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# Effect of Technological Factors on Freeze-Thaw Resistance of Alkali-activated Slag Cement Concrete in NaCl Solution

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**Abstract.** The application of alkali-activated slag cement concrete (hereinafter AASC concrete) is relevant for building constructions which are exploited in aggressive environments with exposed class XF4. It is due to increased freeze-thaw resistance of AASC concrete in water solutions of salts if compared with portland cement concrete. The aim of this work was to investigate the effects of technological factors on porous structure and freeze-thaw resistance of plasticized AASC concrete in NaCl solution. It was shown that increasing of fresh concrete consistency from class S1 up to class S4 due to plasticization by complex admixture "polyorganohydrosiloxane - sodium lignosufonate - polyethylene glycol" as well as application of alkaline component in dry form, in contrast to liquid form, ensures negative changes in porous structure of AASC concrete. These changes cause decreasing of freeze-thaw resistance from mark F500 down to F200. It was revealed that hardening of plasticized AASC concrete under normal conditions (t =  $20\pm2$  °C, RH =  $95\pm5\%$ ), compared with hardening in water or under steam curing (t =  $85\pm5$  °C), ensures more effective porous structure which causes maintained freeze-thaw resistance of F300 in contrast to F200 and F250 agreeable. Effective technological decisions for advanced freeze-thaw resistant of AASC concrete were determined.

#### **INTRODUCTION**

Ensuring the durability of constructions is current world tendency of building industry. This fact can be confirmed by numerous scientific researches concerning durability of structures which are exposed to aggressive environments (atmospheric, chemical, abrasive, etc.) [1, 2, 3, 4, 5, 6]. It's well known that the durability of concrete structures cannot be evaluated using only one performance. The most important properties of concrete for a specified case are used for evaluation of durability depending on destination and environment [7]. Resistance of concrete to freeze-thaw cycles and sodium chloride scaling is one of the criteria. The mentioned environment can be classified as exposure class XF4 (road and bridge decks exposed to deicer agent, splash zones of marine structures, etc.) according to [8]. It's well known that NaCl is the most demanded salt among deicers [7, 9, 10] as well as the predominant one in seawater [11, 12]. The above results have been defined the choice of sodium chloride as corrosion environment to evaluate the durability of concrete to freeze-thaw resistance.

Alkali-activated slag cement (further, AASC) is the most perspective one to ensure advanced service life of concrete structures. The ecological benefits of AASC are caused not only by effective consumption of raw recourses as well as by reduction of  $CO_2$  emission due to application of by-products or waste products [13, 14, 15], but also by possibility to utilize manufacturing waters in safety building materials [16]. In general cases, AASC materials are characterized by advanced performances in aggressive environments such as corrosion resistance [17], sulfate resistance [18] and freeze-thaw resistance [19], including salt scaling resistance [20], in comparison with analogues based on traditional clinker cements.

Increased freeze-thaw resistance of AASC concrete in NaCl solution is caused by several factors, including features of hydrated phases. It's known, that interaction of sodium chloride with hydration products of portland cement ensures destruction of concrete. Particularly, decreasing of  $Ca(OH)_2$  in hydration products in consequence of leaching as well as exchange reaction with sodium chloride NaCl with formation of  $CaCl_2$  leads to decreasing of

Reliability and Durability of Railway Transport Engineering Structure and Buildings AIP Conf. Proc. 2684, 040011-1–040011-8; https://doi.org/10.1063/5.0120034 Published by AIP Publishing. 978-0-7354-4501-7/\$30.00 basicity of highly-calcium hydrosilicates (the main hydration products of portland cement) [7, 21]. Besides, participation of sodium chloride in hydration processes of portland cement ensures transformation of monosulfate  $3CaO\cdotAl_2O_3\cdot CaSO_4\cdot 10H_2O$  to Friedel's salt  $3CaO\cdotAl_2O_3\cdot CaCl_2\cdot 10H_2O$  (AFm-phase) as well as to secondary ettringite  $3CaO\cdotAl_2O_3\cdot 3CaSO_4\cdot 32H_2O$  (AFt-phase) [22, 23]. Formation of secondary ettringite can cause destruction of concrete due to crystallization pressure on porous sides while volume increases. Advanced freeze-thaw resistance of AASC concrete in solution of NaCl is caused by the absence of portlandite in hydration products [13] as well as by the absence of ettringite or due to changes in its morphology in highly-alkaline hydration medium from filamentous, needle to prismatic, plate shape [24]. Solution of NaCl can also provide steel reinforcement corrosion in constructions in consequence of transport of aggressive Cl<sup>-</sup> ions in concrete [25]. AASC concrete is characterized by increased protective properties to steel reinforcement due to high content of gel-like hydrosilicates and formation of alkaline hydroaluminosilicates (analogues of natural zeolites), which can bind Cl<sup>-</sup> ions [13, 26, 27]. The enhancement of steel reinforcement protection in AASC concretes, obtained from high consistency mixes, was proposed [2, 28, 29, 30].

Increased freeze-thaw resistance of AASC concrete compared with portland cement concrete is caused also by influence of alkaline component on decreasing of freezing temperature of solution in porous space [13, 31]. Well known, that increasing of water volume while formation of ice is 8...9 % ensures pressure on side of pores and causes destruction of concrete [7]. However, freezing of liquid in pores occurs at temperatures below 0 °C because of solution in pores of stone is not pure water and contains soluble substances (alkalis, oxides and hydroxides of alkaline-earth metals, sulfates, etc.) [32]. Increased content of compounds of alkaline metals in porous solution causes increased freeze-thaw resistance of AASC concrete compared with portland cement [13, 33].

The peculiarities of porous structure cause advanced freeze-thaw resistance of AASC concrete. In common case, the porous structure of cement stone is presented by gel (1.5 to 10.0) nm, capillary (0,01...1,00 nm) and closed (10 to 500  $\mu$ m) pores [34]. At that, freeze-thaw resistance and accordingly durability of concrete are caused mainly by capillary porosity in contrast to strength of concrete, which depends on total porosity [7]. Capillary effect, which is caused by dependence of freeze point from the size of pores, causes the influence of porous structure on freeze-thaw resistance of concrete. Water firstly freezes in capillary pores while freezing whereas one remains in liquid form in smaller gel pores. Thermodynamic unbalanced state, which causes motion force for removal of water from smaller to larger pores, occurs because the pressure under water is higher than under ice [7]. Increased gel phase while decreased volume of capillary pores compared with portland cement [35, 36] causes advanced freeze-thaw resistance of AASC concrete.

Porous structure of AASC concrete in one's turn is caused by technological factors such as consistency of fresh concrete, form (state) of alkaline component, conditions of hardening, etc. The modern requirements to consistency fresh concretes are governed by practice [37, 38, 39]. Consistency of fresh concrete is regulated by surfactants [40]. Principles for choice of surfactants as the bases of complex admixtures were proposed [40, 41, 42, 43]. Effectiveness of complex admixture «polyorganohydrosiloxane - sodium lignosufonate - polyethylene glycol» for AASC concrete was determined while providing both electrostatic and steric mechanism of plasticization [40]. However, increasing of consistency causes negative changes in concrete structure, which lead to increasing of porosity and consequently less freeze-thaw resistance.

The features of AASC technology, which are caused by different aggregative state of alkaline components and chemical admixtures (dry form or liquid form), provide various intensity in formation of hydrosilicate gel and, consequently, different performances of AASC concrete [13, 40]. Thus, the aim of this research was to investigate the effects of technological factors on porous structure and, consequently, freeze-thaw resistance of plasticized AASC concrete in solution of sodium chloride.

#### MATERIALS AND TESTING TECHNIQUES

Aluminosilicate components of AASC were presented by:

- ground-granulated blast furnace slag (further, GBFS) (CaO – 47.30 %; SiO<sub>2</sub> – 39.00 %; Al<sub>2</sub>O<sub>3</sub> – 5.90 %; Fe<sub>2</sub>O<sub>3</sub> – 0.30 %; MgO – 5.82 %; SO<sub>3</sub> – 1.50 %; TiO<sub>2</sub> – 0.31 %), basicity modulus= 1.11, content of glass phase = 84.0 %, specific surface= 450 m<sup>2</sup>/kg (by Blaine);

- Portland cement CEM I 42,5 R (CaO - 64.13 %; SiO<sub>2</sub> - 25.14 %; Al<sub>2</sub>O<sub>3</sub> - 5.17 %; Fe<sub>2</sub>O<sub>3</sub> - 4.12 %; MgO - 0.88 %; SO<sub>3</sub> - 1.27 %; K<sub>2</sub>O+Na<sub>2</sub>O - 0.99 %).

The alkaline component (Na<sub>2</sub>CO<sub>3</sub> 33 % by mass + Na<sub>2</sub>O·SiO<sub>2</sub>·5H<sub>2</sub>O 67 % by mass) was introduced into a concrete mixer in dry form (powder) or in liquid form (water solution,  $1180 \text{ kg/m}^3$ ) in such a way that its content in

the concrete (as  $Na_2O$ -equivalent) would be equivalent. The contents of alkali metal compounds (alkaline activators) were taken over 100 % of the aluminosilicate components in accordance with [31].

A river silica sand (fineness modulus 1.8) was used. A granite gravel with grain sizes between 5...10 mm (fr. 5/10) and 10 to 20 mm (fr. 10/20) was used as coarse aggregate.

Reference composition of AASC concrete was used according to [44], while application of alkaline component in dry form or in liquid form, kg/m<sup>3</sup>: AASC - 350; silica sand - 740; granite gravel: 330 (fr.5/10) and 780 (fr.10/20).

AASC concrete was modified by complex admixture (CPA) with the main plasticizing effect. CPA was presented by the components:

- sodium lignosulfonate (further, LST) according to CAS 8061-51-6 ( $pH \ge 8.5$ );

- waterproofing agent based on ethyl hydro-siloxane polymer (further, WA) according to CAS 63148-57-2;

- surfactant based on polyether (polyethylene glycol "PEG-400", JSC "Barva") according to CAS 25322-68-3.

WA was used to intensify grinding and to prevent sorption of water from air and to retain the properties of AASC. Contents of CPA components, % by mass of AASC, were: LST -1.00, WA -0.06, polyethylene glycol -0.50.

The AASC components and a half of aggregates together with LST and mixing liquid (water or solution of the alkaline component) were properly mixed in mixer for 1 min, then the remaining part of aggregates was added and mixed together for the next 2 min.

Consistency (workability) was determined by cone slump according to the Ukrainian National Standard [45].

The prepared concrete mixtures were placed into moulds and compacted under vibration at a vibrating table, then covered with a plastic film and placed into a chamber for hardening under normal conditions ( $t = 18\pm2^{\circ}C$  and RH = 95±5%), where it was stored for 2 days until demoulding. A part of the specimens after taken from the moulds was placed for further hardening in water, the other part was left for hardening under normal conditions, and some specimens were steam cured at t = 85±5°C.

Water absorption and porosity of the AASC concretes were tested in accordance to national standard of Ukraine [46]. The concrete cubes (100 mm) after 28 days of hardening were dried up to a constant weight at t=  $105\pm10$  °C. Then, the specimens were saturated with water until a constant weight would be obtained at t=  $20\pm2$  °C. The values of porosity were calculated from the values of average density and water absorption.

Freeze-thaw resistance of AASC concrete (Fig.1) was studied according to the third test method prescribed by the national standard of Ukraine [46]. According to this accelerated method, the concrete cubes (100 mm) were saturated with a 5 % solution of NaCl at  $t= 18\pm2$  °C and after that were subjected to freezing at t= -50 °C. Thawing was done in a 5 % solution of NaCl. A class of concrete in freeze-thaw resistance was designated as a number of alternate freezing and thawing at which a mean compressive strength decreased by no more than 5%. The freeze-thaw resistance of concrete was assessed by the correspondence between permissible number of freezing-thawing cycles by the mentioned method and by the first (basic) method prescribed in mentioned standard.



**FIGURE 1.** A freezing chamber for testing freeze-thaw resistance

#### **RESULTS AND DISCUSSIONS**

The porous structure and corresponding values of freeze-thaw resistance of AASC concrete were compared. AASC concrete was obtained with different consistency (Table 1, Fig. 2-4): class S1 (reference) and class S4 (plasticized by CPA). It was revealed, that consistency of fresh concrete is important factor of porous structure. Thus, increasing of consistency from class S1 up to class S4 while application of alkaline component in *dry form* ensured deterioration of porous structure, i.e. increasing of volume of open capillary pores by 9.1 % (Fig.2, a) and decreasing volume of conditionally closed pores by 41.2 % (Fig.2, b). Less volume of conditionally closed pores

determined formation of minor dense and more permeable structure, which caused deterioration of physical and mechanical properties of AASC concrete, including freeze-thaw resistance decrease from mark F400 down to mark F200 (Fig.3, a). Application of alkaline component in *liquid form* provided the similar dependence. Changes in consistency from class S1 up to class S4 ensured increasing volume of open capillary pores by 14.3 % and corresponding decreasing of conditionally closed pores by 20.7 % (Fig.2, b), that was factor of reduction of freeze-thaw resistance from mark F500 down to mark F300 (Fig.3, b).

	consistency								
Nº	Strength class of concrete	W/C (S/C)	Consistency, cm	Water absorption W <sub>m</sub> , %	Changes in mass, %	Changes in strength, %	Mark of freeze-thaw resistance		
Dry form of alkaline component									
1-1	B35	0.36	18	3.39	+1.05	-9.0	F200		
1-2	B40	0.34	2	3.12	+0.8	+0.5	F400		
Liquid form of alkaline component									
2-1	B35	0.34	20	3.70	+0.04	-1.0	F300		
2-2	B40	0.32	3	2.88	+0.19	-5.7	F500		

<b>TABLE 1</b> . The porous	structure and freeze-thaw resist	ance of AASC concrete ve	ersus form of alkaline component and
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Note. The specimens hardened in water

Specified changes in porous structure and freeze-thaw resistance of AASC concrete was caused by increasing water/cement ratio (W/C) from 0.34 up to 0.36 or solution/cement ratio (S/C) from 0.32 up to 0.34 while application of alkaline component in dry form or liquid form agreeably. Less freeze-thaw resistance of AASC concrete was also caused by increased air-entraining due to CPA. That is explained by decreasing of surface tension between water and air [47, 48].



FIGURE 2. The influence of consistency and form of alkaline component on the volumes of open capillary pores (a) and conditionally closed pores (b) of AASC concrete

Thus, increasing consistency caused negative effect on freeze-thaw resistance of AASC concrete, that is in dissonance with the modern requirements to high consistency of fresh concretes.

Application of alkaline component in dry form, in contrast to liquid form, ensured higher volume of open capillary pores by 5.0 % and 10.0 % at consistency classes S1 and S4 agreeably. Lack in filling intensity of porous space by hydrosilicate gel caused this phenomenon (Fig.2, a). Decreasing volume of conditionally closed pores by 58.0 % and 43.3 % consequently occurred (Fig.2, b). Specified changes in porous structure ensured decreasing tendency in freeze-thaw resistance of AASC concrete from F500 down to F400 (Fig. 4, a) as well as from F300 down to F200 (Fig. 4, b).

Obtained regularities confirm expediency of alkaline component exactly in the liquid form, that is on contrary to modern requirements concerning production of AASC's namely under «all-in-one» technology [40].

Normal conditions for hardening of AASC concrete was more advisable if compared with hardening in water or under steam curing in the view of formation of effective porous structure (Table. 2).



FIGURE 3. Open capillary porosity and freeze-thaw resistance of AASC concrete vs. form of alkaline component: dry form (a), liquid from (b)



FIGURE 4. Open capillary porosity and freeze-thaw resistance of the AASC concrete vs. consistency: class S1 (a), class S4 (b)

N⁰	Conditions of hardening	Strength class of concrete	W/C	Consistency, cm	Water absorption W <sub>m</sub> , %	Changes in mass, %	Changes in strength, %	Freeze-thaw resistance	
	Dry form of alkaline component								
3-1	Water	B35	0.36	18	4.0	`- 0.12	-1.68	F200	
3-2	Steam curing	B35	0.36	19	4.2	+ 0.16	+1.85	F250	
3-3	Normal conditions	B35	0.36	19	4.1	+ 0.12	+4.60	F300	

TABLE 2. Porous structure and freeze-thaw resistance of AASC concrete versus conditions

Porous structure of plasticized AASC concrete, at consistency of class S4 and after hardening during 28 d under normal conditions, was characterized by decreased volume of open capillary pores by 5.0 % and 1.3 % as well as by increased volume of conditionally closed pores by 35.7 % i 20.0 % compared with analogues under water or steam curing (Fig.5). Specified changes in porous structure contributed to formation of AASC concrete with more dense and impermeable structure, which is able for self-healing. This phenomenon provided advanced freeze-thaw resistance mark F300 in contrast to marks F200 i F250 of analogues (Fig.6).

FIGURE 5. Porous structure of AASC concrete vs. conditions

FIGURE 6. The volume of open capillary pores and freeze-thaw resistance of AASC concrete vs. conditions of hardening

#### CONCLUSION

1. Influence of technological factors on peculiarities of porous structure and accordingly freeze-thaw resistance of AASC concrete in solution of sodium chloride was revealed. The most significant technological factors, which determine performances of structure, durable in environment with exposure class XF4, were consistency of fresh concrete, aggregate state of alkaline component and hardening conditions.

2. It was shown, that increasing of fresh concrete consistency from class S1 up to class S4 by means of chemical modification while application of alkaline component in dry form caused decreasing of freeze-thaw resistance of AASC concrete in solution of NaCl as a result of negative changes in porous structure. Thus, application of CPA «polyorganosiloxane - sodium lignosufonate - polyethylene glycol» ensured increasing open capillary porosity within (5.0...14.3) % and decreasing of conditionally closed porosity within (20.7...58.0) % that was accompanied by less freeze-thaw resistance of AASC concrete within (20.0...50.0) %.

3. It was revealed, that negative effect of plasticization can be compensated while dry form of alkaline component and sustainable durability of AASC concrete can be ensured under freeze-thawing resistance in solution of NaCl due to appropriate temperature-humidity conditions of hardening. Freeze-thaw resistance of plasticized AASC concrete, while hardening in normal conditions in contrast to hardening in water or under steam curing, increased up to 1.3...1.5 times in consequence of reduced by 5.0 % open capillary porosity and enlarged by 36.0 % volume of conditionally closed pores.

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