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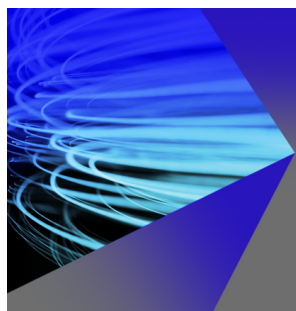


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Effect of Sodium Phosphate and Sodium Nitrate on Microstructure of Alkali-activated Slag Cement Pastes and Properties of Reinforced Concrete Under Cyclic Drying-Wetting in Sea Water

Pavel Krivenko¹, Igor Rudenko¹, Oleksandr Konstantynovskiy^{1,a)}, Olga Boiko¹ and Danutė Vaičiukynienė²

¹Scientific Research Institute for Binders and Materials, Kyiv National University of Construction and Architecture, Povitroflotskyi Avenue, 31, Kyiv, 03037, Ukraine.

²Faculty of Civil Engineering and architecture, Kaunas University of Technology, Studentu st. 48, LT-51367 Kaunas, Lithuania.

^{a)} Corresponding author: alexandrkp@gmail.com

Abstract. The relevance of alkali activated slag cement (AASC) concretes for marine structures is due to their enhanced resistance to sea water. However, cyclic influence of sea water and drying under the action of atmospheric carbonic gas in actual operating conditions cause risks of both deterioration of concrete and corrosion of steel reinforcement. These risks increase in case of fresh concretes with high consistency. Application of salts of strong acids, i.e. sodium phosphate and sodium nitrate, in combination with complex multifunctional additive «portland cement - alumina cement - clinoptilolite» was proposed to protect plasticized AASC concrete from the influence of cyclic drying-wetting in sea water with combination of exposure classes XC4 and XS3. It was shown the advanced crystallization of AASC microstructure due to the mentioned salts as admixtures. Corrosion resistance potential of AASC concrete can be improved due to application of specified salts in combination with the mentioned complex additive as factor of aggressive ions (Cl^- , SO_4^{2-} and CO_3^{2-}) binding. The modified in proposed way plasticized AASC concrete was characterized by the advanced performances, i.e. pore structure, structural density, strength, corrosion resistance, state of steel reinforcement after 90 cycles of wetting/drying in sea water.

INTRODUCTION

To ensure the durability is current world tendency in building industry. This fact is confirmed by numerous scientific researches concerning durability of different structures, such as reinforced concrete [1], concrete [2, 3], brick [4], wood [5, 6], etc. Reinforced concrete structures exploited under the influence of seawater (berths, piers, coast-protecting structures, dams, etc.) need special attention concerning their ensuring durability. This is because of deterioration of concrete [7] as well as corrosion of steel reinforcement [8, 9] under the action of chlorides (NaCl , MgCl_2 , CaCl_2 , KCl) and sulfates (MgSO_4 , CaSO_4) as the main salts in seawater.

Interaction of chlorides and sulfates with hydration products of portland cement causes destruction of concrete in seawater. Thus, gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and secondary ettringite $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 3\text{CaSO}_4 \cdot 32\text{H}_2\text{O}$ are formed due to interaction of SO_4^{2-} -ions with portlandite $\text{Ca}(\text{OH})_2$ and calcium hydroaluminates accordingly [10]. Crystallization pressure of the mentioned phases in micropores can cause the destruction of concrete. Exchange reaction of sodium chloride NaCl with portlandite $\text{Ca}(\text{OH})_2$ with formation of CaCl_2 decreases basicity of the main hydration products of portland cement, i.e. the highly-calcium hydrosilicates [11].

The advanced corrosion resistance of alkali-activated slag cement (further, AASC) concrete in seawater is due to absence of portlandite in hydration products [12] as well as lack of ettringite or changes in its morphology from filamentous, needle to prismatic, plate shape in highly-alkaline hydration medium [13].

The peculiarities of AASC hydration products also cause advanced protection of steel reinforcement. Minor transport of aggressive ions can be provided due to their chemical adsorption by gel-like phases [14], chemical binding by (Mg, Al) LDH-phases (hydrotalcite-group minerals) [15] as well as their occluding by alkaline aluminosilicates as analogues of natural zeolites [12]. Mitigation of drying shrinkage as well as enhanced crack resistance by application of surfactants [16], salts of strong acids [17] and the modifying complexes based on them [18] was proposed to prevent corrosion of steel reinforcement in AASC concrete. It was shown the restriction of aggressive ions transport in plasticized AASC concrete due to complex multifunctional additive (further, CA) including portland cement, calcium aluminate cement and zeolite [19]. Advanced protection of steel reinforcement is due to chemical binding of aggressive ions by (Ca, Al) LDH-phases (Kuzel's salt $3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 0,5\text{CaCl}_2 \cdot 0,5\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and chlorapatite $\text{Ca}_5(\text{PO}_4)_3\text{Cl}$) as well as occlusion by zeolite-containing admixtures.

However, cyclic influence of sea water and drying under the action of atmospheric carbonic gas affect mentioned marine structures in real operating conditions. At that, risks connected with deterioration of AASC concrete [20] also due to increased content of gel phase [12] as well as corrosion of steel reinforcement are increased [21]. The activation of ground granulated blast furnace slag by the salts of sea water was confirmed [22]. This effect is additional to the main one of compounds with highly alkali reaction in water solution and can be caused by advanced crystallization of hydrates. The additive of calcium aluminate cement in presence of portlandite $\text{Ca}(\text{OH})_2$ promotes the accelerated chemical binding of Cl^- and SO_4^{2-} -ions of sea water, while additive of clinoptilolite occludes these aggressive ions.

Influence of cyclic drying-wetting in sea water can be classified as combination of exposure classes XC4 (effect of carbon dioxide while periodical contact with water) and XS3 (periodical effect of seawater or air containing aerosols of seawater) according with [23].

The subject of discussions is to evaluate the corrosion resistance of AASC concrete under action of the mentioned aggressive factors. It's well known that methods of accelerated carbonation are used to determine the atmospheric CO_2 action on concrete in the experimentally available period of time, for instance in [24, 25, 26]. However, there is a discrepancy in evaluation of accelerated and natural carbonation on AASC concrete although the last one is the most realistic [27]. Besides, in case of accelerated carbonation conditions it's difficult to simulate drying-wetting cycles, which affect structures in fact [28].

The absence of portlandite, low Ca/Si ratio in hydrate gel as well as high alkali porous solution cause considerable extremely high sensibility of hydration products of AASC to accelerated carbonization [29, 30]. Increased permeability to CO_2 under these conditions is also caused by prevailing content of nahcolite (NaHCO_3) in porous solution [31]. This phase is characterized by less molecular volume compared to natrone ($\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$), which form under nature carbonation. Changes in carbonate/bicarbonate equilibria under accelerated carbonization also can lead to considerable decreasing of pH unlike to nature conditions [32]. Mentioned processes lead to decalcification of C-S-H and C-A-S-H gel during activation of slag under accelerated carbonization that ensures formation of microcracks and decreasing of AASC strength [33].

Consistency is one more factor, which influences on corrosion resistance of AASC concrete. The high consistency fresh concrete is governed by practice [34, 35, 36]. This way, the increasing porosity and, consequently, permeability of hardened concrete can be caused by changes in its structure. This causes the increasing transport of aggressive ions in AASC concrete and risk of destruction with less protective properties to steel reinforcement [37, 38, 39, 40].

The well-known mean to increase corrosion resistance of plasticized AASC concrete, which is exploited under the influence of seawater, is application of salts of strong acids [19]. Application of these salts leads to higher crystallization of microstructure that causes its densification, enhanced porous structure, higher strength as well as corrosion resistance of AASC concrete [1, 41]. Such salts can be presented, for example, by chlorides, nitrates, sulfates of metals (Na, K, Mg, Zn, Mn, Ni, Cu), which can bind free alkalis in insoluble substances [12, 42].

The above results allow to predict the advanced corrosion resistance of AASC concrete under periodical external sea water attack due to complex of additives. Specified complex should decrease diffusion of atmospheric CO_2 due to densification of microstructure as well as restrict transport of aggressive ions from seawater as a result of their binding. At that, realistic assessment of the proposed decision needs the objective method to evaluate aggressive effect of environment with combination of expose classes XC4 and XS3. Specified environment affects marine reinforcement structure in fact.

Thus, the aim of this research was to investigate the action of salts of strong acids on acceleration of AASC crystallization as well as evolution of performance properties of reinforced AASC concrete, modified by CA, consisting portland cement, alumina cement and clinoptilolite, under cyclic drying-wetting in sea water.

RAW MATERIALS AND TESTING TECHNIQUES

Ground-granulated blast furnace slag (further, GGBFS) ($\text{CaO} - 47.30\%$; $\text{SiO}_2 - 39.00\%$; $\text{Al}_2\text{O}_3 - 5.90\%$; $\text{Fe}_2\text{O}_3 - 0.30\%$; $\text{MgO} - 5.82\%$; $\text{SO}_3 - 1.50\%$; $\text{TiO}_2 - 0.31\%$), basicity modulus= 1.11, content of glass phase= 84.0 %, specific surface= 450 m^2/kg (by Blaine), was used as aluminosilicate component of AASC.

Polyorganohydridosiloxane (liquid 136-41) was used for milling intensification of GBFS and stabilization of AASC properties. Content of the admixture was 0.1 by mass of GGBFS.

Soda ash (Na_2CO_3), in accordance with CAS 497-19-8, and sodium metasilicate ($\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$), in accordance with CAS 10213-79-3, dry state, were used as alkaline components.

Two reference compositions of AASC were used:

- based on soda ash (GBFS – 93.50 %, soda ash – 6.50 % (3.80 % by Na_2O));
- based on sodium metasilicate (GBFS – 88.50 %, sodium metasilicate – 11.50 % (3.36 % by Na_2O)).

The AASC concrete was modified by salts of strong acids in combination with CA.

The salts of strong acids were presented by:

- sodium phosphate $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in accordance with CAS № 7601-54-9;
- sodium nitrate NaNO_3 in accordance with CAS 7631-99-4.

The mentioned salts of strong acids were taken in a quantity 1.5 % in terms of anhydrous salt by mass of AASC.

The components of CA were presented by:

- portland cement CEM I 42,5 R in accordance with EN 197-1:2011;
- calcium aluminate cement ISTRA 40 in accordance with EN 14647:2005;
- natural zeolite (clinoptilolite) powder (by mass, %: $\text{SiO}_2 - 72.5$, $\text{Al}_2\text{O}_3 - 13.1$, $\text{Fe}_2\text{O}_3 - 0.9$, $\text{TiO}_2 - 0.2$, $\text{CaO} - 2.1$, $\text{MgO} - 1.07$, $\text{P}_2\text{O}_5 - 0.003$, $\text{K}_2\text{O} + \text{Na}_2\text{O} - 5.03$), fr. 0 - 0.1 mm, content of clinoptilolite $\leq 93.0\%$, porosity 54.0 %.

The content of CA was 10.0 % by mass of AASC.

Surfactant was presented by sodium lignosulphonate according to CAS 8061-51-6 ($\text{pH} \geq 8.5$), dosage 0.8 by mass of AASC.

Standard quartz sand according to EN 196-1 was used in AASC fine aggregate concretes (ratio AASC to sand = 1:3).

Aqueous solution of the salts, which simulates 99.90 % of ones in seawater, was used in investigations. The composition of aqueous solution, % by mass of mixture: $\text{NaCl} - 78.70$, $\text{MgCl}_2 - 9.80$, $\text{MgSO}_4 - 5.76$, $\text{CaSO}_4 - 3.75$, $\text{KCl} - 1.73$, $\text{CaCO}_3 - 0.29$. Total concentration of the salts was 35 g/l.

Cement pastes were prepared in Hobart mixer. Consistency of AASC pastes was determined according to EN 197-3:2005. Monitoring of the structure formation was carried out by X-ray diffraction (XRD), differential-thermal analysis (DTA) and electronic microscope with microanalyzer.

Fresh concretes were prepared in mixer «Raimondi Iperbet» (Italy). Consistency (workability) was determined by cone slump according to EN 12350-2:2019.

Corrosion resistance potential of AASC concrete under cyclic drying-wetting in sea water was determined using the author's methodology. Specimens of AASC concrete after 28 days of hardening under normal conditions ($t = 20 \pm 2^\circ\text{C}$, $\text{RH} = 95 \pm 5\%$) were stored under periodical wetting (immersion) for 3 hours in seawater and drying for 21 hours ($t = 105 \pm 3^\circ\text{C}$) under the influence of atmospheric concentration of CO_2 ($K \approx 0.04\%$). The performances of AASC concrete (strength, corrosion resistance coefficient, pore structure, ultrasonic pulse velocity, and carbonation) were determined in control term, i.e. after 90 cycles of wetting in sea water and drying. Protective properties of plasticized AASC concrete to steel reinforcement were evaluated by the state of embedded steel rebars.

Strength of AASC concrete was determined according to EN 196-1:2016 using specimens 40x40x160 mm.

Porosity of the AASC concrete was measured in accordance with the following method. The concrete cubes (100 mm) after 28 days of hardening ($t = 20 \pm 2^\circ\text{C}$, $\text{RH} = 95 \pm 5\%$) were dried up to a constant weight at $105 \pm 5^\circ\text{C}$. Then, the specimens were saturated with water at $t = 20 \pm 2^\circ\text{C}$ until a constant weight. The values of porosity were calculated using the obtained values of average density and water absorption.

Density of the structure was evaluated by ultrasonic pulse velocity of AASC concrete. The settings of the ultrasonic pulse velocity tester UKB-1M: indirect and direct transmission; longitudinal and surface waves; working frequency – 100 kHz.

Depth of carbonation was determined by qualitative reaction due to spraying of ethyl alcohol solution of phenolphthalein (concentration 0.1 %) on surface of AASC concrete specimens right after their breaking.

Corrosion resistance coefficient (K_{cr}) of AASC concrete was determined as ratio of flexural strength of specimens after 28 days of storing under normal conditions and further 90 cycles of drying-wetting in sea water to flexural of specimens after 28 days under normal conditions. Concretes can be classified as unresistant ($K_{cr} < 0.3$), low-resistant ($0.3 < K_{cr} < 0.5$), resistant ($0.5 < K_{cr} < 0.8$) and high-resistant ($K_{cr} > 0.8$) ones in corrosion mediums.

The state of the embedded steel rebars in the plasticized AASC concretes, was estimated according to the following method: the basic rebars, with a length of 120 ± 2 mm and a diameter between 3 mm and 6 mm, were embedded in $40 \times 40 \times 160$ mm AASC concrete specimens. The rebars were degreased with acetone and weighed, to an accuracy of ± 0.001 g, before embedding. After the specimens hardened under normal conditions, the basic bars were removed from AASC concrete and etched for 25 ± 5 min in 10 % hydrochloric acid solution, with an addition of urotropine (1 % by mass of the acid), to remove any remaining cement stone and corrosion products. The reference rebars, which were not embedded in the concrete, were weighed and etched simultaneously with the basic rebars. After etching, the basic and reference rebars were cleaned with distilled water and immersed in a fat solution of sodium nitrate for 5 min. The rebars were then wiped with filter paper, dried and weighed. The mean mass loss of the basic and reference rebars was calculated as the ratio of the mean differences of the mass of the rebars, before and after etching, to surface area. Mass loss was calculated as a difference between the mean loss of the basic and reference rebars.

RESULTS AND DISCUSSIONS

Crystallinity of microstructure

AASC Based on Soda Ash

The effects of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and NaNO_3 on the structure formation of AASC pastes were investigated. The choice of these salts as modifiers was caused by their known positive effect on porous structure, acceleration of crystallization, etc. [17, 41]. Besides, the mentioned salts are the most widespread corrosion inhibitors [18, 19, 43, 44].

By DTA the low-calcium hydrosilicates were identified in hydration products of the reference AASC after 28 d of hydration (FIGURE 1, curve 1). The formation of low-calcium silicate hydrates CSH(B) were confirmed by the endothermic effect at 185 °C (dehydration) and the exothermic effect at 840 °C (recrystallization into wollastonite).

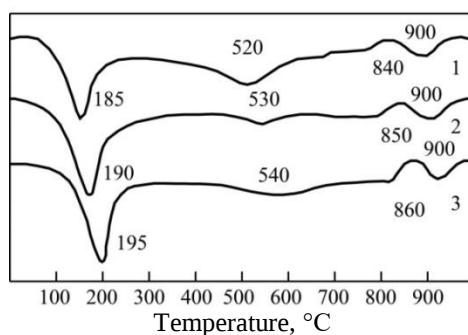


FIGURE 1. DTA of alkali-activated slag cement based on soda-ash after 28 d of hydration:
1 – the reference; 2 – modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$; 3 – modified by NaNO_3 .

The endothermic effects at 185 °C and 520 °C (stepped dehydration) and the exothermic effect at 840 °C (recrystallization into wollastonite) are typical for gyrolite $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$. The endothermic effect at 900 °C confirmed the presence of CaCO_3 . Specified phases are typical for AASC based on soda-ash [45].

Zeolite-like alkaline hydroaluminosilicates can also be predicted according to [11, 46]. However, these hydrates were not identified because of their submicrocrystalline state.

The application of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and NaNO_3 resulted in formation of low-calcium silicate hydrates with higher level of crystallization. This phenomenon was confirmed by relocation of effects to higher temperatures (FIGURE 1, curve 2, 3). The use of NaNO_3 ensured higher crystallization than $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$.

The electron microscopy confirmed advanced crystallization of microstructure while modification of AASC by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (FIGURE 2, b) and NaNO_3 (FIGURE 2, c) compared to the reference one without salt (FIGURE 2, a).

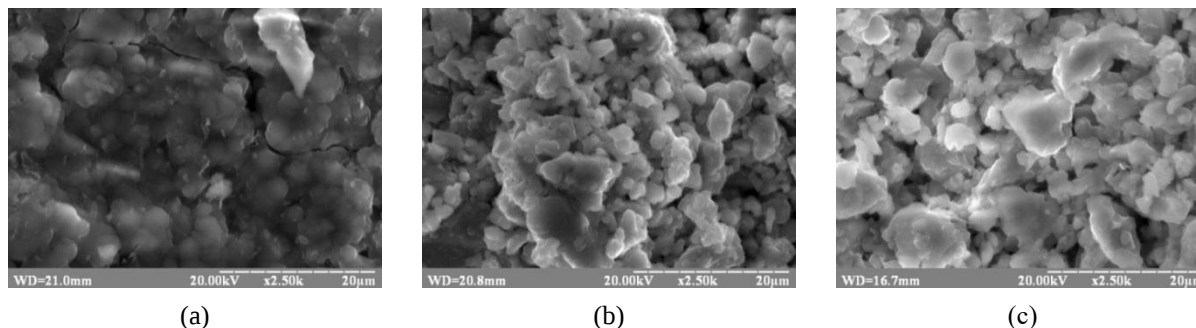


FIGURE 2. SEM images of 28 d hydrated alkali-activated slag cement based on soda-ash: reference (a), modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (b) and NaNO_3 (c).

AASC Based on Sodium Metasilicate

The presence of low-calcium silicate hydrates, such as CSH(B), and gyrolite (FIGURE 3, curve 1) after 28 d of hardening was confirmed by DTA. Modification of AASC by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and NaNO_3 ensured formation of CSH(B) and $2\text{CaO} \cdot 3\text{SiO}_2 \cdot 2\text{H}_2\text{O}$ with advanced crystallization (FIGURE 3, curve 2, 3). The displacement of the mentioned effects to higher temperatures verified this fact. The presence of the zeolite-like minerals may be also assumed.

The results of electron microscopy confirmed the advanced crystallization of modified AASC (FIGURE 4, b, c) compared with the reference one (FIGURE 4, a).

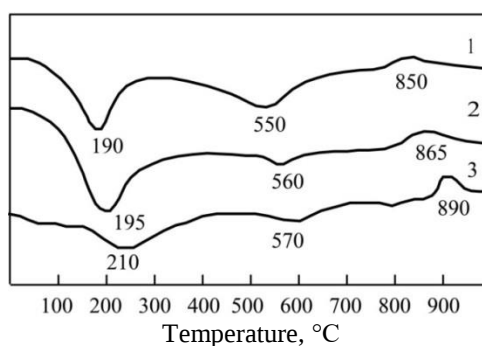


FIGURE 3. DTA of alkali-activated slag cement based on sodium metasilicate after 28 d of hydration: 1 – the reference; 2 – modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$; 3 – modified by NaNO_3 .

The above-mentioned hydration of AASC modified by NaNO_3 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ caused densification of structure and allowed to predict the advanced corrosion resistance potential of plasticized AASC concrete in aggressive environment due to application of specified salts in combination with CA «portland cement - alumina cement - clinoptilolite».

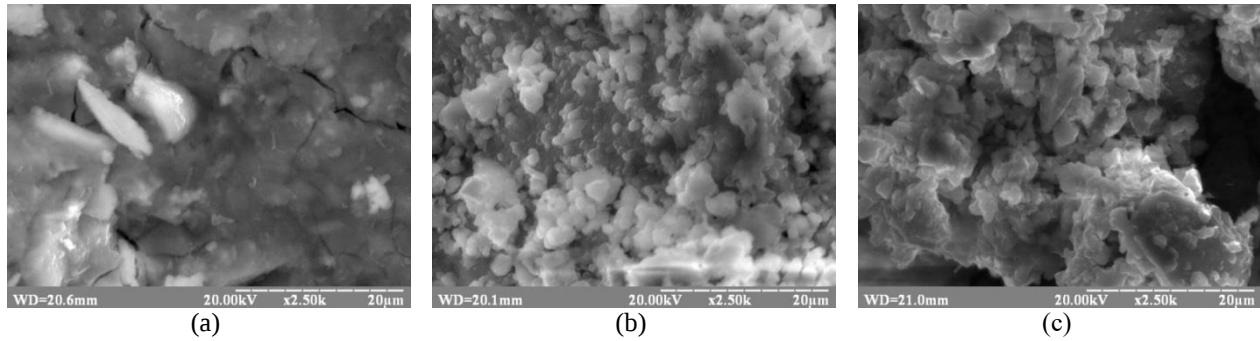


FIGURE 4. SEM images of 28 d hydrated alkali-activated slag cement based on sodium metasilicate: the reference (a), modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ (b) and NaNO_3 (c).

Performance Properties Of The Plasticized AASC Concretes Under Cyclic External Sea Water Attack

Effectiveness of mentioned salts of in combination with CA was tested while consistency class S4 [22] for AASC fresh concrete was provided. The performance properties of plasticized AASC concrete after 90 cycles of wetting in sea water and drying were fixed (Table 1).

TABLE 1. The performance properties of plasticized AASC concrete after 90 cycles of drying- wetting in sea water

Admixture	W/C Ratio	Compressive Strength, MPa	K_{cr}	Open Capillary Porosity, %	Conditionally Closed Porosity, %	Total Porosity, %
AASC concrete based on soda ash						
without salt (reference based on soda ash)	0.38	39.5	0.88	7.3	2.8	10.1
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.39	41.3	0.93	6.2	3.5	9.7
NaNO_3	0.39	42.4	0.96	5.8	4.1	9.8
AASC concrete based on sodium metasilicate						
without salt (reference based on sodium metasilicate)	0.37	51.3	0.92	5.0	2.4	7.4
$\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$	0.37	53.9	0.97	4.2	3.1	7.3
NaNO_3	0.37	56.2	0.99	3.3	3.7	7

Compressive Strength

The compressive strength of AASC concrete based on soda ash and modified by NaNO_3 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in combination with CA was by 4.6 % and 7.3 % higher than that of the reference one (table 1). The modified AASC concrete based on sodium metasilicate in the case of NaNO_3 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ was characterized by compressive strength 5.1 % and 9.6 % higher than the reference.

Corrosion resistance

The corrosion resistance coefficient (K_{cr}) of AASC concrete based on soda ash and modified NaNO_3 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in combination with CA was by 5.7 % and 9.1 % higher than that of the reference one without admixture of salt. In case of AASC based on sodium metasilicate application of NaNO_3 or $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ in combination with CA caused 5.4 % and 7.6 % higher the corrosion resistance coefficient than the reference.

Increase of compressive strength as well as corrosion resistance coefficient was caused by densification of structure due to advanced crystallization of AASC microstructure while application of salts of strong acids as

admixtures. The absence of strength losses due to crystallization pressure of gypsum $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ as a result of interaction of GGBFS with sulphates from sea water [47] can be attributed to the chemical binding of SO_4^{2-} -ions by CA [19].

Pore structure

The modification of AASC concrete based on soda ash by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA allowed to decrease the part of open capillary pores in total porosity from 72 % down to 64 % and 58 % respectively (FIGURE 5, a) and to increase the part of conditionally closed pores from 28 % up to 36 % and 42 % (FIGURE 5, b), accordingly, compared to the reference one. For AASC concrete, based on sodium metasilicate, application of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA caused lessening in the part of open capillary pores from 68 % down to 58 % and 47 % (FIGURE 5, a) and to increasing part of conditionally closed pores from 32 % up to 42 % and 53 % in total porosity (FIGURE 5, b), accordingly, compared to the reference one.

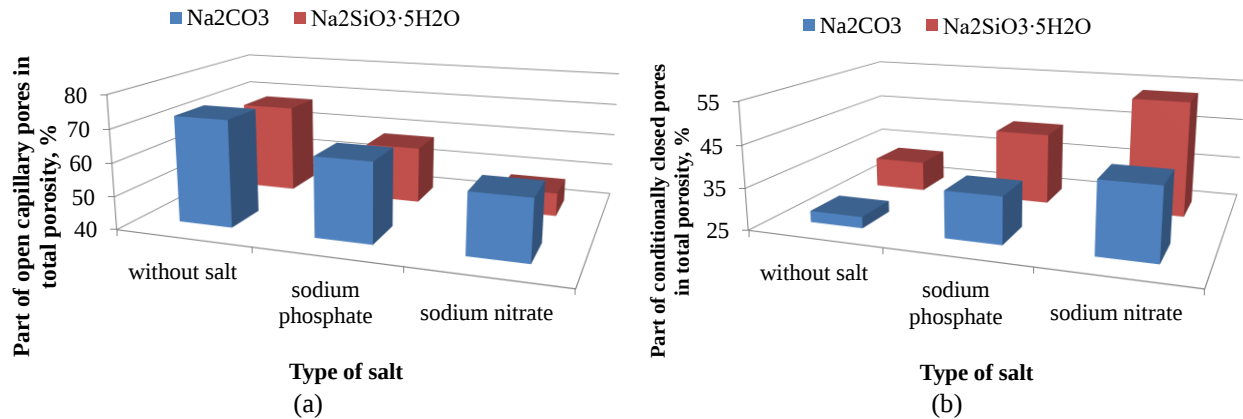


FIGURE 5. Specific volume of open capillary pores (a) and conditionally closed pores (b) in the plasticized alkali-activated slag cement concrete after 90 cycles of drying-wetting in sea water.

The enhanced pore structure of AASC concrete is reached due to filling of pore space both by gel phases with higher crystallinity due to action of the mentioned salts and by AFm phases (Kuzel's salt) as a result of chemical binding of Cl^- and SO_4^{2-} -ions from sea water due to the action of CA [19].

Ultrasonic pulse velocity

It was confirmed that the specified changes in the pore structure resulted in densification of the plasticized AASC concrete. Thus, the ultrasonic pulse velocity measured in the structure of AASC concrete based on soda ash and modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA was by 5.0 % and 16.7 % higher than that of the reference one (FIGURE 6). In case of sodium metasilicate, application of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA caused 6.1 % i 21.9 % higher ultrasonic pulse velocity than that of the reference one.

Carbonation

Application of mentioned salts in combination with CA caused higher resistance of plasticized AASC concrete to carbonation under cyclic drying-wetting in seawater. Specified effect was provided due to densification of the structure while binding of aggressive ions (Cl^- , SO_4^{2-} and CO_3^{2-}) [15, 19, 48] by CA and because of higher crystallinity of microstructure in presence of the mentioned salts.

The application of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA provided minor mean depth of carbonation in specimens of plasticized AASC concrete based on soda ash from 2.0 mm to 1.5 mm compared to the reference one. In case of sodium metasilicate, the mean depth of carbonation of plasticized AASC concrete modified by $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ or NaNO_3 in combination with CA was decreased from 2.0 mm to 1.0 mm compared to that of the reference one.

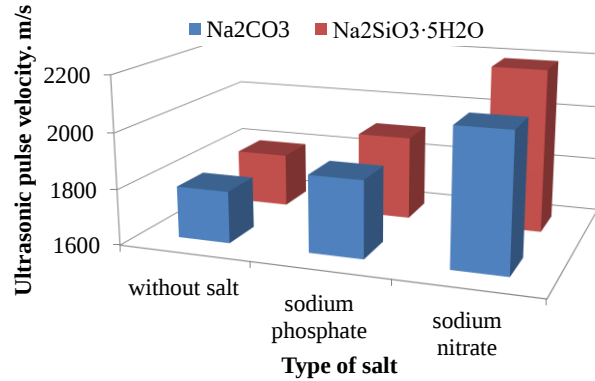


FIGURE 6. Ultrasonic pulse velocity in plasticized plasticized alkali-activated slag cement concrete after 90 cycles of drying-wetting in sea water

State of steel reinforcement

The effects of mentioned salts as admixtures in combination with CA «portland cement - alumina cement - clinoptilolite» on protective properties of plasticized AASC concrete were evaluated by mass losses of embedded steel rebars after 90 cycles of drying- wetting in sea water (Table 2).

TABLE 2. The state of the steel rebars embedded in AASC concretes 90 cycles of drying and wetting in sea water

Type of AASC Concrete	Mass Loss, g/m ²
reference AASC concrete based on soda-ash	4.18
AASC concrete based on soda-ash and modified by the CA	1.25
AASC concrete based on soda-ash and modified by the CA in combination with Na ₃ PO ₄ ·12H ₂ O	1.05
AASC concrete based on soda-ash and modified by the CA in combination with NaNO ₃	0.87
reference AASC concrete based on sodium metasilicate	3.85
AASC concrete based on sodium metasilicate and modified by the CA	1.03
AASC concrete based on sodium metasilicate and modified by the CA in combination with Na ₃ PO ₄ ·12H ₂ O	0.84
AASC concrete based on sodium metasilicate and modified by the CA in combination with NaNO ₃	0.67

The values of mass loss were in compliance with mandatory requirements, i.e. not more than 10 g/m² in accordance with [49]. For AASC concrete, based on soda ash or sodium metasilicate, application of CA caused 3.3 times and 3.7 times lesser mass losses than for the reference ones. The restriction of aggressive ions (Cl⁻, SO₄²⁻, CO₃²⁻) transport into plasticized AASC concrete caused its advanced protective properties. The obtained results correlate with ones, concerning the effectiveness of specified CA [19]. Mitigation of ions transport from aggressive environment was caused by their chemical adsorption by gel-like phases, chemical binding in AFm phases, which were formed due to co-acting of portland cement and calcium aluminate cement in hydration process, as well as because of occluding by zeolite-containing admixture and hydrates presented by alkaline hydroaluminosilicates.

Application of specified salts together with CA ensured higher protective properties of AASC concrete. In case of AASC concrete, based on soda ash, application of Na₃PO₄·12H₂O or NaNO₃ in combination with CA caused 1.19 times and 1.44 times lesser mass losses of the embedded steel rebars compared to those of analogues without admixture of salts. For AASC concrete, based on sodium metasilicate, application of Na₃PO₄·12H₂O or NaNO₃ in combination with CA resulted in 1.23 times and 1.54 times smaller mass losses.

CONCLUSION

1. The acceleration effects of salts of strong acids (Na₃PO₄·12H₂O and NaNO₃) on crystallization of hydrates of alkali-activated slag cement were investigated and the evolution of performance properties of reinforced plasticized

concrete modified by these salts in presence of multifunctional complex additive «portland cement - alumina cement - clinoptilolite» under cyclic wetting in sea water and drying under the influence of atmospheric CO_2 has been shown as well. Increasing crystallinity of hydrates under the action of the mentioned salts along with binding of aggressive ions (Cl^- , SO_4^{2-} and CO_3^{2-}) by the multifunctional additive determine densification of the concrete, that in turn limits CO_2 diffusion and mitigates transport of aggressive ions from sea water.

2. The higher effectiveness of the salts in case of sodium metasilicate compared to soda ash, used as alkaline components, is due to higher volume of gel-like phases with advanced crystallization during hydration of alkali-activated slag cement. The change of anion in alkaline component from carbonate to silicate ensures the lower open capillary porosity (by 32.3...42.1 %) and the higher conditionally closed porosity (by 9.8...11.4 %) in alkali-activated slag cement concrete after 90 cycles of drying-wetting in sea water depending on salt admixture cation, i.e. PO_4^{3-} or NO_3^- . The perfection of pore structure is accompanied by higher density (by 1.5...5.0 %), major strength (by 30.5...32.5 %), greater coefficient of corrosion resistance (by 3.1...4.3 %) of plasticized alkali-activated slag cement concrete as well as by lower weight losses of the embedded steel rebars (by 20.0...23.0 %).

3. The effectiveness of proposed modification was confirmed by performance properties of plasticized alkali-activated slag cement concrete after 90 cycles of drying-wetting in sea water. Application of the mentioned salts as admixtures in combination with the multifunctional complex additive ensures the lower open capillary porosity (by 15.1...34.0 %) and the higher volume of conditionally closed pores (by 25.0...54.2 %) of the concrete compared to the not modified reference one, depending on anion in sodium salts of strong acids (phosphate, nitrate). These identified effects are accompanied by higher density (by 5.0...21.9 %), advanced strength (by 4.6...9.6 %) and coefficient of corrosion resistance (by 5.4...9.1 %) as well as by lower rate of carbonation (by 25.0...50.0 %). The 4.0...5.7 times lesser mass losses of embedded steel rebars confirm the enhanced protective properties of plasticized alkali-activated slag cement concrete obtained due to its modification.

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