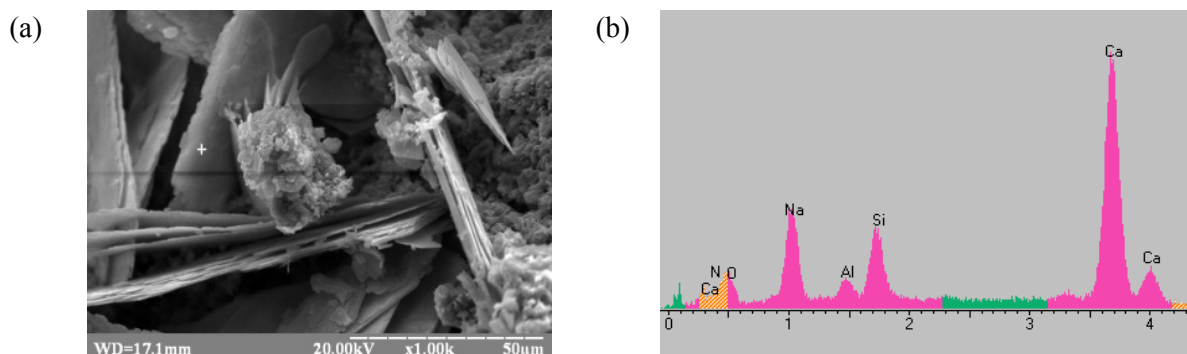


Figure 5. Electronic micrographs of cleavage surface (a) and probe analysis (b) of 28 d AAPC modified with CA system “ $\text{NaNO}_3 - \text{LST} - \text{GL}$ ”.

The microstructures of AAPC in presence of CA based on Na_2SO_4 and NaNO_3 were investigated (Figure 4, 5). In case of Na_2SO_4 the data indicate the hexagonal lamellar crystalline structures of minamiite ($(\text{Na}, \text{Ca}_{0.5})\text{Al}_3(\text{SO}_4)_2(\text{OH})_6$) [35, 36] along with hydrosilicates and hydroaluminates with a

higher degree of crystallization. In the case of NaNO_3 the layered lamellar crystalline formations of calcium hydronitrioluminate $3\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot\text{Ca}(\text{NO}_3)_2\cdot 10\text{H}_2\text{O}$ (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 “ Na_2SO_4 – LST – GL” and “ NaNO_3 – 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 Na_2SO_4	based on NaNO_3
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 Na_2SO_4 provides initial setting time 30 min, final setting time 35 min and expansion within 0.062 mm/m. AAPC modified by CA based on NaNO_3 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 Na_2SO_4 -based system) and crystalline calcium hydronitroaluminate (for NaNO_3 -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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References

- [1] Kropyvnytska T, Rucinska T, Ivashchyshyn H and Kotiv R 2019 Development of Eco-Efficient Composite Cements with High Early Strength *International Conference Current Issues of Civil and Environmental Engineering Lviv-Košice-Rzeszów* (CEE 2019: Proceedings of CEE 2019) 211–218

- [2] Solodkyy S, Markiv T, Sobol K and Hunyak O 2017 Fracture properties of high-strength concrete obtained by direct modification of structure *MATEC Web of Conferences* **116** 01016
- [3] Xing J, Zhao Y, Qiu J and Sun X 2019 Microstructural and mechanical properties of alkali-activated materials from two types of blast furnace slags *Materials* **12** 2089
- [4] Awoyera P 2019 Durability properties of alkali-activated slag composites: short overview *Silicon* 1-10
- [5] Fernández-Jiménez A, Pastor J Y, Martín A, Palomo A 2010 High-Temperature Resistance in Alkali-Activated cement *Journal of the American Ceramic Society* **10** 3411–3417
- [6] Xie Y, Lin X, Ji T, Liang Y and Pan W 2019 Comparison of corrosion resistance mechanism between ordinary Portland concrete and alkali-activated concrete subjected to biogenic sulfuric acid attack *Construction and Building Material* **228** 117071
- [7] Kovalchuk O, Grabovchak V and Govdun Y 2018 Alkali-activated cements mix design for concretes application in high corrosive conditions *MATEC Web of Conferences* **230** 030077
- [8] DSTU B V.2.7-181:2009: Alkaline cements. Technical conditions. National standart of Ukraine
- [9] Gelevera A G and Munzer K 1994 Alkaline portland and slag portland cements *First Int. conf. on alkaline cements and concretes* (Kiev: Vipol Stock company) 173-180
- [10] Ma C, Tan Y and Li E 2015 High-performance grouting mortar based on mineral admixtures *Advances in Materials Science and Engineering* **260** 1-11
- [11] Fang Zhi and Shao-hua He 2012 High-Performance Grouts for Rock Anchor *Key Engineering Materials Trans Tech Publications* **517** 946-951
- [12] DSTU B V.2.7-126:2011: Mixes building dry modified. National standart of Ukraine
- [13] Rudenko I, Konstantynovskiy O, Kovalchuk A, Nikolainko M and Obremsky D 2018 Efficiency of redispersible polymer powders in mortars for anchoring application based on alkali-activated Portland cements *Key Engineering Materials* **761** 27-30
- [14] Krivenko P V 2017 Why Alkaline Activation – 60 Years of the Theory and Practice of Alkali-Activated Materials *Journal of Ceramic Science and Technology* **8** 323-334
- [15] Shpynova L G, Sanitskiy M A, Shyiko O Ya and Kostiuk P Ya 1985 Effectiveness of ordinary and free-gypsum Portland cement with additives of potassium during winter concreting *Building and architecture* **10** 65-69
- [16] Sanitskiy M A, Sobol' H S, Shevchuk G Ya and Loskutov Yu A 1989 Effective high strengthened free-gypsum portland cements *Cement* **8** 16-17.
- [17] Yuan X-H, Chen W, Lu Z-A and Chen H 2014 Shrinkage compensation of alkali-activated slag concrete and microstructural analysis *Construction and Building Materials* **66** 422-428
- [18] Shtark Y. and Vicht B. 2008 *Cement and lime* [ed P Krivenko] p 480
- [19] Kharchenco I, Alekseev V 2019 Effect of ettringite morphology on the properties of expanding cement systems *E3S Web Conf* **110** 01037
- [20] Teilor H F 1996 *Cement chemistry* (Moscow: Mir) p 560
- [21] Samchenko S V 2016 *Formation and genesis of cement stone structure* (Moscow: NIU MGSU) p 284
- [22] Plugin A A and Runova R F 2018 Bonding calcium chloride and calcium nitrate into stable hydration portland cement products: Stability conditions of calcium hydrochloraluminates and calcium hydronitroaluminates *International Journal of Engineering Research in Africa* **36** 69–73
- [23] Chen K, Yang C-H and Yu Z-D 2011 Effect of admixture on drying shrinkage of alkali-activated slag mortar *Chongqing Daxue Xuebao/Journal of Chongqing University* **34** 38-40.
- [24] Bílek, V, Pařízek L and Kosár P 2016 Strength and porosity of materials on the basis of blast furnace slag activated by liquid sodium silicate *Materials Science Forum* **851** 45-50.
- [25] Palacios M and Puertas F 2005 Effect of superplasticizer and shrinkage-reducing admixtures on alkali-activated slag pastes and mortars *Cement and Concrete Research* **35** 1358-1367

- [26] Palacios M and Puertas F 2007 Effect of shrinkage-reducing admixtures on the properties of alkali-activated slag mortars and pastes *Cement and Concrete Research* **37(5)** 691-702
- [27] Runova R F, Kochevyh M O and Rudenko I I 2005 On the slump loss problem of superplasticized concrete mixes *Proceedings of the International Conference on Admixtures, Enhancing Concrete Performance* 149-156
- [28] Batrakov V G 1998 *Modified concretes. Theory and practice* 2-d ed (Moscow: Tehnoproekt) p 768
- [29] Kryvenko P, Runova R, Rudenko I, Skoryk V and Omelchuk V 2017 Analysis of plasticizer effectiveness during alkaline cement structure formation *Eastern-European journal of Enterprise Technologies* **4(6-88)** 35-41
- [30] Runova R F, Gots V I, Rudenko I I, Konstantynovskiy O P and Lastivks O 2018 The efficiency of plasticizing surfactants in alkali-activated cement mortars and concretes *MATEC Web of Conferences* **230** 03016
- [31] Palacios M, Houst Y F, Bowen P and Puertas F 2009 Adsorption of superplasticizer admixtures on alkali-activated slag pastes, *Cement and Concrete Research* **39(8)** 670-677
- [32] Najimi M, Ghafoori N and Sharbaf M 2019 Alkali-activated natural pozzolan/slag binders: limitations and remediation *Magazine of Concrete Research* 1-48
- [33] Krivenko P, Petropavlovskiy O, Rudenko I and Konstantynovskiy O 2019 The influence of complex additive on strength and proper deformations of alkali-activated slag cements *Materials Science Forum* (Trans Tech Publications Ltd, Switzerland) **968** 13-19
- [34] Omelchuk V, Ye G, Runova R and Rudenko I 2018 Shrinkage behavior of alkali-activated slag cement pastes *Key Engineering Materials* **761** 45-48
- [35] Minamiite Mineral Data. Available at: webmineral.com/data/Minamiite.shtm
- [36] Bayliss P, Kolitsch U, Nickel E H and Pring A 2016 Alunite supergroup: recommended nomenclature *Mineralogical Magazine* **74 (5)** 919-927