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PERFORMANCE OF CONCRETE EXPOSED TO FREEZING AND THAWING IN DIFFERENT SALINE ENVIRONMENTS

Jana Šelih
University of Ljubljana, Faculty of Civil and Geodetic Engineering, Jamova 2,
1000 Ljubljana, Slovenia, e-mail: jana.selih@fgg.uni-lj.si

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Abstract. Selection of de-icing agent applied to the road surfaces can crucially affect the winter driving conditions as well as the deterioration of materials employed in the road structures in cold climates. In particular, concrete as one of the main construction load bearing materials can be affected. Road managers should therefore base their decisions regarding the selection of de-icing agent not only on data regarding their defrosting potential but also on data related to deterioration rates of materials built in the road infrastructure system. The paper presents the results of a study where the influence of different types of de-icing salts upon concrete performance was assessed in laboratory conditions. The theoretical background of freezing and thawing in the presence of de-icing salts in concrete is summarized. Salt scaling tests were performed using 3 selected de-icing salts on 3 different types of concrete. The mass scaled off the surface was weighed after every 5 freeze-thaw cycles. The results obtained show that a $CaCl_2$ solution has the most destructive effect upon concrete performance, regardless of the type of concrete. Deterioration was the least when a $MgCl_2$ solution was applied to the concrete surface.

Keywords: concrete, surface scaling, freeze-thaw resistance, de-icing agent, operation and maintenance management, road infrastructure.

1. Introduction

During their service life, concrete structures comprising the infrastructure systems which have been built in cold, harsh climates are frequently subjected to freezing and thawing. These systems need to exhibit constant adequate functional performance in terms of traffic safety (Baltrenas *et al*. 2009), which means that the elements and structures within the system are subjected to de-icing agents' application throughout the winter time. As a consequence, these elements experience freezing and thawing in the presence of de-icing salts that can have a devastating effect upon their long time performance and associated service time.

Various types of de-icing salts and their mixtures in various proportions are employed in order to ensure the required road conditions. The selection is mainly based on criteria related to their effectiveness in terms of their defrosting potential and effective temperature range (Table 1).

In addition to ensuring traffic safety provided by the salt application, the road managers have to be able to predict the deterioration progress of concrete structures and elements. This information has to accompany the knowledge related to current state of the road infrastructure in order to establish and implement rational and effective maintenance and rehabilitation plans (Šelih *et al.* 2008). Comprehensive fundamental understanding of the influence of deterioration processes occurring in concrete is therefore required.

With regard to the application of de-icing salts, insight into the behaviour of concrete when exposed to different saline environments can provide the additional information required for the selection of an appropriate de-icing agent.

The purpose of the study presented in this paper was to evaluate different types of de-icing agents in terms of their effect on concrete at low temperatures under controlled laboratory conditions. Three different salts with different effective temperature range (Table 1) that are commonly used as road de-icing agents were considered: sodium, magnesium and calcium chloride. Concrete resistance to freezing and thawing in the presence of salts was determined for these de-icing agents by standard salt scaling test.

Table 1. Effective temperatures of the selected salts (Winter … 2009)

De-icing salt	Formula	Effective temperature (°C)
Sodium chloride	NaCl	–11
Magnesium chloride	$MgCl_2$	–24
Calcium chloride	$CaCl_2$	–25

Two different types of concrete were tested: structural concrete suitable for highway structures and earth moist concrete suitable for the production of highly exposed prefabricated concrete road elements such as pav-

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ing blocks or kerbs. To ensure the quantitative evaluation of the de-icing salt effect, two types of structural concrete were further designed. The first type was designed to have a low, and the second type a high salt scaling resistance.

2. Literature review

2.1. The mechanism of water freezing in concrete pores and salt scaling

Freezing and thawing in the presence of salts is one of the most destructive deterioration processes a concrete structure can be exposed to. The exposure damage to concrete is manifested as “salt scaling” of the material – superficial damage caused by freezing a saline solution on a surface of a cementitious body, that causes the performance of the structure to decrease.

Due to the severity of this kind of exposure, several researchers, e.g. Hudec 2000; Kaufmann 2000, 2004; Marchand *et al.* 1999; Setzer *et al*. 1996, have studied the theoretical background of this degradation process, which is complex and governed by several different mechanisms.

If de-icing salts are applied during the freeze-thaw process, the freeezing/melting point of the pore solution is depressed by the dissolved alkali or chloride ions. Additionally, due to surface tension effects, the water in the small pores is at a lower energy level than the free water. When the pore water freezes, the solid-liquid interface curvature depends upon the pore diameter and therefore the freezing/melting temperature in the small pores is depressed when compared to the bulk water (Kaufmann 2000; Valenza and Scherer 2007a, b). In pores smaller than 1.5 nm, the freezing point is lower than –70 °C (Rostam 1992). In addition, the hydraulic underpressures that develop in small pores during cooling induce diffusion of liquid water from the small pores to the larger pores.

Ice formation can take place in the shape of a front, or as a nucleation process in each pore. Considering that the specific volume of ice is larger than that of liquid water, the nucleation process results in an increase in pore pressure, and consequent expression of the liquid water out of the pore. If empty pore space where the expressed water can be expelled to is available in the neighbourhood of the pore, no damage will occur to the solid matrix (Valenza and Scherer 2007).

If freezing is governed only by an ice front penetrating the pore space, poor connectivity of the pores, where wide pores are connected by narrow necks, may lead to super-cooling. In this process, poorly connected large pores freeze at a much lower temperature than they would if nucleation ice formation was present.

The presence of de-icing salts additionally affects the freezing and thawing process in terms of temperature redistribution. Melting of the ice at a concrete surface occurs at a lower temperature when de-icing salts are present. Thermal energy has to be supplied from the environment if the phase change from ice to water is to take place. As a consequence, the concrete surface is additionally cooled (Rostam 1992). The resulting temperature gradients may cause additional internal stresses and associated cracking and scaling of the outer layer of concrete.

Another destructive mechanism that takes place during the freezing and thawing of concrete in the presence of de-icing salts is osmotic flow. Osmotic pressure depends on the difference of the number of solute ions in the pore solution. In concrete, the adsorbed water occupying the small connecting neck pores provides resistance to the free flow of ions, and therefore serves as a semi-permeable membrane which is usually required to establish osmotic differences (Hudec 2000).

Empirical evidence supported by theoretical studies has shown that the freeze-thaw process is the most destructive when a 3% salt solution is applied to the tested concrete surface (Marchand *et al.* 1999; Valenza 2007), regardless of the salt type.

2.2. Influence of concrete composition, supplementing materials and surface finish upon concrete deterioration rate

The influence of concrete composition upon performance of concrete is well known (Mačiulaitis *et al.* 2009). In particular, the behaviour of various types of concrete when subjected to freezing and thawing in the presence of de-icing salts has been investigated extensively, e.g. (Setzer *et al.* 2002; Talbot *et al.* 2000). It has been shown that the pore structure of concrete and water content has a crucial influence upon surface salt scaling resistance (Copuroglu 2008). Large air pores resulting from adding air entraining agents to the fresh concrete mixture provide extra space in the pore structure where excess liquid water can be expelled during freezing.

Comprehensive studies have be carried out in order to demonstrate the effectiveness of various additives to concrete, such as supplementary cementing materials, in enhancing salt scaling resistance. The rate of deterioration (i.e. the quantity of material scaled off the surface) depends significantly upon concrete composition. For concrete types with added supplementary cementing materials, it has been shown that the deterioration rate is more rapid during the first few cycles of freezing (Talbot *et al.* 2000).

Further proof of the pore size distribution importance is provided by the influence of the selection of the tested surface. Salt scaling resistance was much higher (by a factor of 3) on a trowelled surface when compared to a sawn surface, as a trowelled surface is more porous. The scaling process was almost linear for the sawn surfaces, but not for the trowelled surfaces, where, during the first few cycles, the weak and porous surface layer was lost. Afterwards, the deterioration rate decreased. This is in accordance with the finding of the other researchers (Miragliotta *et al.* 2000), who detected a large variation in pore size distribution on the free and moulded faces of prefabricated concrete elements.

The available literature does not, however, report on the effect of salt type upon concrete performance, neither during laboratory de-icing salt scaling tests nor during in-situ exposure.

3. Materials and mix proportions

3.1. Selection of concrete types

Three types of concrete were investigated. The designed properties, especially the anticipated salt scaling resistance, were designed in such a way that the influence of the salt type could be quantitatively assessed.

The first type (designated A) was designed to be poorly resistant to salt scaling freeze-thaw exposure, so no air-entraining agent was added to the mixture.

Concrete mixes B and C were designed to have a high freeze-thaw resistance in the presence of salts. Mixture B was designed as a structural type of concrete, whereas the intended use of concrete type C is for the production of prefabricated concrete elements, where a low water to cement ratio is required. A schematic presentation of the selected concrete types is given in Fig. 1.

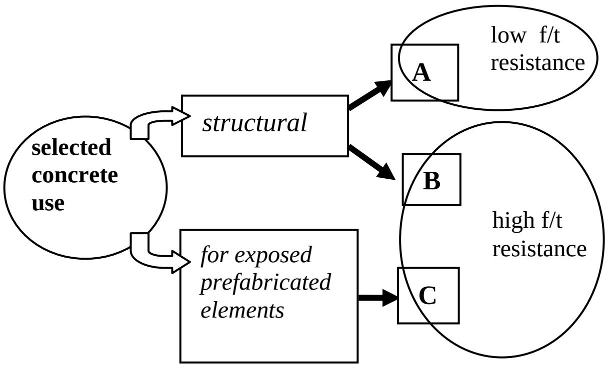

Fig. 1. Selection of concrete types to be tested (f/t = freeze/thaw)

3.2. Constituent materials and mix design

Locally obtainable constituent materials were employed. Tap water was used for all mixtures. Type CEM I 42,5 cement and crushed aggregate were employed in all mixtures. A sulfonate naphtalene formaldehyde condensate superplasticizing agent was added to the mixtures to obtain the required consistence.

The designed compressive strength class was C 30/37 according to the standard EN 206-1:2000 for all of the designed concrete mixtures. The designed consistence class was S3 for the A and B concrete mixtures according to the standard EN 206-1:2000. Concrete mixture C was designed as an earth-moist concrete.

The concrete was mixed in a drum mixer under laboratory conditions. The mix design of all tested mixtures is presented in Table 2.

Table 2. Concrete mix design

Label	A	B	C
Cement, kg/ m^3	410	410	410
Water, kg/m^3	175	175	142
Fine aggregate, kg/ m^3	839	789	830
Coarse aggregate, kg/ m^3	1021	960	1010
Air entraining agent, l/m^3	–	0.26	0.30
Superplasticizer, l/m^3	5.54	5.54	5.54

4. Experimental results

4.1. Fresh concrete properties

Air content, slump and density were measured for concrete types according to the series of European standards EN 12350. The obtained values are presented in Table 3.

A high air content level was achieved for concrete types B and C. The corresponding densities for these two concrete types were lower than the density of concrete type A. The targeted consistence class (S3) was achieved for concrete mixture A, whereas the achieved consistence class of concrete mixture B was S4 according to the standard EN 206-1:2000.

Table 3. Fresh concrete properties

Label	A	B	C
Air content, %	1.3	5,4	3,8
Slump, cm	15	18	0
Density, kg/ m^3	2485	2350	2430

Table 4. Hardened concrete properties after 28 days

Label	A	B	C
Comp. strengh, MPa	51.7	46.4	56.6
Flex. Strength, MPa	7.2	7.4	8.8

4.2. Hardened concrete properties

Compressive and flexural strength were measured after 28 days in conformity with the requirements of the EN 12350 series of standards. The results are presented in Table 4. The lower compressive strength of concrete type B when compared to that of type A can be attributed to this concrete’s larger air void space and lower density. The high compressive strength of concrete mix C results from the lower w/c ratio compared to concrete mixtures A and B.

4.3. Salt scaling testing

Standard procedure (CEN/TS 12390:9, 2006) was employed to measure the resistance of concrete to scaling. According to the standard, a 3% sodium chloride solution has to be used.

The sample consisted of three 15×15×15 cm cubes. The samples were cured for 28 days at 20 °C and at 100% relative humidity, and were then exposed to conditioning under ambient conditions of 20±2 °C and 65±5% relative humidity for 7 days. After conditioning, the samples were exposed to 25 freeze-thaw cycles, where the temperature of the air in the testing chamber reached –20±2 °C in the freezing phase, and +20±2 °C in the thawing phase. The freezing and thawing phases were 16 to 18, and 6 to 8 hours long, respectively. A 3% de-icing salt solution was poured over the surface of the test sample before exposure. The liquid height was maintained at 3 mm throughout the test.

The mass of material scaled off the surface of the test sample was determined every 5 cycles, and the maximum depth of damage on the tested surface was measured.

The criterion for scaling resistance is a maximum of 0.20 g/m^2 for the average cumulative mass loss after 25 freeze-thaw cycles, where the average value is obtained from measurements on 3 specimens. In addition, the maximum final mass loss obtained among the 3 measurements should not exceed 0.25 g/ m^2.

4.4. Results of the salt scaling test

The average mass losses after 5, 10, 15, 20 and 25 freeze thaw cycles for concrete types A, B and C exposed to selected types of de-icing salts are presented in Table 5. The corresponding cumulative losses of mass are depicted in Figs. 2, 3 and 4.

Table 5. Loss of mass after 5, 10, 15, 20 and 25 freeze/thaw cycles for concrete types A, B and C when exposed to varying de-icing salt solutions

	Salt type	No. of cycles				
		5	10	15	20	25
		g/m^2				
A	NaCl	0.052	0.086	0.056	0.063	0.059
	$CaCl_2$	0.090	0.062	0.093	0.096	0.087
	$MgCl_2$	0.000	0.001	0.003	0.002	0.007
B	NaCl	0.000	0.014	0.008	0.014	0.011
	$CaCl_2$	0.000	0.011	0.003	0.003	0.005
	$MgCl_2$	0.000	0.000	0.003	0.002	0.003
C	NaCl	0.000	0.010	0.019	0.033	0.035
	$CaCl_2$	0.022	0.010	0.014	0.011	0.014
	$MgCl_2$	0.000	0.000	0.000	0.000	0.009

The influence of the de-icing salt type is clear. The degradation rate for concrete type A is the fastest for the calcium chloride solution, which also causes the greatest final mass scaling. This trend is less pronounced for concrete types B and C, where the final amounts of mass scaled off the surface are of the same order of magnitude as the estimated measuring uncertainty of the testing method. The least destructive scaling action occurs when a magnesium chloride solution is poured over the tested surface, where the final amount of the scaled mass is well below the threshold level of 0.20 g/m^2.

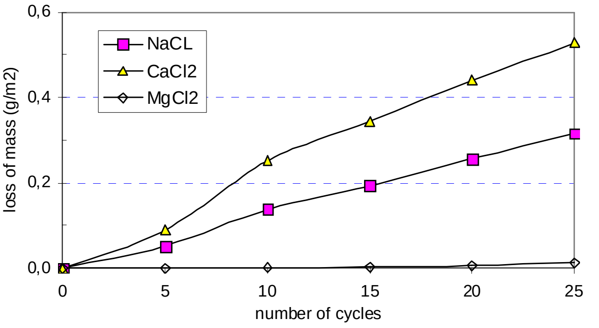

Fig. 2. Increase in cumulative mass loss for concrete type A with the number of freeze-thaw cycles

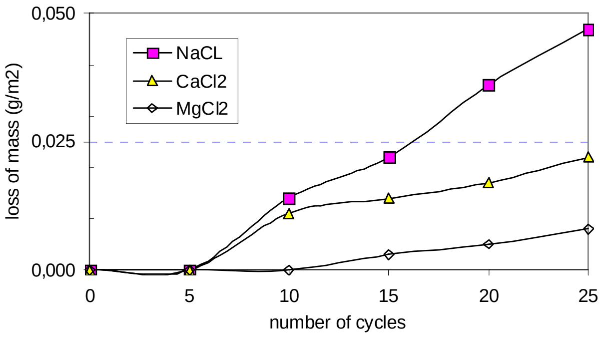

Fig. 3. Increase in cumulative mass loss for concrete type B with the number of freeze-thaw cycles

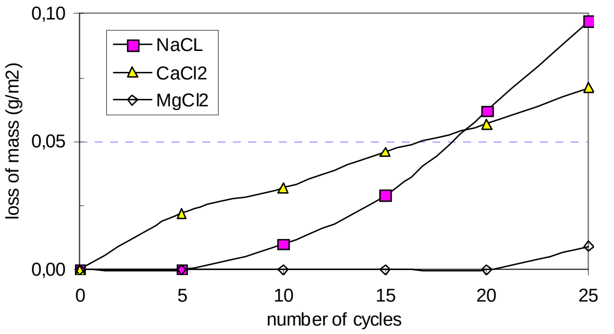

Fig. 4. Increase in cumulative mass loss for concrete type C with the number of freeze-thaw cycles

The results show that, in the case of concrete type A, the scaling rates decreases with the increasing number of freeze-thaw cycles. For concrete types B and C, the mass scaled off the surface and the corresponding scaling rates are very small (Table 5). This implies that the scaling process is stable.

From Figs. 2, 3 and 4, it can be seen that the targeted scaling resistance was achieved. The scaling resistance of concrete type A was much smaller that that of concrete types B and C: the cumulative average mass losses for concrete types A, B and C after 25 freeze-thaw cycles were, for NaCl, 0.315, 0.046 and 0.097 g/m^2, respectively.

It is well known that the performed test is associated with a large uncertainty of measurement. In this study, each test was performed on 3 specimens as prescribed by the standard CEN/TS 12390-9:2006 and other similar testing procedures. The scatter of the measured values is presented in Fig. 5 for the largest mass losses, i.e., for the case of concrete type A when exposed to $CaCl_2$ solution.

Parallel to the measurements of scaled mass, the maximum depth of damage to the tested surface was measured. This is a subjective test as the location of the maximum damage depth is assessed by the operator. The measurements do, however, provide an overall feeling of the surface degradation degree.

The results of the average depths of damage and their development over time, and the number of freeze-thaw cycles, respectively, are presented in Table 6 for all tested concrete types. The measured changes of depth show the same trends as measured losses of mass given in Table 5.

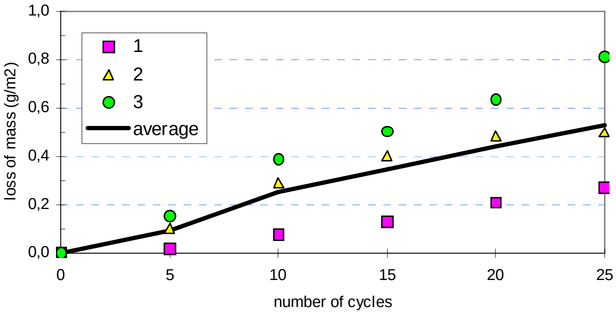

Fig. 5. Scatter of values measured on 3 specimens for concrete type A when exposed to $CaCl_2$ solution

The largest damage depth was observed for the case of the calcium chloride solution and concrete type A that contains no air-entraining agent. The depth of damage increases as the number of freeze-thaw cycles is increased. The obtained values are the smallest for concrete type B, which is consistent with the results presented in Table 5.

Table 6. Average depth of damage after 5, 10, 15, 20 and 25 freeze/thaw cycles for concrete types A, B and C, exposed to varying de-icing salt solutions

Salt type		No. of cycles				
		5	10	15	20	25
				mm		
A	NaCl	0.5	0.8	0.9	1.1	1.4
	$CaCl_2$	0.5	0.7	0.9	1.0	1.2
	$MgCl_2$	0.0	0.1	0.2	0.2	0.3
B	NaCl	0.0	0.2	0.3	0.3	0.4
	$CaCl_2$	0.0	0.2	0.3	0.4	0.5
	$MgCl_2$	0.0	0.0	0.1	0.1	0.2
C	NaCl	0.0	0.3	0.5	0.6	0.7
	$CaCl_2$	0.3	0.3	0.4	0.5	0.5
	$MgCl_2$	0.0	0.0	0.0	0.0	04

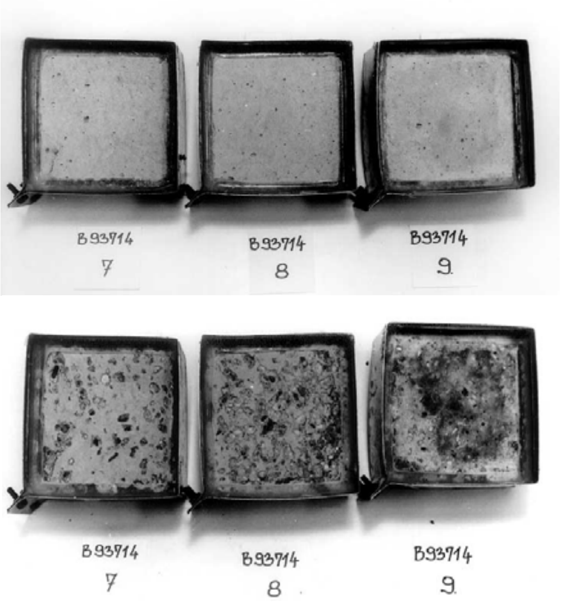

Fig. 6. Concrete type A (low freeze/thaw resistance) samples exposed to 3% NaCl solution, a) at the beginning of test, b) after 30 cycles

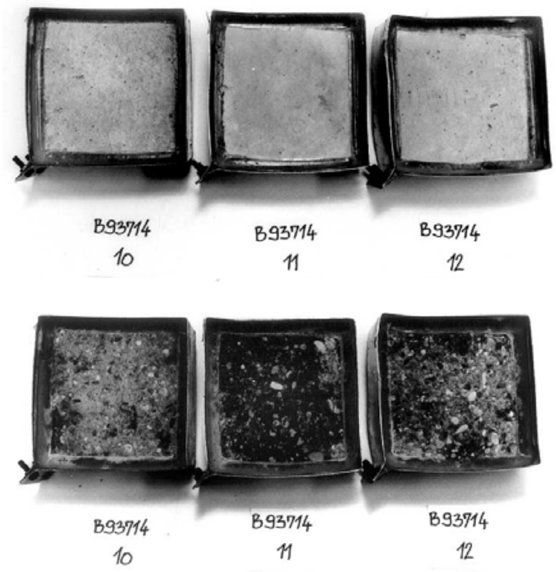

Fig. 7. Concrete type A (low freeze/thaw resistance) samples exposed to 3% $CaCl_2$ solution: a) at the beginning of test, b) after 30 cycles

Visual inspection of the tested samples can give a general idea of the degree of deterioration. This is confirmed by Figs. 6 and 7, where illustrations of the actual damage caused by the salt scaling test when different types of salt are applied are presented for concrete type A.

5. Conclusions

The presented results clearly show that the selection of de-icing agent significantly affects the onset, rate and final level of freeze-thaw damage occurring in a concrete structure. When tested under laboratory conditions, the most severe degradation (measured in mass of the scaled surface) was observed when calcium chloride solution was applied to the concrete surface.

It should be noted that all the solutions had the same mass concentration of de-icing salt (3%), as suggested by Valenza and Scherer (2007). To experimentally confirm his findings and the present results for different salts, salt scaling tests should be carried out also with varying levels of salt concentration, as presented by Marchand *et al.* (1999) for sodium chloride solutions.

When designing concrete to be used in structures exposed to the salt scaling process, one should bear in mind that standard laboratory salt scaling tests are carried out by applying a sodium chloride solution. Other types of de-icing salts, or their mixtures, are also frequently used in practice due to their different effective temperature ranges. The results presented in this paper show that they can have more devastating effects on concrete. Therefore, additional test methods should be developed for the assessment of concrete behaviour when exposed to various combinations of different types of de-icing salts.

References

Baltrenas, P.; Kazlauskiene, A. 2009. Sustainable ecological development reducing negative effects of road maintenance salts, *Technological and Economic Development of Economy* 15(1): 178–188. doi:10.3846/1392-8619.2009.15.178-188

CEN/TS 12390-9: 2006. Testing hardened concrete – Part 9: Freeze-thaw resistance – Scaling., European Committee for Standardization, Brussels.

Copuroglu, O.; Schlangen, E. 2008. Modeling of salt scaling, *Cem. & Concr. Res*. 38: 27–39. doi:10.1016/j.cemconres.2007.09.003

Hudec, P. 2000. The three percent deicer solution (why it is the most destructive in freezing and thawing tests), in Malhotra, V. M. (Ed.). *Durability of Concrete, Suppl. papers 5th Intern. Conference, Barcelona, 4–9 June 2000*. Farmington Hills: American Concrete Institute, 585–598.

Kaufmann, J. P. 2000. Freezing and thawing hysteresis effects in experimental analysis of frost de-icing salt resistance of cementitious materials, in Malhotra, V. M. (Ed.). *Durability of Concrete; Proc. 5th Intern. Conference, Barcelona, 4–9 June 2000;* SP-192, 677–692. Farmington Hills: American Concrete Institute.

Kaufman, J. P. 2004. Experimental identification of ice formation in small concrete pores, *Cement & Concrete Research* 34(8): 1421–1427. doi:10.1016/j.cemconres.2004.01.022

Mačiulaitis, R.; Vaičienė, M.; Žurauskienė, M. 2009. The effect of concrete composition and aggregates properties on performance of concrete, *Journal of Civil Engineering and Management* 15(3): 317–324. doi:10.3846/1392-3730.2009.15.317-324

Marchand, J.; Pigeon, M.; Bager, D.; Talbot, C. 1999. Influence of chloride solution concentration on salt scaling deterioration of concrete, *ACI Mat. J.* 96(4): 429–435.

Miragliotta, R.; Ait-Mokhtar, A.; Rougeau, P.; Dumargue, P. 2000. Concrete carbonation, a predicting methodology of the front advance, in Naus, D. (Ed.). *Life Prediction and Aging Management of Concrete Structures, Proc. Intern. Workshop, Cannes, 16–17 October 2000*; PRO 16, 35–42. Cachan: RILEM.

Rostam, S., *et al.* 1992. *Durable concrete structures – design guide.* Comite Euro-International du Beton, London: Thomas Telford.

Setzer, M. J.; Auberg, R.; Keck, H. J. (Eds.). 2002. Frost resistance of concrete from nano-structure and pore solution to macroscopic behaviour and testing, in *Proc. Intern. Workshop, Essen, 18–19 April 2002.* Cachan: RILEM.

Setzer, M. J.; Fagerlund, G.; Janssen, D. J. 1996. CDF Test – Test method for the freeze-thaw resistance of concrete – tests with sodium chloride solution (CDF), *Materials and Structures* 29(193): 523–528. doi:10.1007/BF02485951

Šelih, J.; Kne, A.; Srdić, A.; Žura, M. 2008. Multiple-criteria decision support system in highway infrastructure management, *Transport* 23(4): 299–305. doi:10.3846/1648-4142.2008.23.299-305

Talbot, C.; Pigeon, M.; Marchand, J. 2000. Influence of fly ash and slag on deicer salt scaling resistance of concrete, in Malhotra, V. M. (Ed.). *Durability of Concrete*, *Proc. 5th Intern. Conference, Barcelona, 4–9 June 2000*; SP-192, 645-658. Farmington Hills: American Concrete Institute.

Talbot, C.; Pigeon, M.; Marchand, J. 1996. Influence of supplementary cementing materials on the deicer salt scaling resistance of concrete, in *Proc. of the 7th Int. Conf. on the Durability of Building Materials and Components,* Stockholm.

Valenza, J. J.; Scherer, G. W. 2007a. A review of salt scaling: I. Phenomenology, *Cement and Concrete Research* 37: 1007–1021. doi:10.1016/j.cemconres.2007.03.005

Valenza, J. J.; Scherer, G.W. 2007b. A review of salt scaling: II. Mechanisms, *Cement and Concrete Research* 37: 1022–1034. doi:10.1016/j.cemconres.2007.03.003

Winter maintenance materials: What are you using? [online], [accessed Dec. 10, 2009]. Available from Internet: <www.saltinstitute.org/content/download/4264/23275)>.

UŽŠALDYMO IR ATŠILDYMO CIKLAIS VEIKIAMO BETONO ELGSENA SKIRTINGOJE DRUSKŲ APLINKOJE

J. Šelih

Santrauka

Kelių paviršiams barstyti naudojamos druskos gali iš esmės pakeisti vairavimo sąlygas žiemą ir paskatinti šalto klimato regionuose keliams naudojamų medžiagų senėjimą. Šios druskos ypač veikia betoną kaip vieną pagrindinių statybinėms konstrukcijoms naudojamų medžiagų. Parinkdami barstyti naudojamų medžiagų tipą kelių prižiūrėtojai turi atkreipti dėmesį ne tik į atitirpimo pajėgumą, bet ir į duomenis, susijusius su kelių infrastruktūros sistemoje naudojamų medžiagų senėjimu. Straipsnyje pateikti skirtingų tipų druskomis veikiamų betonų elgsenos eksperimentiniai tyrimai. Apibendrinti užšaldymo ir atšildymo ciklais druskų aplinkoje veikiamo betono elgsenos teoriniai tyrimai. Nagrinėtas trijų skirtingų druskų tipų poveikis trims skirtingų tipų betonams. Nuo paviršių atšokusios masės buvo sveriamos kas penkis užšaldymo ir atšildymo ciklus. Gauti rezultatai, parodė, kad $CaCl_2$ turi didžiausią ardomąjį poveikį betono elgsenai nepriklausomai nuo betono tipo. Senėjimas buvo mažiausias naudojant $MgCl_2$.

Reikšminiai žodžiai: betonas, paviršiaus aižėjimas, atsparumas užšaldymui ir atšildymui, druskos, operacijų ir priežiūros valdymas, kelių infrastruktūra.

Jana ŠELIH is an Assistant Professor at University of Ljubljana, Faculty of Civil and Geodetic Engineering, where she teaches Construction management. Her research interests include construction materials, construction management, quality management, maintenance management and decision methods in construction.