Microstructure Changes in Hardened Cement Paste after Freezing – Thawing Cycles

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This article analyses the results of the freezing – thawing with deicing salt test where changes in the microstructure of the surface layer in contact with aggressive environment of hardened cement paste produced with and without sodium silicate (hereinafter NTS) admixture were observed after freeze-thaw cycles in the presence of calcium chloride. After 56 cycles of freezing – thawing with deicing salt test micro-cracks and cavities were observed in the microstructure of the surface layer of hardened cement paste with and without NTS admixture. In the case of hardened cement paste with NTS admixture changes in the microstructure of the surface layer are less prominent: the number and size of cavities and micro-cracks are smaller. The test revealed that compressive stress, which before freezing – thawing with deicing salt test was very similar in hardened cement paste with and without NTS admixture (85.4 MPa and 82.8 MPa respectively), changed after 56 cycles of freezing – thawing with deicing salt test as follows: reduced by 39.5 % in concrete without NTS admixture and increased slightly (2.5 %) in hardened cement paste with NTS admixture. Based on the test results the authors arrived at the conclusion that sodium silicate solution can be effectively used to extend the useful life of hardened cement paste exposed to freeze-thaw cycles and affected by $CaCl_2$.
Keywords: hardened cement paste, microstructure, freeze-thaw cycle, sodium silicate, calcium chloride.
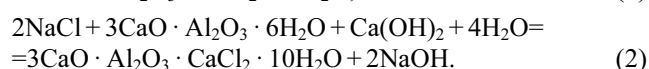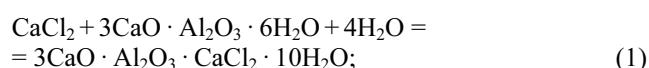
INTRODUCTION

When concrete is exposed to cyclic freezing and thawing with de-icing salt the frost salt scaling (FSC) of concrete surface occurs.

The results of investigations of frost salt scaling in the presence of saline water [1 – 5] revealed that the reason of this defect is the cracking of the brine ice layer formed on the surface of hardened cement paste. It is explained [1 – 4] that cracks formed in brine ice layer having good adhesion to the surface of concrete penetrate into the substrate, resulting in near-surface damage of concrete. The concentration of salt in the ice layer causing its cracking and concrete defects must be low. It has been shown [4] that maximum damage is caused by 3 % salt and that FSC increases with increased thickness of the ice layer on the surface of concrete and with the increase of stiffness. It has been noted [2] that significant FSC occurs at salt concentration in the ice layer of a few per cent but when the salt concentration exceeds 6 % the ice does not form a rigid enough structure to result in significant stress, so no damage occurs. There is no consensus on the salt type influence on concrete damage. Some reports [1] indicate that FSC does not depend on the type of salt, or the influence of salt type is not evident [2, 4], while others [3, 5] report that $CaCl_2$ salt has the most damaging effect compared to other salts used in the investigation, including NaCl.

Analysis of the results of research work [1, 3] show that damaging impact of various salts is not a simple process and that this process is influenced by the chemical composition of salts, by diffusion of salts forming ions onto the hardened matrix and by the products of its chemical interaction with the components of hardened cement matrix.

As previously reported [1] the reason of concrete FSC is not only the cracking of small amount of salt (solute) having ice layer formed on the surface of concrete but also the expansion of paste resulting from the precipitation of Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$). The authors note that crystallization pressure caused by the growth of Friedel's salt crystals cause significant expansion of the paste and results in high stresses on local scale near ice/paste boundary. This can substantially weaken the concrete surface layer and facilitate scaling.

It is known that Friedel's salt (F_s) in concrete can be formed during chemical interaction of chloride salt with calcium aluminate hydrate. Reaction schemes can be found in a series of research articles [6, 7]. The schemes of reactions can be described as follows:

$$CaCl_2 + 3CaO \cdot Al_2O_3 \cdot 6H_2O + 4H_2O =$$
$$= 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O; \tag{1}$$

$$2NaCl + 3CaO \cdot Al_2O_3 \cdot 6H_2O + Ca(OH)_2 + 4H_2O =$$
$$= 3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O + 2NaOH. \tag{2}$$

Some authors [3] investigated the damaging impact of five deicing chemicals – calcium chloride ($CaCl_2$), calcium chloride with corrosion inhibitor ($CaCl_2$-inhib), sodium

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chloride (NaCl), potassium acetate (K Acetate) and an agricultural deicing product (Agr-deicing) – on concrete produced using the cement of composition C_3S – 53.09 %, C_2S – 19.44 %, C_3A – 6.04 %, C_4AF – 10.50 %. Freezing-thawing and wetting-drying exposure conditions were considered. Investigation results show that various deicing chemicals penetrated into a given paste and concrete at different rates resulting in different degrees of damage. Among the deicing chemicals tested two calcium chloride solutions had the most adverse effects, where was as follows: loss of sample weight and strength, salt crystallization and precipitation, leaching of cement hydration products (CH and ettringite), chemical reaction between deicing chemicals and concrete materials by forming calcium aluminum chloride hydrate $Ca_8Al_4O_{12}Cl_2SO_4 \cdot 24H_2O$ (Ca-Al-Cl-S hydrate) in near surface layers. It was estimated that in the case of $CaCl_2$ the diffusion of chloride ions was faster than in the case of NaCl. Potassium acetate caused minor scaling, associated with alkali carbonation on the surface layer of concrete. Chemical penetration and scaling damage of the paste and concrete was the least with Agr-deicing product.

As previously reported [3] the damage of concrete is related with the diffusion (migration) of deicing chemical ions into the matrix, the leaching of calcium hydroxide (CH) and chemical alterations in concrete. The relationship between chloride ions diffusion and CH dissolution was also estimated [8]. Conclusions were made [9] that chloride ions migration coefficients are influenced by the capillary pore volume and by the connectivity or pores in the specimens. It was also stated that the migration coefficient of chloride ions of non-steady state is higher than the steady-state and the possibility that part of chloride ions is bound to the hydration products and block some pores in the steady-state and reduce the steady-state migration coefficient was noted, but others [10] have concluded that the decisive parameter for chloride resistance is the permeability influenced by pore size characteristics while the chloride binding is less important.

Chloride ions migration can be slowed down by enhancing the matrix density, forming the pore structure that is less permeable for chloride ions diffusion. Matrix density was increased and less permeable pore structure was achieved by adding superplasticizers, decrease of w/c ratio [10], by adding silica fume [11], the granulated blast furnace slag [12]. At early exposure period the chloride ions diffusion can be decreased by adding sulphate ions, because at its presence gradual formation of ettringite crystals in early period leads to compacted microstructure of concretes surface layer and decrease of ingress of chloride into concretes for some time [7]. The chloride ions diffusion can be slowed down as well by creating the concrete skin effect [13, 14]. The skin effect may be created by rendering concrete surface by mortar layers [13], by using the curing methods that ensure the formation of dense membrane on the surface of concrete [14].

The analysis of the results of the abovementioned investigations of concrete resistance to chloride ions attack show that in this respect a very important role is played by concrete surface layer resistance to chloride ions diffusion

and to leaching compounds from this layer and that have been efforts to slow the diffusion.

No research studies investigating into the possibilities of enhancing the resistance of the surface layer of concrete to chloride diffusion by using sodium silicate solution were found. This study investigates the possibility of using NST admixture in concrete manufacturing to increase concrete's resistance to freeze-thaw cycles (in the presence of $CaCl_2$ salt). This possibility is explained by investigating the resistance of the surface layer of concrete matrix (hardened cement paste) containing sodium silicate admixture focusing on the explanation of the changes in the microstructure of the surface layer of hardened cement paste.

MATERIALS AND TEST METHODS

Test hardened cement paste specimens were produced from Portland cement CEM I 42.5 N manufactured by AB "Akmenės cementas". The parameters of the cement paste of normal thickness were as follows: water content 24.2 %, specific surface 360 m^2/kg, particle density 3110 kg/m^3, bulk density 1240 kg/m^3. Specific surface of the cement was determined by air-permeability method using apparatus PSCH-4 (LST EN 196-6; 2004).

The following admixtures were used to produce hardened cement paste specimens: a) superplasticizer (concentration of dry particles 36.1 %, pH 4.4, electrical conductivity 1.480 mS/cm) based on modified polycarboxylic ether; b) sodium silicate water solution (NST – $Na_2O \cdot nSiO_2$), having silicate module 3.3, dry $Na_2O \cdot nSiO_2$ and water ratio 60:40, and the average density value of liquid glass solution of 1382 kg/m^3. The two admixtures were added to 0.5 % of cement weight. W/C ratio was constant (0.27) during the test.

Cement was added by mass, whereas water and chemical admixtures were added by volume. Superplasticizer and NST admixtures in the form of solution were added to cement together with water.

Cement pastes were mixed in a forced mixing blender by using dry materials and following test requirements given in LST EN 196-1.

Hardened cement paste specimens were formed in impermeable prism moulds ($40 \times 40 \times 160$ mm). Settled specimens were left in moulds for 24 hours and protected from drying with polyethylene film. After 24 ±2 hours the specimens were taken out of the moulds and placed into a tub filled with tap water of 20 °C ± 2 °C. The specimens were left to harden in water for 28 days.

On day 20 three 40 mm-thick samples were cut out from each prism perpendicularly to the test surface to determine the weight of the matter peeled away from the surface of hardened cement paste prisms during the established number of freeze-thaw cycles. The cut surface was regarded as test surface.

Prepared samples were washed with tap water and returned to the water tub. After 28 days of ageing the samples were taken out of the water tub. All surfaces of the sample except for the test surface were covered with 3 mm-thick rubber sheet resistant to salt solutions used in the test. The edge of the rubber sheet was 20 mm above the test surface. The connection of the test surface between the

sample and the rubber sheet was sealed by silicon strip resistant to aggressive environment.

The compressive strength of the samples was determined in accordance with LST EN 196-1:2005 when the samples were taken out of water after 28 days of hardening in water of 20 °C ±2 °C. Before the compressive strength test the samples were kept covered in humid environment.

Prior to starting the cyclic freezing and thawing test natural carbonation of the test surface was enabled by leaving the samples in ambient air. 5 % solution of technical calcium chloride ($CaCl_2$) salt and tap water was used as freezing medium applied onto the surface of the samples. Freeze-thaw testing of hardened cement paste samples in the presence of $CaCl_2$ salt was started by pouring a 3 mm layer of 5 % $CaCl_2$ solution onto the test surface of samples prepared in the manner described above. Freeze-thaw testing (in the absence of salt) was done by pouring a 3 mm layer of tap water on the test surface.

Freeze-thaw cycle was controlled by computer software connected to the freezing chamber. The freezing chamber has a heating system with controlled temperature and heating duration and digital thawing and ventilation control. The samples were placed into 20 mm-thick expanded polystyrene thermal insulation cells to ensure that only the test surface is subjected to freezing during the test.

The freeze-thaw test was started by placing the samples into the freezing chamber with cycle phase duration of 0 min ±30 min. During the test the freezing medium temperature must be within the limits of temperature cycle presented in Figure 1.
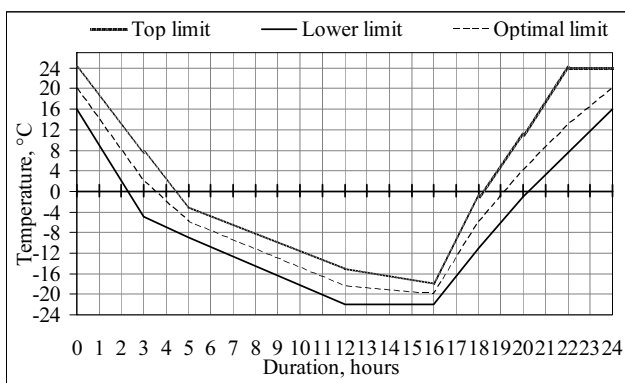

Fig. 1. Freeze-thaw cycle diagram and control of upper and lower temperature limits

One test cycle consists of a programmed model freeze-thaw phase. The total duration of the cycle is 24 ±0.5 hours. During each cycle the temperature is maintained above 0 °C for at least for 7 hours, however not longer than 9 hours. Air temperature in the freezing chamber does not fall below −22 °C.

The layer of freezing medium together with the peeled away surface mortar was collected from the test surface into a container every 14th freeze-thaw cycle starting at the 23rd hour until the 24th hour during the thawing phase (at this time the ambient temperature was within the limits of 16 °C ÷ 21 °C). A new 3 mm-thick layer of freezing medium was poured onto the test surface and the sample was returned to the freezing chamber.

The collected liquid with the peeled away surface mortar was poured out from the container onto the paper filter, which was dried to the constant weight, weighted and marked. At the end of filtration the flakes deposited on the filter were thoroughly washed with distilled water and then the filter with the flakes was dried to the constant weight. Prior and after the filtering the filter (with deposited flakes) was dried to the constant weight in the oven at the temperature of 110 °C ±10 °C and weighted on analytical balance having the precision of 0.0001 g.

The weight of peeled away surface mortar is the weight of the filter with deposited flakes after filtration less the weight of the filter before filtration.

The mass per unit area of peeled away surface mortar after n freeze-thaw cycles is calculated from the equation:

$$S_n = \frac{m_{s,n}}{A} \cdot 10^3 ,$$
(3)

where: S_n is the mass of peeled away surface mortar after n freeze-thaw cycles, kg/m^2; $m_{s,n}$ is the total weight of dry peeled away surface mortar after n freeze-thaw cycles, g; A is the test surface area, mm^2.

JEOL scanning electron microscope (SEM) JSM-6490 LV with 3.0 nm resolution and magnification from 5 to 300 000 times was used to investigate the microstructure of the surface layer of hardened cement paste. The split face of the sample's surface layer covered with electrically conductive carbon in vacuum was tested with SEM. The test was performed at accelerating voltage 20 kV. The microstructure of the surface layer of hardened cement paste was also tested with a computerized optical microscope OLYMPUS (magnification up to 1000 times) equipped with a digital camera.

Electric conductivity and pH values of the admixture were determined by the instrument Mettler-Toledo MPC 227 (pH electrode InLab 410, 0.01 pH; electrical electrode InLab 730, measuring range 0 μS/cm − 1000 μS/cm). The measuring was done at ambient temperature of 21 °C ±0.5 °C in accordance with testing procedure defined by LST EN 1262:2004.

X-ray diffraction analysis was done by a diffractometer "ДРОН-6". Test specifications: CuK_α radiation, Ni filter, detector step 0.02°, intensity measuring span 0.5 s, anode voltage $U_a = 30$ kV, current $I = 20$ mA.

TEST RESULTS AND DISCUSSION

The test revealed that changes in the microstructure of the surface layer of hardened cement paste without NST admixture (Composition I) occur when the samples are subjected to freeze-thaw cycles in the presence of calcium chloride ($CaCl_2$) salt (Fig. 2). SEM images presented in Figure 2 show significant decrease in density of hardened cement paste test surface after 56 freeze-thaw cycles and treatment with 5 % $CaCl_2$ solution (Fig. 2, b) compared to the density of the same test surface before freezing (Fig. 2, a); there are cracks (Fig. 2, b$_1$) and voids containing large crystals of different shapes (Fig. 2, b$_2$, and enlarged fragment in 2, b$_3$).

In the case of hardened cement paste with NST admixture (Composition II) (Fig. 3) the density of the surface layer before freezing (Fig. 3, a) is slightly higher compared to the hardened cement paste of Composition I (Fig. 2, a). After 56 freeze-thaw cycles and treatment with 5 % CaCl$_2$ solution the density of the surface layer of hardened cement paste of Composition II (Fig. 3, b) does not lower compared to the density before freezing in contrast with the behaviour of hardened paste of Composition I.

Very complex processes occur in the system Portland cement – superplasticizer – NST – H$_2$O. They are explained based on the results of researches published in scientific literature and their analysis.

a_1 b_1

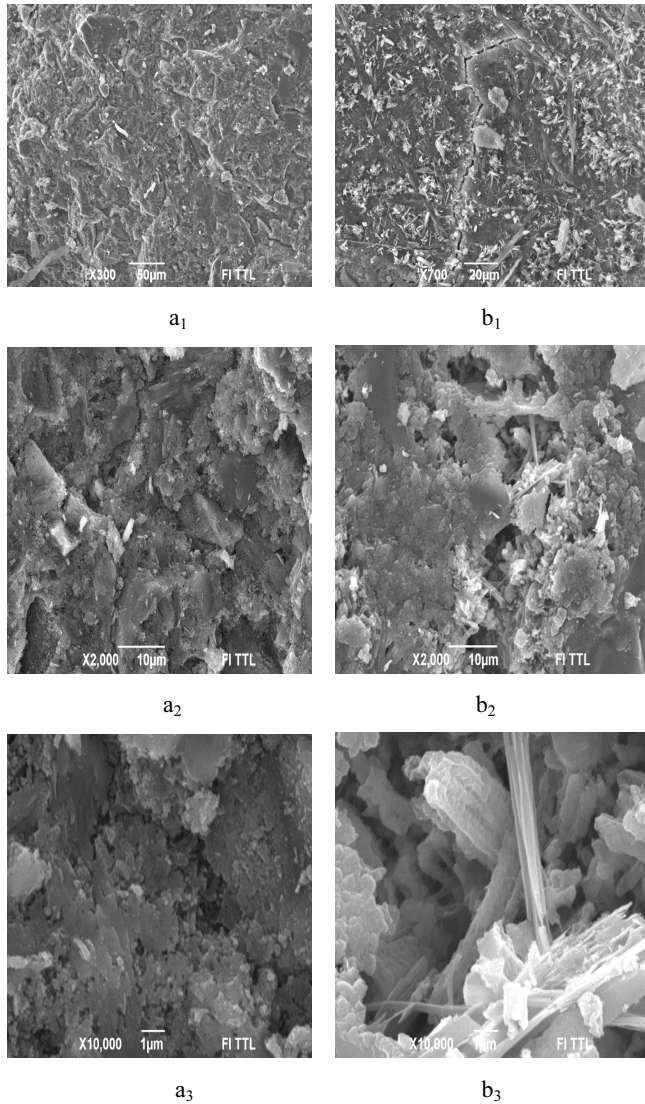a_2 b_2

a_3 b_3

Fig. 2. Microstructure of the surface layer of hardened cement paste without NST admixture: a – before freezing; b – after 56 freeze-thaw cycles and treatment with 5 % CaCl$_2$ salt solution

Superplasticizer, when mixed with cement and water, adsorbs on the surface of cement particles C$_2$S, C$_3$S, C$_3$A, C$_4$AF. For this reason particles of all types, irrespective of their initial charge (before adding superplasticizer particles C$_2$S and C$_3$S are negative and particles C$_3$A, C$_4$AF are positive) become negatively charged, i. e. all particles have the same charge and therefore particle sticking and coagulation is disturbed [15]. Adsorbed plasticizer improves the workability of the cement paste and reduces the amount of water required to produce the wet mix. Superplasticizer improves the distribution of ultra-fine particle admixtures (amorphous SiO$_2$) in concrete matrix [16], reduces the risk of cracking due to drying shrinkage [17].

a_1 b_1
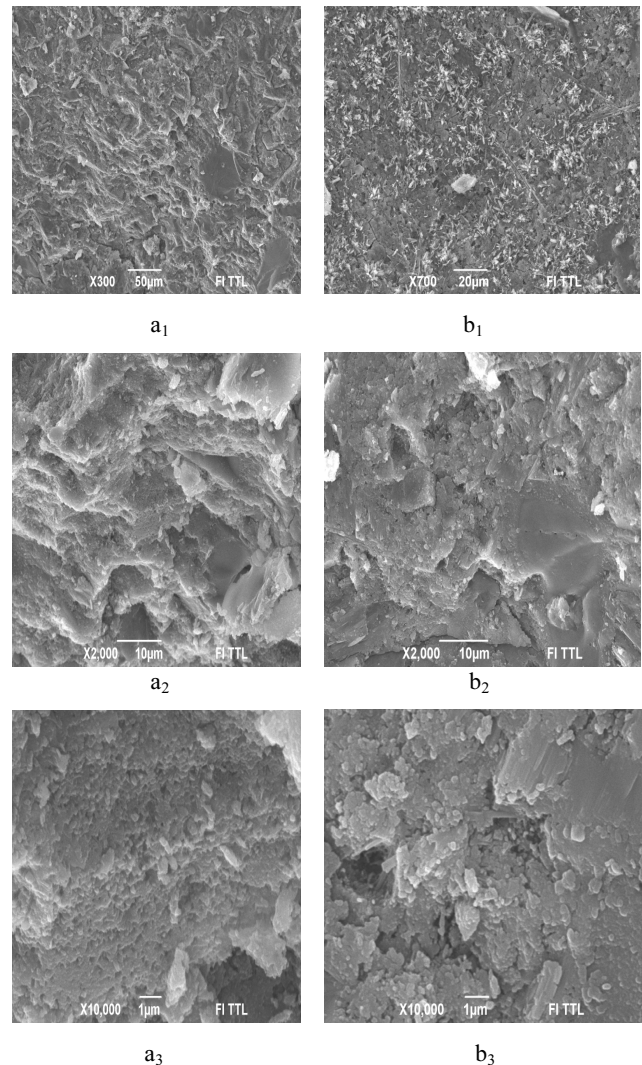
a_2 b_2

a_3 b_3

Fig. 3. Microstructure of the surface layer of hardened cement paste with NST admixture: a – before freezing; b – after 56 freeze-thaw cycles and treatment with 5 % CaCl$_2$ salt solution

XRD test results presented in Figure 4 show that before freeze-thaw testing (curve 1) the surface layer of hardened cement paste of both Composition I (Fig. 4, a) and Composition II (Fig. 4, b) contains some alite (much more in the sample of Composition II than in the sample of Composition I), and also vaterite, aragonite, while the biggest part of the crystal phase on the surface of hardened cement paste is taken by calcite, the amount of which is much higher in the sample of Composition I than in the sample of Composition II. The XRD pattern of the surface layer of hardened cement paste of Composition I before freeze-thaw test shows two reflections of low intensity (at diffraction angles 2θ 11.25° and 14.25°) and there is one obscure reflection in the XRD pattern of the paste of

Composition II (at diffraction angle 2θ 14.25°) (curve 1) that were impossible to interpret.

Freeze-thaw tests in CaCl$_2$ salt solution resulted in the following changes in the sample of Composition I (Fig. 3, a, curve 2): calcite content reduced, alite remained, small amount of portlandite occurred (this phase is represented by low intensity reflections), aragonite and vaterite disappeared, reflections at diffraction angles 2θ 11.25° and 14.25°, which were impossible to interpret before the test, also disappeared. The changes in the sample of Composition II (Fig. 3, b, curve 2) after freeze-thaw tests in CaCl$_2$ salt solution were as follows: calcite content increased significantly, alite almost disappeared, aragonite and vaterite disappeared, reflection at diffraction angle 2θ 14.25°, which was impossible to interpret before the test, disappeared, and very obscure reflections at diffraction angles 2θ 15.25° and 18° came out but were impossible to interpret.
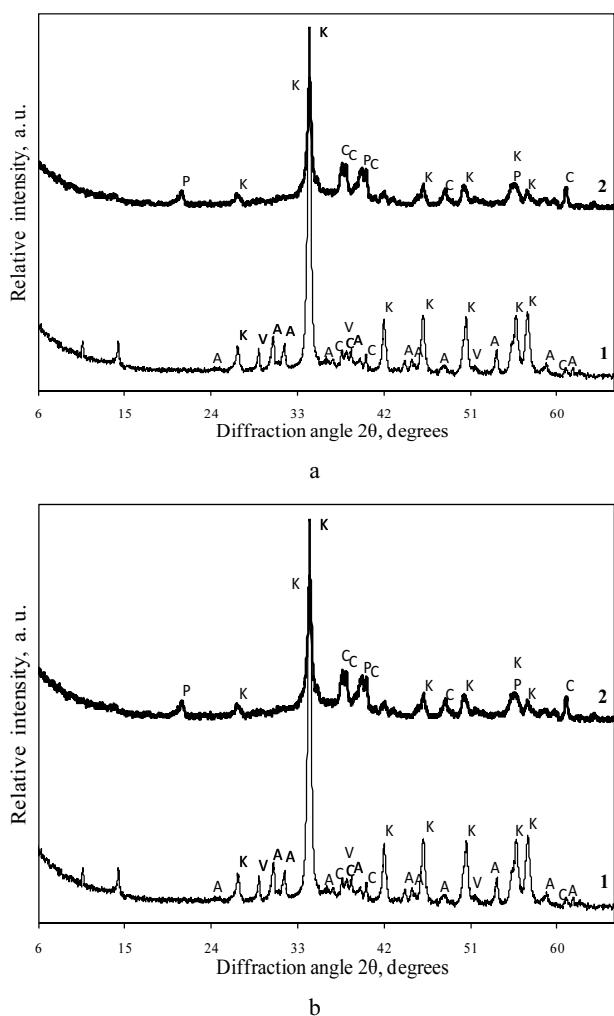

a

b

Fig. 4. X-ray diffraction patterns of samples without NST admixture (Composition I) (a) and samples with NST admixture (Composition II) (b): 1 – after 28 days hardening in water before freezing; 2 – after 56 freeze-thaw cycles with 5 % calcium chloride solution. Symbols: P – portlandite; C – alite; K – calcite; V – vaterite; A – aragonite

Basing on the afore-described results of SEM and XRD tests we may claim that in cement paste hardening phase the

NST admixture acts as an active hydraulic admixture. It was noted [18] that sodium silicate solution contains undissolved SiO$_2$ particles of 1 nm – 2 nm in size, whereas others [19] describe 10 nm – 60 nm isometric particles observed while testing sodium silicate (liquid glass) dried in ambient air. Particles about 100 nm in size are seen in the photo of liquid glass containing sodium silicate of module 3.3 presented were reported [20]. That means that sodium silicate solution contains colloidal SiO$_2$ particles, the fineness of which creates a very big surface area even in a small amount of liquid glass. Reports [21] based on other investigations, analysing the effect of active SiO$_2$ in Portland cement reaction with water, as well as other tests [21] that confirmed the results of investigations in this field state that colloidal SiO$_2$ particles accelerate the reaction (participate in the reaction) of cement phases C$_3$S and C$_3$A with water by producing C–S–H, which deposits on the surface of SiO$_2$ particles in the first stage of the reaction of cement minerals with water, i.e. the surface of SiO$_2$ acts as C–S–H deposition area. As SiO$_2$ particles are very fine, the size of SiO$_2$ particle surface area is very big even in the small amount of liquid glass used as an admixture. As previously reported, the amount of crystalline portlandite, which is formed in the cement matrix containing micro and nano particles of pozzolans, is much smaller than the amount formed in cement matrices without these admixtures. The admixture with such particle size results in the reduced porosity of the binder. The results obtained from the investigation in the microstructure of hardened cement paste matrix without and with NST admixture (Figures 2, a, and 3, a, respectively) correspond to previously reported results [21], i.e. the matrix of hardened cement paste containing NST admixture is denser than the matrix obtained without this admixture.
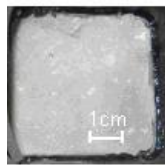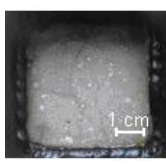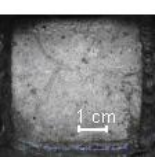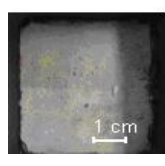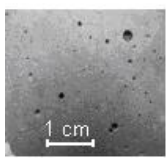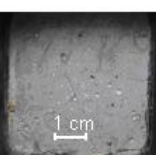
Some tests [22] have showed that the use of SiO$_2$ nanoparticles in cement matrix result in its resistance to C–S–H disturbance due to calcium washout because the admixture reduces the porosity of the matrix, portlandite is transformed into C–S–H gel, silicate chains of C–S–H gel are longer in the matrix with NST admixture. The analysis of investigations in the carbonization of synthetic C–S–H specimens surface and results of the tests [23] have revealed that fresh synthetic C–S–H phases were rapidly carbonated upon exposure to air with the initial formation of amorphous calcium carbonate, then aragonite and/or vaterite, together with silicate anion polymerisation. C–S–H decalcification upon carbonation leads to silicate polymerisation with the ultimate product being silica gel and calcium carbonate. The precise nature of the silica gel is uncertain, although it is known to be highly polymerised. The results of our investigation presented on Fig. 4 as well as on Fig. 2 and Fig. 3 agree with the results presented in articles [22] and [23] and also with the results of other articles mentioned above: with liquid glass added to Portland cement colloidal SiO$_2$ particles lead to the decrease of porosity and increase of density of hardened cement paste matrix. The surface layer of fresh hardened cement paste is carbonated, as it was not protected against contact with air, (Fig. 4).

From the images presented in Table 1, visual assessments of the changes in the samples subjected to 56

freeze-thaw cycles with calcium chloride salt solution used as ice melting agent can be made.

Photos of sample surfaces presented in Table 1 show that surfaces of samples of Composition I and II were not damaged when the surface was covered with water as freezing medium. After 56 freeze-thaw cycles in water minor defects appeared on the surface of the sample of Composition I. Minor defects occurred on the surface of samples modified with NST admixture (composition II) after 56 freeze-thaw cycles and treatment with $CaCl_2$. Distinctly visible defects are seen on the surface of samples of Composition I (without NST admixture) after 56 freeze-thaw cycles and treatment with $CaCl_2$. These results are confirmed by quantitative assessment of the peeled away surface mortar.

Table 1. Visual appearance of hardened cement paste before freezing and after 56 freeze-thaw cycles with calcium chloride salt solution

Sample marking	Before freezing	After 56 freeze-thaw cycles	
	H_2O	H_2O	5 % $CaCl_2$
I			
II			

The test revealed that after 56 freeze-thaw cycles with 5 % $CaCl_2$ applied as freezing medium on the surface of the sample, the amount of flakes collected from the surface of hardened cement paste modified with NST admixture was 0.0220 kg/m^2 and the flakes collected from the surface of unmodified cement paste was 0.060 kg/m^2. The investigation into the weight loss of concrete samples with NST admixture caused by cyclic freezing and thawing and treating the surface with deicing solution has shown that the effect of 5 % $CaCl_2$ solution applied on the surface of concrete modified with NST admixture is 3 times lower compared to the weight loss in samples with Portland cement only. Nevertheless, the fact that the amounts of peeled away surface mortar are relatively small (grams per $1m^2$) should be taken into account. Low values of weight loss can be explained by low w/c ratio (0.27) in both compositions and the absence of contact zone between the cement paste and aggregates.

Optical microscope images presented in Table 1 and quantitative assessment of surface scaling confirm the effect of freezing and thawing in the presence of $CaCl_2$ on the surface of concrete: very small amount of sodium silicate solution in the cement paste together with superplasticizer particles effectively extend the durability of hardened cement paste matrix.

The results of compressive strength testing performed on hardened cement paste samples (Fig. 5) revealed that in freezing and thawing conditions the compressive strength of concrete without NST admixture is much more adversely affected by 5 % $CaCl_2$ deicing salt solution than concrete modified with NST admixture. Test data presented in Figure 5 show that 56 freeze-thaw cycles in the presence of 5 % $CaCl_2$ solution had negligible effect on the strength of hardened cement paste with NST admixture; after cyclic freezing and thawing the compressive strength increased 2.5 % (up to 84.9 MPa) compared to the compressive strength before freezing. The compressive strength of hardened cement paste without NST admixture decreased 39.5 % (down to 50.1 MPa) after 56 freeze-thaw cycles with 5 % $CaCl_2$ solution.
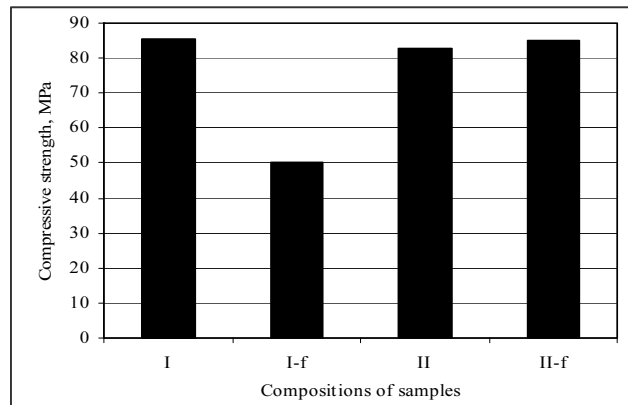

Fig. 5. Compressive strength of hardened cement paste samples before and after freezing: (I) and (II) before freezing, without and with NTS admixture respectively; (I-f) and (II-f) after freezing, without and with NTS admixture respectively

The obtained results allow suggesting that the structure of surface layer of cement binder produced with water glass (NST) admixture (composition II) resulted in very low permeability of water and chloride ions. It is the reason why the surface layer of hardened cement paste practically was not damaged under aggressive environment attack (Fig. 3, b) and why there is no indication of the beginning of the FSC (Table 1) and also why the strength of hardened cement matrix was not lowered (Fig. 6). The permeability of the surface of cement paste produced without liquid glass (NST) admixture (composition I) is evidently much higher than in the case of cement binder produced with liquid glass admixture. That explains why this binder was much less resistant to the aggressive environment (Fig. 2, b, Table 1) and why the compressive strength reduced so much (Fig. 6). The overall results of investigating the microstructure of the surface layer of hardened cement paste with and without liquid glass admixture and mechanical tests show that NST may be used as effective admixture to extend the durability of hardened cement paste treated with $CaCl_2$ salt solution and subjected to cyclic freezing and thawing.

CONCLUSION

1. Sodium silicate solution added to cement paste extends the durability of cement matrix because introduction of

NST admixtures to cement mixtures enable SiO_2 to bind free $Ca(OH)_2$ in hardened cement paste and produce stable and less water soluble hydrosilicates that enhance concrete durability and strength.

2. SEM micrographs and the results of chemical analysis confirm the propositions that in the presence of NST admixture $Ca(OH)_2$ react with SiO_2, formed in sodium silicate hydrolysis, and produce calcium hydrosilicates (C–S–H). NST content up to 0.5 % enable to bind free $Ca(OH)_2$ portlandite in hardened cement paste.

3. Investigation into the microstructure of the surface layer of hardened cement paste before and after 56 freeze-thaw cycles in the presence of $CaCl_2$ and mechanical tests showed that NST may be used as effective admixture to extend the durability of hardened cement paste treated with $CaCl_2$ salt solution and subjected to cyclic freezing and thawing.

4. After cyclic freezing and thawing in the presence of 5 % $CaCl_2$ deicing salt solution, the compressive strength of hardened cement paste samples with NST admixture is in average 1.7 higher compared to the samples made of Portland cement only.

5. It is difficult to assess the impact of salt solutions on the degradation of hardened cement paste microstructure by the weight of peeled away surface mortar without using additional test methods as the amount of peeled away matter is rather small due to the absence of aggregates in the cement paste and their contact zone.

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