RESISTANCE OF MODIFIED HARDENED CEMENT PASTE TO FROST AND DE-ICING SALTS

Gintautas Skripkiūnas[1], Džigita Nagrockienė[2]✉, Giedrius Girskas[3], Eugenijus Janavičius[4]

[1, 2, 3]*Dept of Building Materials, Vilnius Gediminas Technical University,
Saulėtekio al. 11, 10223 Vilnius, Lithuania*
[4]*Dept of Building Materials, Kaunas University of Technology, Studentų g. 48, 51367 Kaunas, Lithuania*
*E-mails: [1]gintautas.skripkiunas@vgtu.lt; [2]dzigita.nagrockiene@vgtu.lt; [3]giedrius.girskas@vgtu.lt;
[4]Eugenijus.Janavicius@mc-bauchemie.com*

Abstract. Concrete is widely used in the structures of bridges, flyovers, sidewalks and carriageways that are exposed to freeze-thaw cycles in wet conditions and are treated with de-icing salts. Tests were made to examine the effect of sodium silicate solution on the resistance of hardened cement paste to frost and de-icing salts. 5% sodium chloride, calcium chloride and manganese chloride solutions were used as de-icing salts. The deterioration of hardened cement paste was assessed by the changes in compressive strength, ultrasonic pulse velocity, specimen deformations and amount of scaled matter during cyclic freezing and thawing. Test results have revealed that hardened cement paste modified with sodium silicate solution is less subject to destruction when the surface of cement paste is treated with de-icing salt solutions under cyclic freeze-thaw conditions. The research has proved that sodium silicate solution increases the durability of concrete used in road structures.

Keywords: concrete, hardened cement paste, frost resistance, salt solution, sodium silicate solution, durability.

1. Introduction

When de-icing salts are applied on bridges and carriageways in winter, part of the salt usually gets onto road and bridge structures. Studies of Lithuanian scientists have revealed that the highest chloride concentrations in snow-melt runoff are observed in highways (Storpirštytė *et al.* 2003) where the majority of bridges and flyovers are also located. NaCl and $CaCl_2$ solutions are used to reduce the slipperiness of roads (Baltrėnas *et al.* 2009; Rimkus 1999) where chlorides turn snow or ice to brine. Rimkus (1999) states that lately about 100 000 t of white technical salt is used on Lithuanian roads during the winter season. Reduced durability of concrete is one of the biggest concerns for the operators of road structures in cold climates. The complexity of chemical composition and structure of hardened cement paste and the variety of factors affecting concrete structures under the afore-described conditions makes it difficult to assess explicitly the chemical and physicochemical processes that occur simultaneously in hardened cement paste. Investigation into the resistance of concrete to aforementioned factors is focused on the resistance of the binding phase in concrete, i.e. hardened cement paste (matrix).

The decrease in the durability of concrete exposed to de-icing salt solutions (DSS) is described as superficial damage caused by a salt solution on top of the frozen layer. This damage is progressing and is observed in the form of scaled concrete pieces (Jana 2004; Valenza II, Scherer 2007). It should be noted that salt scaling is not the same as freeze-thaw damage, which is characterized by the reduction of the entire structure strength, because superficial scaling of concrete initially causes no threat to mechanical integrity of concrete. Research into the alternatives of using secondary materials to ensure the durability of concrete is done for the sake of global climate protection and with the aim to reduce the use of clinker Portland cement (Nili, Zaheri 2011; Skripkiūnas *et al.* 2009).

The properties of modern building materials containing cement and various modifying agents (SiO_2 micro particles, ash, sodium silicate solution, plasticizers) highly depend on nanostructures formed during cement hydration. These structures influence the key properties of the material, i.e. strength and durability. It is hard to retain materials in nanodispersion under natural conditions because of thermodynamic instability, whereas the disadvantage of artificial nanodispersions is low production capacity.

Nanodispersions in the form of by-products, such as SiO_2, are an exception. Nano SiO_2 dispersion is unique because it has a big amount of free surface energy. This free energy is generated by high chemical activity of the material (Beaudoin *et al.* 2009; Jo *et al.* 2007; Lotov 2006).

To obtain better characteristics of construction materials at macro level the formation of nano phases must be controlled and properties of such materials have to be analysed at micro level because nano additives act as supplementary crystallization centres in cementations materials and change the direction and rate of physical and chemical processes (Raki *et al.* 2010; Skripkiūnas *et al.* 2008b; Sobolev *et al.* 2008). Sodium silicate solution additive ($Na_2O \cdot nSiO_2$) as well as super plasticizer (PCE) have nanostructures in their composition. Sodium silicate solution contains undissolved SiO_2 nano particles of 1–2 nm in size and even a small amount of sodium silicate solution (0.03–1%) influences cement hydration (Kiricsi *et al.* 2006; Pundiene *et al.* 2005; Sandberg *et al.* 1989; Skripkiūnas *et al.* 2008). High SiO_2 activity enables SiO_2 to bind free $Ca(OH)_2$ (portlandite) in hardened cement paste. Stable and less water soluble hydro silicates formed in the reaction enhance concrete durability and strength. Studies of researchers (Gartner *et al.* 2002) have shown that the use of SiO_2 nano particles in the production of cement matrix influences the material's resistance to C–S–H destruction, whereas portalindite is transformed into C–S–H gel. According to Lotov (2006) cement starts binding due to the formation of nanodispersion particles that bind the bigger part of water. Concrete strength starts increasing with the increase of solid phase concentration in the system cement-water. Observation and examination of hydration processes at nano level is important for a new approach to cement hydration (Chen *et al.* 2004; Gartner *et al.* 2002,) values. G. Skripkiūnas and M. Daukšys with colleagues (Daukšys *et al.* 2009; Skripkiūnas *et al.* 2008b; Skripkiūnas *et al.* 2010) examined the effect of various nanomodifiers on the strength of hardened cement paste matrix, durability and rheological properties.

Nanodispersion system is formed in the initial stage of hydration of binding phase (Portland cement, aluminous cements) (Kiricsi *et al.* 2006). It is therefore necessary to explore the possibilities of halting the formation of large crystallized hydration products in the initial stage of structure formation by inducing the formation of amorphous nano-sized hydration structures where more energy is accumulated. Another group of researchers claims that nano additives in the material (new nanostructures, i.e. super plasticizers, super strong nanofiber, SiO_2, Fe_2O_3, AI_2O_3 and organic montmorinollite nanoparticles) may improve the nanostructure of cementations materials (Asao 2003; Jo *et al.* 2007; Kuo *et al.* 2006).

Super plasticizer, when mixed with cement and water, adsorbs on the surface of cement particles C_2S, C_3S, C_3A, C_4AF. For this reason particles of all types, irrespective of their initial charge (before adding super plasticizer particles C_2S and C_3S are negative and particles C_3A, C_4AF are positive) become negatively charged, i.e. all particles have the same charge and therefore particle sticking and coagulation is disturbed (Yoshioka *et al.* 2002), the workability of cement paste improves, less amount of water is required to produce the paste. To this end, the binding phase consisting of colloidal sodium silicate solution ($Na_2O \cdot nSiO_2$) and suspension super plasticizer based on modified polycarboxylic ether may be used. H. Hommer, K. Wutz and H. Li (Hommer, Wutz 2005; Li *et al.* 2004) have noted in their research papers that super plasticizers of new generation not only disperse the material and actively influence cement hydration process but also improve the structure of cementations materials due to nanodispresion particles present in their composition.

According to research results (Skripkiūnas *et al.* 2008) sodium silicate solution changes the microstructure of the hardened cement paste, accelerates binding time, enhances closed porosity and has insignificant effect on the strength of hardened cement paste. The said factors have a positive effect on frost resistance of hardened cement paste. It is therefore necessary to explore the possibilities of halting the formation of large crystallized hydration products in the initial stage of structure formation by inducing the formation of amorphous nano-sized hydration structures where more energy is accumulated. To this end, the binding phase consisting of colloidal sodium silicate solution and suspension super plasticizer based on modified polycarboxylic ether may be used.

A three-component binding phase consisting of colloidal sodium silicate solution, Portland cement and super plasticizer was used in the research into the effect of multicomponent disperse systems on the durability of binder matrix. The research revealed the effect of sodium silicate solution on the durability of hardened cement paste exposed to de-icing salts under cyclic freeze-thaw conditions.

2. Materials

Portland cement CEM I 42.5 R manufactured by *SC Akmenės cementas* was used for the tests. The parameters of the cement paste of normal thickness were as follows: water content 25.4%; specific surface 360 m^2/kg; particle density 3110 kg/m^3; bulk density 1220 kg/m^3.

Two types of suspension super plasticizers were used as concrete additives: polycarboxylic ether based super plasticizer with dry particle concentration of 18.7%, pH value 6.4; electrical conductivity 4.390 mS/cm (hereinafter – super plasticizer R) and modified polycarboxylic ether based super plasticizer with dry particle concentration of 36.1%, pH value 4.4; electrical conductivity 1.480 mS/cm (hereinafter – super plasticizer F). Electric conductivity and pH values were determined by Mettler-Toledo Device MPC 227 (pH electrode InLab 410, 0.01 pH, and electric InLab electrode 730, the measurement range of 0–1000 µS/cm). Measuring was made at the ambient temperature of 21 ± 0.5 °C.

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, average density value of liquid glass solution of 1382 kg/m^3 was also used as an additive. The hydrolysis reaction in sodium silicate solution is expressed by the equation:

$$Na_2O \times SiO_2 + H_2O = 2Na^+ + 2OH^- + SiO_2.$$
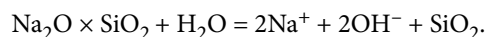
5% sodium, 5% calcium and 5% magnesium chloride solutions were used as freezing media. Tap water was used as freezing media for control specimens.

3. Research methodology

Cement pastes were made of dry matter and mixed in forced action mixer Auto mix. Concrete specimens were formed in impermeable prism moulds 40×40×160 (mm). Settled specimens were left in moulds for 20 h at the ambient temperature of 20 °C ± 2°C. Hardened cement specimens were left for 28 days at the ambient temperature of 20 °C ± 2 °C and ≥ 95% humidity. Prior to the experimental research the compressive strength, the initial length of the specimens and the initial ultrasonic pulse velocity were determined according to *LST EN 196-1:2005 "Methods of Testing Cement – Part 1: Determination of Strength"* after 28 days of hardening. The change in compressive strength, relative deformations, loss of weight and ultrasonic pulse velocity in specimens was measured after 56 freeze-thaw cycles where the surface of specimens was treated with different saline solutions.

Glass plates were inserted at the ends of 40×40×160 (mm) concrete prisms during the experimental research into the change of relative deformations and ultrasonic pulse velocity in order to determine the deterioration of the internal concrete structure.

An ultrasonic wave propagation time measuring method was used in ultrasonic test. The method is based on electronic modelling of the leading short pulse propagation, i.e. the propagation of the pulse between two transducers placed at a certain distance. Ultrasonic pulses transmitted by the generator are turned into mechanical pulses in the transducer and propagate in the form of elastic waves across the researched material. The receiving transducer converts the mechanical pulse, which has propagated through the material, into electric pulse and displays it on the screen. The experimental research employs universal transducers where electric pulse is converted into mechanical pulse and vice versa. In the experimental research relative deformation (relative elongation) after 56 freeze-thaw cycles of specimens exposed do de-icing solutions is calculated as the ratio of absolute deformation and initial length of the specimen. Repeated saturation of the specimen surface covered with 3 mm layer of water for (72 ± 2) h at room temperature was assumed as the initial length of the specimen for deformation measuring.

To determine the amount of scaled matter after freeze-thaw cycles the specimens were cut into 40×40×40 (mm) cubes and the cut surface was used as the test surface. Freezing and thawing was conducted by leaving the specimens for 56 days in a climatic chamber with controlled temperature and heating time and digital defrosting and ventilation controller (Dixell digital controller with defrost and fans management min set point –50 °C /–58 °F; max set point 110 °C/230 °F). One freeze-thaw cycle lasted for 24 h at the temperature changing from –22 °C to 24 °C. During one cycle the temperature was above 0 °C from 7 to 9 h.

4. Research results

Table 1 shows the change in compressive strength and density of hardened cement paste modified with sodium silicate solution (NST – Na$_2$O·nSiO$_2$).

The results show that the compressive strength as well as density of hardened cement paste after 28 days of setting slightly reduces or increases and mainly depends of the plasticizing additive and water/cement ratio. Irrespective of cement mix composition, the compressive strength and density of hardened cement paste after 28 days of setting did not change or changed insignificantly when NST content was increased up to 0.8%. Based on the evaluation of previous research results and literature analysis the most appropriate cement composition was developed for the experimental research into durability. NST added at 0.5% of the matrix content should react with polycarboxylic ether super plasticizer and water/cement ratio should be 0.27.

Table 1. The change in compressive strength of hardened cement paste

Composition No.	Water/cement ratio	NST content, %	Super plasticizer content, %		Compressive strength, MPa	Density, kg/m^3
			R	F		
1		0	–	0.5	84.6	2140
2		0.2	–	0.5	79.4	2132
3		0.5	–	0.5	81.0	2131
4	0.27	0.8	–	0.5	80.5	2133
5		0	0.5	–	80.0	2106
6		0.2	0.5	–	81.8	2138
7		0.5	0.5	–	82.2	2115
8		0.8	0.5	–	83.2	2130

4.1. Results of research into the effect of NST on the compressive strength of hardened cement paste exposed to de-icing salts

Figs 1 and 2 illustrate the changes in compressive strength of hardened cement paste with and without NST after 56 freeze-thaw cycles when the surface of hardened cement paste is exposed to different de-icing salt solutions. The solid line in the figures illustrates the value of compressive strength prior to freezing; the columns represent the values after 56 freeze-thaw cycles.

Research results have shown that NST additive has an effect on the compressive strength of concrete exposed to de-icing salt solutions under cyclic freeze-thaw conditions. The compressive strength values before freezing were similar in compositions with and without NST additive; the compressive strength of hardened cement paste made of Portland cement without NST additive was 85.4 MPa (standard deviation $\sigma = 2.5$ MPa) and 82.8 MPa in composition without NST additive (standard deviation $\sigma = 2.5$ MPa). After 56 freeze-thaw cycles the adverse
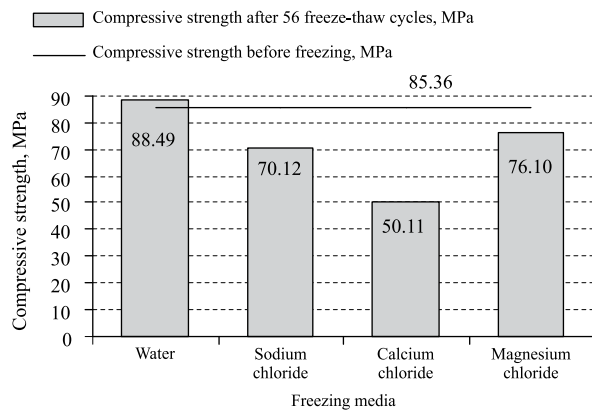

Fig. 1. The dependence of compressive strength on saline solution type in specimens made of Portland cement without additives
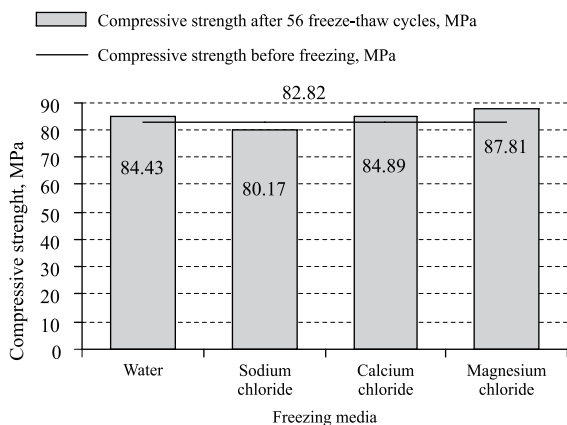

Fig. 2. The dependence of compressive strength on saline solution type in specimens made of Portland cement with NST additive

effect of saline solutions on the compressive strength is mostly expressed in specimens made without NST additive and exposed to 5% $CaCl_2$ solution. The compressive strength in specimens made without NST additive and exposed to 5% $CaCl_2$ solution dropped down to 50.1 MPa ($\sigma = 1.5$ MPa). 5% NaCl and 5% $MgCl_2$ de-icing salt solutions reduced the compressive strength to 70.1 MPa ($\sigma = 0.81$ MPa) and 76.1 MPa ($\sigma = 1.4$ MPa) respectively. NST additive was found to reduce the loss in compressive strength in hardened cement paste with NST additive after 56 freeze-thaw cycles in saline solutions. When NST is added to the cement mix at 0.5% of the matrix content the compressive strength is similar as in specimens before freezing. The biggest drop in compressive strength was observed when the surface of specimens was treated with 5% NaCl solution. The compressive strength value reduced to 80.2 ($\sigma = 3.2$ MPa).

The experimental research results presented in Figs 1 and 2 show that after 56 freeze-thaw cycles and treatment with different salt solutions the biggest drop in compressive strength was observed in specimens without NST additive treated with 5% $CaCl_2$ solution (50.1 MPa), and the least drop was recorded in specimens with 0.5% NST treated with 5% $MgCl_2$ solution (87.8 MPa, $\sigma = 2.0$ MPa).

The standard deviation of compressive strength ranges from 0.8 MPa to 2.5 MPa in hardened cement paste without NST and from 2.0 MPa to 3.2 MPa in hardened cement paste with NST. Therefore, it could be stated that NST additive slightly changes the standard deviation of compressive strength. Low values of standard deviation confirm insignificant variation of research results and prove the reliability of obtained results. Smaller change in compressive strength of hardened cement paste modified with NST additive compared to control specimens exposed to de-icing salt solutions is explained by the following reasons:

1. The amount of sodium silicate solution reacting with polycarboxylic ether super plasticizer in cement paste enables to bind free $Ca(OH)_2$ in hardened cement paste and produce stable and less soluble in water hydrosilicates that increase the compressive strength of concrete.

2. In the presence of NST the matrix contains more hydro silicates during the setting compared to cement mix compositions without NST because $Ca(OH)_2$ react with SiO_2, which is formed during sodium silicate hydrolysis, and produce calcium hydro silicates (C-S-H) from sodium silicate. The amount of NST used in the research (at 0.5% of the total matrix content) enables SiO_2 to bind free $Ca(OH)_2$ portlandite in hardened cement paste.

3. Modification of hardened cement paste with NST enables to change durability parameters.

4.2. Results of research into the effect of NST on ultrasonic pulse velocity in hardened cement paste exposed to de-icing salts

The experimental research in ultrasonic pulse velocity in the structure of hardened cement paste is based on the ratio of ultrasonic pulse propagation time and the distance of travel across the specimen within a specified time period.

Microcracks in the structure of hardened cement paste are filled with air having the acoustic resistance of 43 g/cm²s. This parameter ranges within the limits of (0.9–1.2) × 10⁶ g/cm²s in hardened cement paste, i.e. is 100 000 times higher. That means that microcracks formed in hardened cement paste practically stop the propagation of ultrasonic pulse generated by ultrasonic wave diffractions around the microcrack. The growing number of microcracks increases the pulse propagation distance and reduces the velocity. Figs 3 and 4 illustrate the kinetics of ultrasonic pulse velocity after 56 freeze-thaw cycles when the surface of hardened cement past is treated with different saline solutions.

The curves in Figs 3 and 4 show that ultrasonic pulse velocity after 56 freeze-thaw cycles is lower in specimens with NST additive irrespective of the freezing media on the surface of the specimen. That means that there are smaller microcracks in the cement matrix of specimens with NST additive. From Fig. 3 may see that in hardened cement paste without NST additive and exposed to 5% $CaCl_2$ solution the drop in ultrasonic pulse velocity is 681 m/s (from 3900 m/s to 3219 m/s); whereas in hardened cement paste with NST additive the ultrasonic pulse velocity drops from 3777 m/s to 3698 m/s, i.e. reduces by 79 m/s. The comparison of control specimens and specimens with NST additive has revealed similar trends in the change of ultrasonic pulse velocity.

Figs 3 and 4 show that after 56 freeze-thaw cycles the change in ultrasonic pulse velocity is 2.3 times higher in specimens with NST additive exposed to 5% sodium chloride solution and 3.2 times higher in specimens exposed to 5% magnesium chloride solution compared to control specimens. The lowest ultrasonic pulse velocity after 56 freeze-thaw cycles was observed in hardened cement paste with NST additive and exposed to 5% $MgCl_2$ de-icing solution.

According to experimental research results the standard deviation of ultrasonic pulse velocity in specimens without NST additive was 86.9 m/s and in specimens with NST additive it was 81.5 m/s. Therefore, it could be stated that research results are reliable because the standard deviation values are not big and similar.

The summary of ultrasonic pulse velocity results after 56 freeze-thaw cycles in the presence of de-icing salt solutions shows that introduction of 0.5% NST additive into the mix causes the reduction in ultrasonic pulse velocity. A lower drop in ultrasonic pulse velocity in specimens with NST additive compared to specimens without NST additive may be explained by the bigger amount of amorphous compounds that cover calcium hydro silicate crystals and partly close capillary pores. For this reason smaller microcracks develop in the cement matrix of specimens with NST additive.

4.3. Results of research into the effect of NST on deformations in hardened cement paste exposed to de-icing salts

One of the objectives of experimental research was to determine changes in the relative length of specimens subjected to de-icing salts under cyclic freeze-thaw conditions. The humidity of capillary porous materials is closely related to the expansion-contraction deformations. The volume of hardened cement paste increases with its humidity due to bigger dimensions of polycrystalline material structures and the action of capillary forces. Surface tensions develop because molecular force balance between the particles on the surface of the pores disappears. Partial compensation of surface forces that are not in equilibrium on the surface of the pores occurs during adsorption process, thus reducing the surface tension of hardened cement paste. Hardened cement stone expands under the influence of tension forces. Defects in the structure of hardened cement paste are caused by the variation of sorption capacity of cement under repeated freeze-thaw conditions and exposure to de-icing solutions. Figs 5 and 6 illustrate the kinetics of hardened cement paste deformations after 56 freeze-thaw cycles when the surface of hardened cement paste is exposed to different salt solutions.
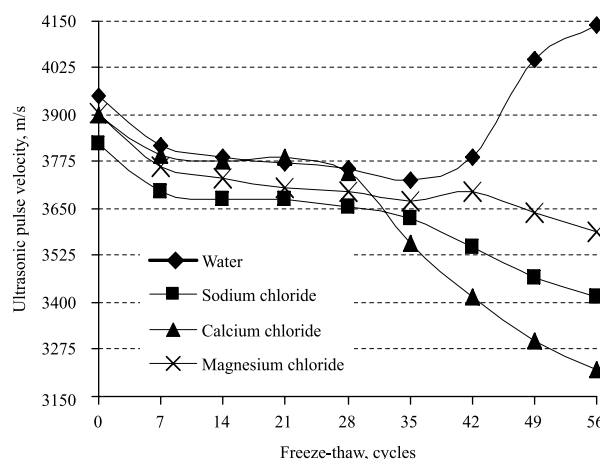

Fig. 3. Kinetics of ultrasonic pulse velocity in specimens made of Portland cement after 56 freeze-thaw cycles in different saline solutions
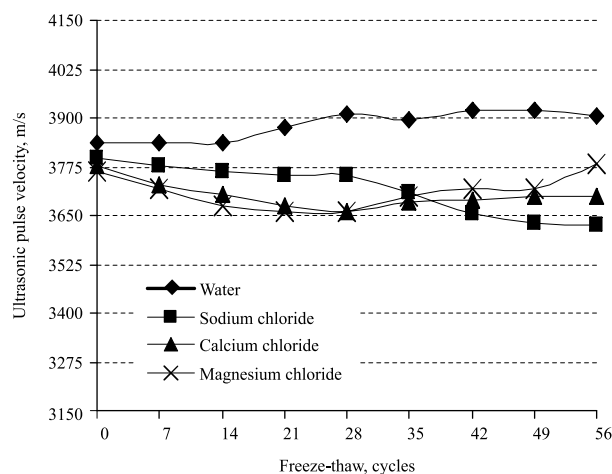

Fig. 4. Kinetics of ultrasonic pulse velocity in specimens made of Portland cement with NST additive after 56 freeze-thaw cycles in different saline solutions
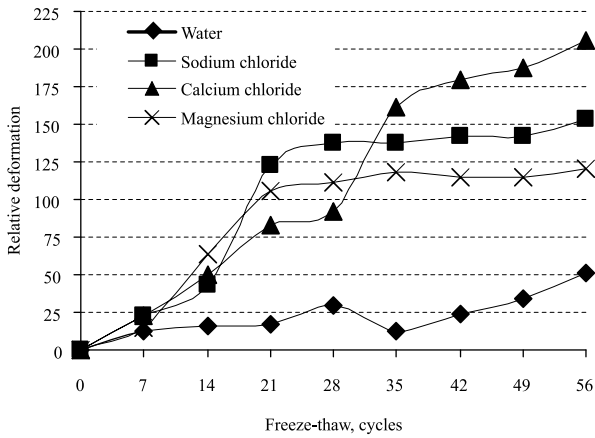
Fig. 5. Kinetics of deformations in specimens made of Portland cement after 56 freeze-thaw cycles in different saline solutions
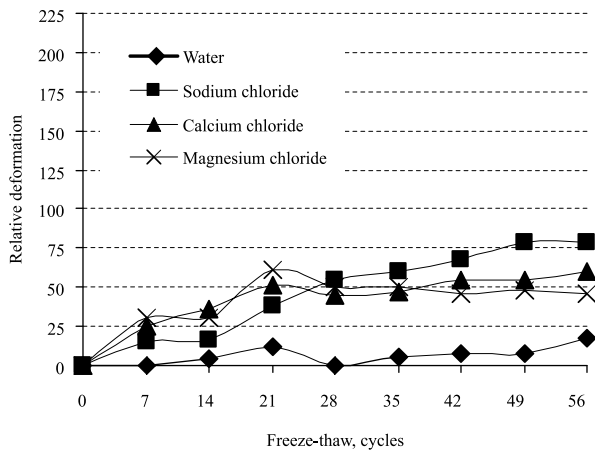

Fig. 6. Kinetics of ultrasonic pulse velocity in specimens made of Portland cement after 56 freeze-thaw cycles in different saline solutions
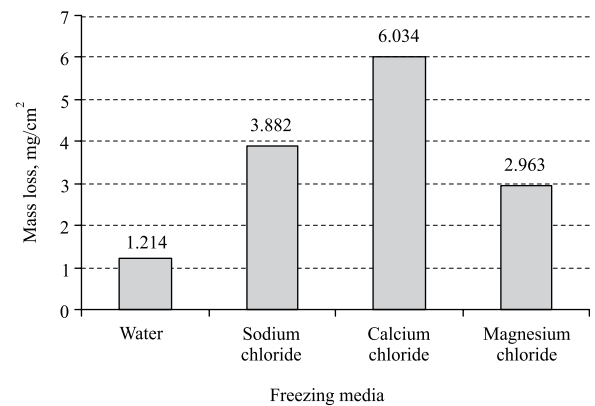

Fig. 7. The dependence of mass loss on saline solution type in specimens with Portland cement after 56 freeze-thaw cycles

The curves in the figures clearly illustrate that after 56 freeze-thaw cycles and exposure to salt solutions relative deformations in hardened cements stone with NST additive (at 0.5% of the matrix content) changed to 78.4×10^{-3} and to 205.9×10^{-3} in specimens without NST additive.

Research results have shown that much smaller deformations occur in hardened cement paste with NST additive after 56 freeze-thaw cycles and exposure do de-icing salt solutions. Therefore, sodium silicate solution is used to improve the durability of hardened cement paste.

The biggest increase in deformations after 56 freeze-thaw cycles is observed in specimens exposed to 5% $CaCl_2$ solution where relative deformations reached 205.9×10^{-3}. In specimens with NST additive exposed to $CaCl_2$ solution relative deformations were 59.8×10^{-3}.

Fig. 6 illustrates that after 56 freeze-thaw cycles the relative deformations in hardened cement paste with NST additive reduced 3.4 times when 5% $CaCl_2$ solution was used as freezing medium, 2.6 times when the freezing medium was 5% $MgCl_2$ solution and 1.9 times when the freezing medium was 5% NaCl solution. It should be noted that relative deformations in specimens with and without NST additive were insignificant when tap water was used as the freezing medium compared to deformations when the freezing medium was de-icing salt solution, i.e. 17.5×10^{-3} and 51.0×10^{-3} respectively. Deformations, however, differ 2.9 times. That means that hardened cement stone with NST additive is more resistant to cyclic freezing and thawing when de-icing salt is applied.

The analysis of relative deformations in cement stone exposed to different salt solutions under cyclic freeze-thaw conditions has shown that after 56 freeze-thaw cycles hardened cement stone with NST additive is mostly affected by 5% $NaCl_2$ de-icing salt solution (relative deformations 78.4×10^{-3}) and least affected by 5% $MgCl_2$ de-icing salt solution (relative deformations 45.8×10^{-3}).

4.4. Results of research into the effect of NST on the surface scaling in hardened cement paste exposed to de-icing salts under freeze-thaw conditions

The research has shown that although surface scaling is relatively insignificant in terms of mass (measuring unit is mg), however general tendencies are observed. Small loss in surface mass is related to low water/cement ratio (0.27, Table 1). The experimental research has revealed that after 56 freeze-thaw cycles the loss in weight in specimens with NST additive (at 0.5% of the total matrix content) is lower compared to control samples irrespective of the freezing medium. Figs 7 and 8 illustrate the amount of scaled matter per area unit after 56 freeze-thaw cycles when the surface of hardened cement paste is exposed to different salt solutions.

After 56 freeze-thaw cycles the specimens with NST additive compared to control specimens had the biggest difference in the mass loss, i.e. 2.7 times, when the freezing medium was 5% $CaCl_2$ solution. When the freezing

medium on the surface of the specimen was 5% NaCl and 5% MgCl$_2$, the mass loss differed 1.3 and 2.0 times, respectively.

The analysis of hardened cement paste surface scaling caused by de-icing salt solutions under cyclic freeze-thaw conditions based on the data presented in Figs 7 and 8 leads to the conclusion that the biggest scaling occurs in specimens without NST additive exposed to 5% CaCl$_2$ solution (6.034 mg/cm^3) and the smallest scaling is observed in specimens with 0.5% NST additive exposed to 5% MgCl$_2$ solution (1.508 mg/cm^3).

5. Conclusions

The biggest drop in compressive strength occurs in specimens without NST additive exposed to 5% CaCl$_2$ solution and the least drop in compressive strength occurs in specimens with 0.5% NST additive exposed to 5% MgCl$_2$ solution.

Compressive strength in specimens with NST additive changes insignificantly after 56 freeze-thaw cycles irrespective of the type of de-icing salt solution used as freezing medium.

Ultrasonic pulse velocity in hardened cement paste without NST additive slows down significantly after 28–42 freeze-thaw cycles depending on freezing media, whereas in specimens with NST additive it remains constant.

Deformations in specimens without NST additive increase significantly with the number of freeze-thaw cycles; specimens with NST additive undergo 2.5 times smaller deformations.

Mass loss in hardened cement paste resulting from surface scaling under cyclic freeze-thaw conditions is insignificant and shall not be used as a parameter to describe deterioration processes.

Research results have shown that hardened cement paste with NST additive is subject to much smaller scale deterioration processes after 56 freeze-thaw cycles and exposure do de-icing salt solutions. Therefore, sodium silicate solution may be used to improve the durability of hardened cement paste and concrete used in road building.

References

Asao, O. 2003. Nano-Fiber Technology Innovating World of Fiber. An Example of Research and Development. Nanomaterial Design by Polymer Blend Method, *Journal of Engineering Materials* 51(9): 42–45.

Beaudoin, J. J.; Dramé, H.; Raki, L.; Alizadeh, R. T. 2009. Formation and Properties of C-S-H-PEG Nano-Structures, *Materials and Structures* 42(7): 1003–1014. http://dx.doi.org/10.1617/s11527-008-9439-x.

Chen, J. J.; Thomas, J. J.; Taylor, H. F. W.; Jennings, H. M. 2004. Solubility and Structure of Calcium Silicate Hydrate, *Cement and Concrete Research* 34(9): 1499–1519. http://dx.doi.org/10.1016/j.cemconres.2004.04.034.

Daukšys, M.; Skripkiūnas, G.; Janavičius, E. 2009. Complex Influence of Plasticizing Admixtures and Sodium Silicate Solution on Rheological Properties of Portland Cement Paste, *Materials Science (Medžiagotyra)* 15(4): 349–355.
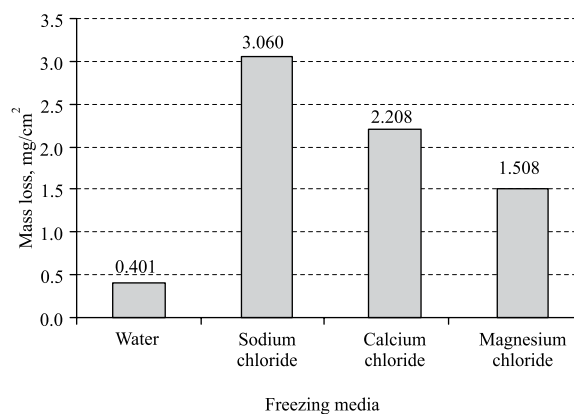

Fig. 8. The dependence of mass loss on saline solution type in specimens with Portland cement and NST additive after 56 freeze-thaw cycles

Gartner, E. M.; Young, J. F.; Damidot, D. A.; Jawed, I. 2002. Hydration of Portland Cement, in *Structure and Performance of Cements,* 57–108. Spoon Press. ISBN 9780419233305.

Hommer, H.; Wutz, K. 2005. Recent Developments in Deflocculants for Castables, in *The 9th Biennial Worldwide Congress on Refractories.* November 8–11, 2005, Orlando, Florida, USA, 2–6.

Yoshioka, K.; Tazawa, E.; Kawai, K.; Enohata, T. 2002. Adsorption Characteristics of Superplasticizers on Cement Component Minerals, *Cement and Concrete Research* 32(10): 1507–1513. http://dx.doi.org/10.1016/S0008-8846(02)00782-2.

Jana, D. 2004. Concrete, Construction, or Salt – which Causes Scaling? Part I: Importance of Air-Void System in Concrete, *Concrete International* 26(11): 31–38.

Jo, B.-W.; Kim, C.-H.; Tae, G.-H.; Park, J.-B. 2007. Characteristics of Cement Mortar with Nano-SiO$_2$ Particles, *Construction and Building Materials* 21(6): 1351–1355. http://dx.doi.org/10.1016/j.conbuildmat.2005.12.020.

Kiricsi, I.; Fudala, Á.; Méhn, D.; Kukovecz, Á.; Kónya, Z.; Hodos, M.; Horváth, E.; Urbán, M.; Kanyó, T.; Molnár, É.; Smajda, R. 2006. Tubular Inorganic Nanostructures, *Current Applied Physics* 6(2): 212–215. http://dx.doi.org/10.1016/j.cap.2005.07.042

Kuo, W.-Y.; Huang, J.-S; Lin, C.-H. 2006. Effects of Organo-Modified Montmorillonite on Strengths and Permeability of Cement Mortars, *Cement and Concrete Research* 36(5): 886–895. http://dx.doi.org/10.1016/j.cemconres.2005.11.013.

Li, H.; Xiao, G.-H.; Ou, J.-P. 2004. A Study on Mechanical and Pressure-Sensitive Properties of Cement Mortar with Nanophase Materials, *Cement and Concrete Research* 34(3): 435–438. http://dx.doi.org/10.1016/j.cemconres.2003.08.025.

Lotov, V. A. 2006. Nanodispersnye sistemy v tekhnologii stroitelnykh materialov i izdelij, *Stroitelnye materialy* 9: 80–82.

Nili, M.; Zaheri, M. 2011. Deicer Salt-Scaling Resistance of Non-Air-Entrained Roller-Compacted Concrete Pavements, *Construction and Building Materials* 25(4): 1671–1676. http://dx.doi.org/10.1016/j.conbuildmat.2010.10.004.

Pundiene, I.; Goberis, S.; Stonys, R.; Antonovich, V. 2005. The Influence of Various Plastizing Elements on Hydration and Physical-Mechanical Properties of Refractory Concrete with Porous Fillers, in *Proc. of the Conference "Refractory".* Castables, Prague, 86–95.

Raki, L.; Beaudoin, J.; Alizadeh, R.; Makar, J.; Sato, T. 2010. Cement and Concrete Nanoscience and Nanotechnology, *Materials* 3(2): 918–942. http://dx.doi.org/10.3390/ma3020918

Rimkus, A. 1999. Chloridų, naudojamų kelių dangų apledėjimui tirpinti, neigiamas poveikis. Inhibicija, *Aplinkos inžinerija* [Environmental Engineering] 7(2): 99–103.

Skripkiūnas, G.; Janavičius, E. 2010. Effect of Na$_2$O·nSiO$_2$ Nanodispersion on the Strength and Durability of Portland Cement Matrix, *Medžiagotyra* (Materials Science) 16(1): 86–93.

Skripkiūnas, G.; Grinys, A; Miškinis, K. 2009. Damping Properties of Concrete with Rubber Waste Additives, *Medžiagotyra* (Materials Science) 15(3): 266–272.

Sobolev, K.; Flores, I.; Hermosillo, R.; Torres-Martínez, L. M. 2008. Nanomaterials and Nanotechnology for High-Performance Cement Composites, in *Proc. of ACI Session on "Nanotechnology of Concrete: Recent Developments and Future Perspectives"*, vol. 254: 91–118. November 7, 2006, Denver, USA.

Storpirštytė, I; Kazlauskienė, A.; Ščupakas, D. 2004. Chloridų koncentracijos sniego dangoje intensyvaus eismo Lietuvos kelių pakelėse tyrimai, *Journal of Environmental Engineering and Landscape Management* 12(Suppl. 2): 60–66.

Valenza II, J. J.; Scherer, G. W. 2006. Mechanism for Salt Scaling, *Journal of the American Ceramic Society* 89(4): 1161–1179.
http://dx.doi.org/10.1111/j.1551-2916.2006.00913.x.