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THE INFLUENCE OF THE DE-ICING SALT ON THE DETERIORATION OF ROCK MATERIALS USED IN MONUMENTAL BUILDINGS

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Abstract: The de-icing salt has been used for decades to increase safety on the roads and sidewalks. In Poland, mainly the sodium chloride is used in order to maintain the roads in good condition during winter. Like other salts used for surface de-icing, it depresses the freezing point to lower temperatures and has an additional thermal effect by an exothermic reaction. However, this salt causes the accumulation of chlorides in the walls and stone buildings contributing to the deterioration of these facilities.

The paper addresses the issue of the influence of salt solutions on the structure and geomechanical properties of rocks at negative temperatures. The study was conducted on the basis of cyclic tests which simulate complex action of both the negative temperature and the salty environment. The conditions for the tests were chosen so as to reflect the actual conditions of the winter in Poland. During the tests, the longitudinal wave propagation velocity, changes in weights of the samples as well as visual changes were recorded which allowed continuous tracking of occurring changes. At the end of the tests, the rock samples were subjected to uniaxial compressive tests. For this purpose, four lithological types were chosen, representing the sedimentary rocks: clastic and carbonate, widely used in stone constructions.

1. INTRODUCTION

De-icing salt has been used for decades to improve traffic safety on roads and sidewalks. Millions of tons of salt have been applied since then for de-icing by lowering the freezing temperature of water. Unfortunately the migration of the de-icing salt to the neighboring buildings causes the accumulation of chloride on their near ground level and the subsequent resulting deterioration [9]. Most of the laboratory studies deal with the role of de-icing salts in the frost damage and emphasize their high harmfulness to the structure of stones [1], [2], [10], [11], although there are some that describe their positive action. McGreevy [7], for example, using more dilute solutions, found that salts could actually inhibit frost weathering under certain conditions. The greatest harmfulness under freeze thaw conditions is attributed to NaCl because of the crystallization of the dehydrate salt [9].

Winter is a period of the saturation of stones with salt solutions and salt nucleation. Intensive growth of salt occurs in the spring, when the evaporation is increasing [6]. In the outdoor masonry the distribution of salt is not homogeneous. In general, higher concentration of salts is found in the subsurface area and additionally at ground level, like in the case of de-icing salts. In the zone affected by rising damp the salt weathering is most noticeable because this process is permanent. Salts dissolved in the solution move upwards by capillary rise at first and then precipitate during evaporation. During capillary rise and evaporation the less soluble salts reach saturation earlier than salts of greater solubility resulting in a fractionation of the salts according to their solubilities. The composition of the pore solution continuously changes during transport and only the very soluble salts are transported as concentrated brine solutions to the upper evaporation zone [9].

The paper addresses the issue of an impact of saline solutions at low temperatures, formed as a result of road de-icing, on the structure of the rock and its geomechanical properties. Four lithological types representing sedimentary rocks: clastic and carbonate with different structure were chosen as an example of stones used in monumental buildings of Poland. Study conditions were chosen so as to reflect actual conditions in the winter in Poland.

2. CHARACTERIZATION OF THE ROCK MATERIAL

The research materials were sedimentary rocks often used in monumental buildings. For the study purposes the clastic rocks – sandstones from Śmiłów and Żerkowice, and carbonate rocks: limestones from Józefów and Raciszyn were used.

The sandstones from Śmiłów, exploited in the Świętokrzyski region, are characterized by fine grains and silica-clay binder. Their mineral content is dominated by well sorted quartz grains (Fig. 1a). In petrographic terms they are quartz arenites.

The sandstones from Żerkowice, exploited in the north Sudeten depression, are also characterized by fine grains and some silica-clay cement (Fig. 1b). These sandstones have a very large effective porosity of about 26%. In petrographic terms they are quartz arenites.

The limestones from Józefów, coming from a closed quarry in Roztocze region, are carbonate organogeneous rocks with a micrite cement. The skeleton grains are dominated by well preserved bioclasts of algae as well as accompanying foraminifera and fragments of bryozoans, crinoids and molluscs, and the nonskeleton grains are dominated by oval ooloids and small grains of quartz (Fig. 1c). In petrographic terms the rock under study is a paxton with bioclasts.

The limestones from Raciszyn, exploited in the Polish Jurassic Highland, are carbonate organogeneous rocks and belong to the group of the zalesiaki limestones. The background of these rocks is formed by fragments of organisms compound by fine grained calcite (Fig. 1d). There are also numerous caverns as well as intergranular, intragranular and intercrystalline pores. In petrographic terms the rock under study is an ooid paxton with bioclasts.

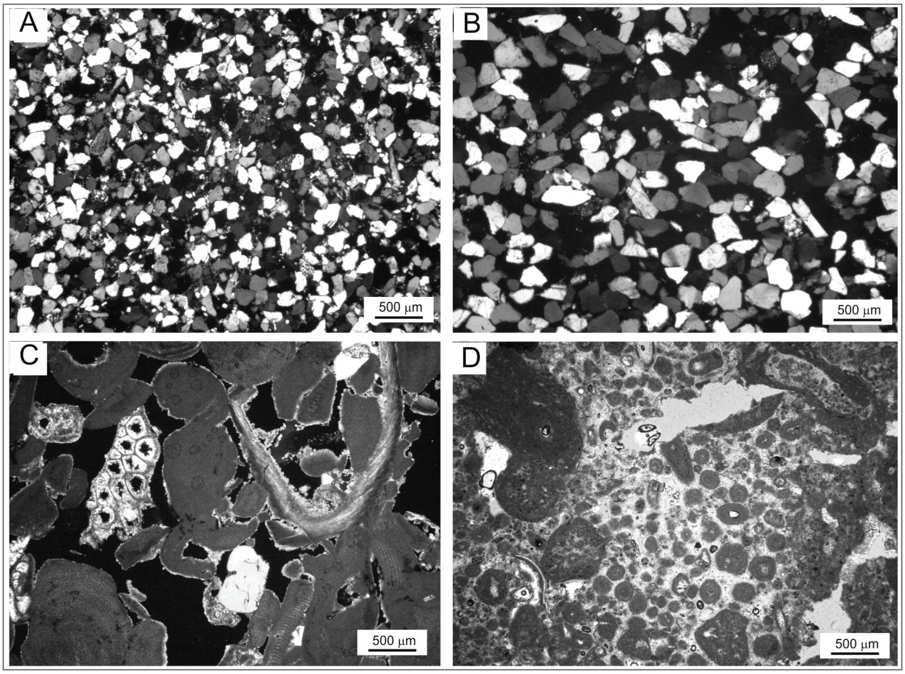

Fig. 1. Photomicroscopy of thin-section of analyzed stones, under transmitted light with crossed polarisers: (a) sandstone from Śmiłów, (b) sandstone from Żerkowice, (c) limestone from Józefów, (d) limestone from Raciszyn

The mineralogical differentiation of the rocks is reflected in the physical and mechanical properties, which have been identified in Table 1.

Table 1

Physical and mechanical properties of the rocks under study

Type of the stone	Bulk density* [kg/m^3]	Apparent (skeletal) density* [kg/m^3]	Effective porosity* [%]	Longitudinal wave velocity [m/s]	Uniaxial compressive strength [MPa]
sandstone from Śmiłów	2070	2620	20.8	2598–2894	34–62
sandstone from Żerkowice	1960	2640	25.7	3694–3808	23–56
limestone from Józefów	1850	2610	23.4	2833–2910	4.4–10.0
limestone from Raciszyn	2360	2710	12.8	4755–5059	30–59

* – result of the mercury intrusion porosimetry

3. METHODS

Determination of resistance to the de-icing salt at negative temperatures was based on the authors' own research methodology. Each test was performed on 4 cylindrical samples with a height of 5 cm and a width of 5 cm. After drying and weighing the samples were immersed in a 10% solution of de-icing salt (minimum NaCl content of 96.5%) and saturated to a constant weight. Thus prepared samples were inserted in a freezer where they were stored at temperatures ranging from –8 °C to –12 °C for 6 hours. After this time, they were placed in a vessel with a 10% salt solution at a temperature of 20 ± 5 °C and left completely immersed for 18 hours. This was one test cycle. The samples were again placed in a freezer and subjected to freezing and then thawing in a salt solution under the same conditions and the same time as previously. After each cycle, the samples were examined to identify any macroscopic changes. 100 cycles of freezing and thawing were performed, assuming that winter in Poland lasts on average 100 days. At the end of the test the samples were dried to a constant weight and the results are shown in percents as a relative difference of weight in relation to the initial weight of a dry sample according to the formula

$$\Delta m = \frac{m_b - m_a}{m_b} * 100 ,$$

where

m_b – weight of a dry sample before the test [g],

m_a – weight of a dry sample after the test [g].

A diagram of the study is presented in Fig. 2.

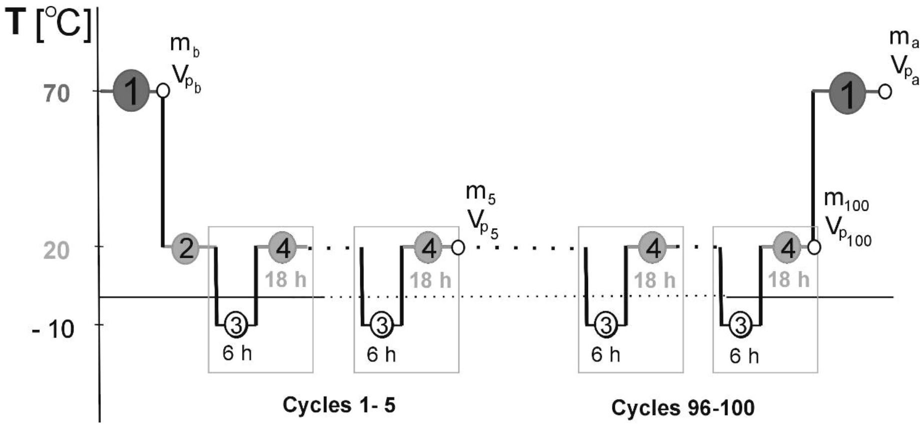

Fig. 2. Diagram of the study: 1 – drying to a constant weight, 2 – saturation with a 10% solution of the de-icing salt to a constant weight, 3 – the action of negative temperatures, 4 – immersion in a 10% solution of the de-icing salt

While performing the tests, the longitudinal wave propagation velocity was recorded (Vp). The changes of the longitudinal wave velocity in relation to the initial longitudinal wave velocity of a dry sample were determined according to the formula

$$\Delta Vp = \frac{Vp_x - Vp_b}{Vp_b} * 100$$

where

- Vp_b – longitudinal wave velocity of a dry sample before the test (in the air-dry state) [g],
- Vp_x – longitudinal wave velocity of a sample during the test [g].

The changes in the properties of the rock under influence of the de-icing salt in the modeled test were described with an integrity index (I_{DS}), which determines the degree of the rock deterioration. This index describes the change of the longitudinal wave velocity recorded for the material after the action of salt in reference to the longitudinal wave velocity measured in an air-dry state and it is expressed by a general formula

$$I_{DS} = \frac{(Vp_a)^2}{(Vp_b)^2}$$

where

- $I_{DS.}$ – integrity index of the longitudinal wave velocity change after the action of the de-icing salt [–];
- Vp_a – longitudinal wave propagation velocity after the action of the de-icing salt [m/s];
- Vp_b – longitudinal wave propagation velocity before the test (in an air-dry state) [m/s].

After the modeling of the action of de-icing salt at negative temperatures, the samples were subjected to an uniaxial compressive strength test. The test was performed in the stiff loading machine MTS-815 in accordance with the Polish standard PN-EN 1926: 2007 [8] and suggestions of ISRM [3]. Based on the acquired values of Rc, the coefficient of resistance (w_{DS}) to de-icing salt was determined according to the general formula

$$w_{DS} = \frac{Rc_a}{Rc_n}$$

where

- w_{DS} – coefficient of resistance to the action of de-icing salt [–],
- Rc_a – uniaxial compressive strength of a sample after completing the test of resistance to the action of de-icing salt [MPa],
- Rc_b – uniaxial compressive strength of a sample before the test in an air-dry state [MPa].

An additional component of the study were the observations in the scanning electron microscope, which enabled the monitoring of microstructural changes after completing the modeled tests as well as identification of newly formed minerals.

4. RESULTS

The visual assessment of the tested rock material does not reveal significant changes due to corrosive action of the de-icing salt on the structure of rocks. During the tests, there were no visible signs of shedding of the surface or chipping of the components of the rocks. No sample was also completely destroyed. The only things that strike the eye are white spots and efflorescences of salt on the outer surfaces of the rock samples, which significantly reduce the aesthetic value of the tested rock material. The condition of the samples after completing the test is shown in Fig. 3. The organogeneous limestones from Józefów were proven to be the most susceptible to color changes, which was observed as thick salt crusts on the surface (Fig. 3g). In the case of organogeneous limestones from Raciszyn, no significant change in appearance was observed (Fig. 3h).

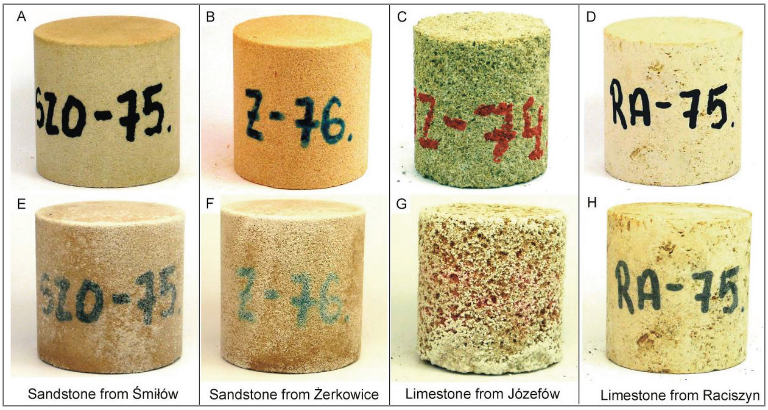

Fig. 3. The appearance of the samples after completing the test of resistance to the action of the de-icing salt: (a)–(d) the reference samples (before the test); (e)–(h) the samples after the test

In the microscopic image (SEM) of the material from the surface of the samples, in all the cases, large quantities of new mineral phases were observed. It was mainly sodium chloride, but calcium sulfate was also occasionally observed (Fig. 4). The sodium chloride was mainly found in the form of discontinued coatings or amorphous crystals merging into larger aggregates (Figs. 5–8) and the calcium sulfate appeared as elongated prismatic crystals (Fig. 4). In the material collected from the center of the samples, in each case fine crystalline forms of halite in the pore space were observed, however, its presence was not as common as on the surface of the samples.

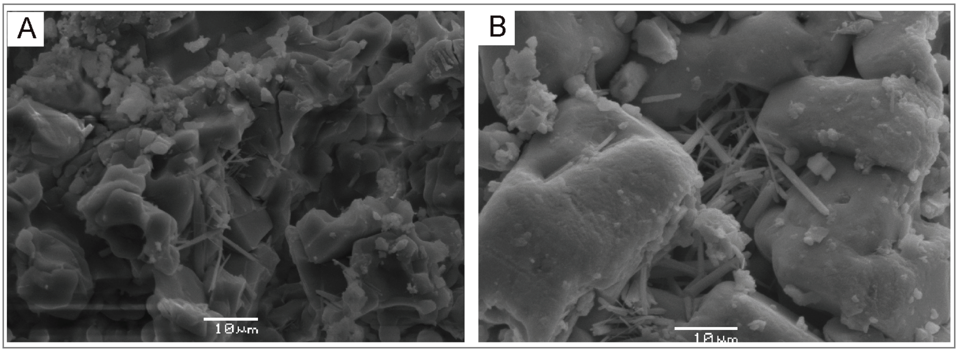

Fig. 4. SEM images of the surface of the sample after completing the test
of resistance to the action of de-icing salt:
(a) elongated gypsum crystals in the pore space of limestone from Józefów,
(b) elongated gypsum crystals in the pore space of sandstone from Żerkowice

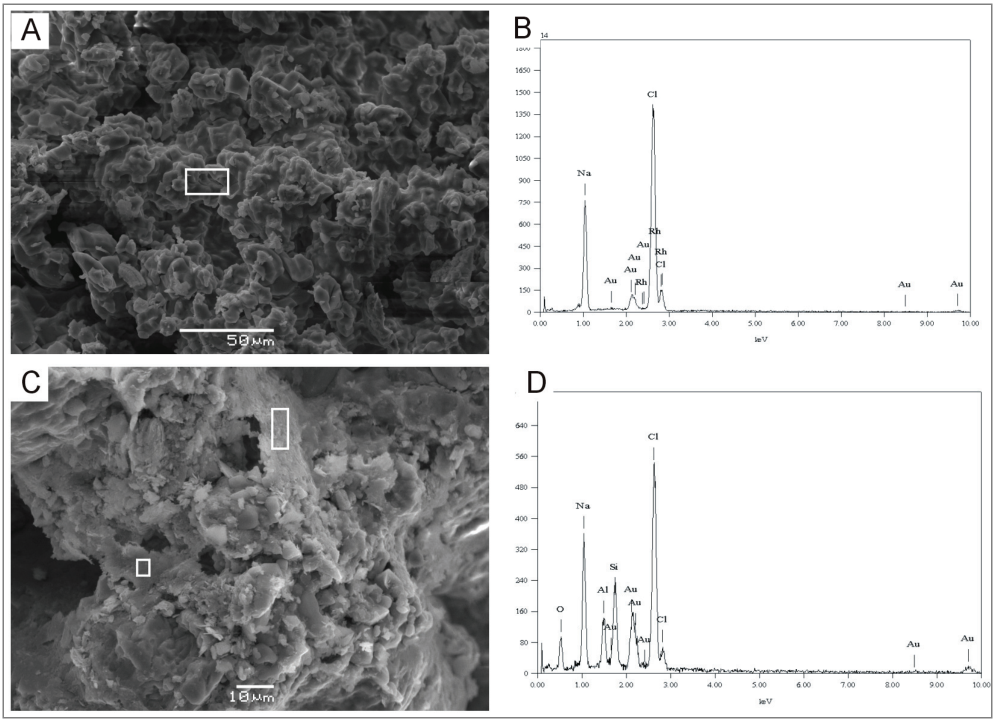

Fig. 5. The sample of sandstones from Śmiłów after completing the test
of resistance to the action of de-icing salt:
(a) SEM images of the surface of the sample, (b) energy dispersive spectrum (EDS) of halite,
(c) SEM images of the interior of the sample, (d) energy dispersive spectrum (EDS) of halite

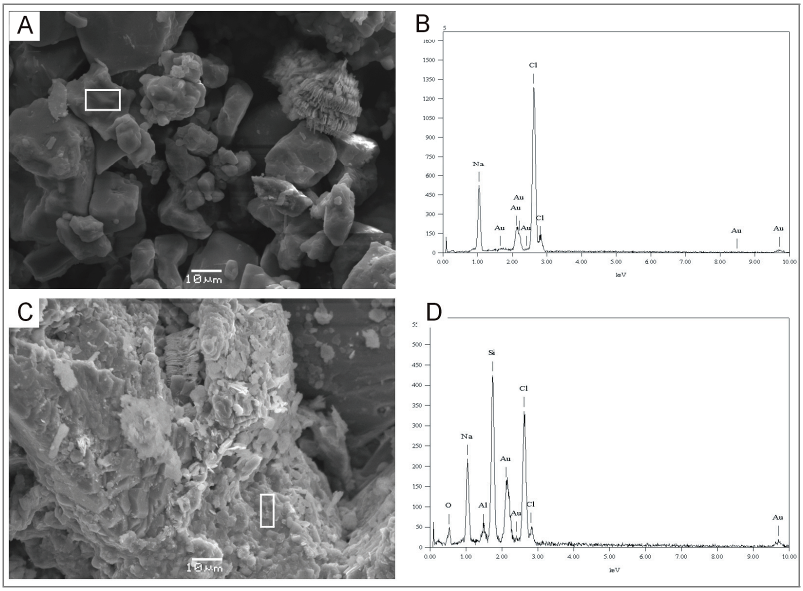

Fig. 6. The sample of sandstones from Żerkowice after completing the test of resistance to the action of de-icing salt: (a) SEM images of the surface of the sample, (b) energy dispersive spectrum (EDS) of halite, (c) SEM images of the interior of the sample, (d) energy dispersive spectrum (EDS) of halite

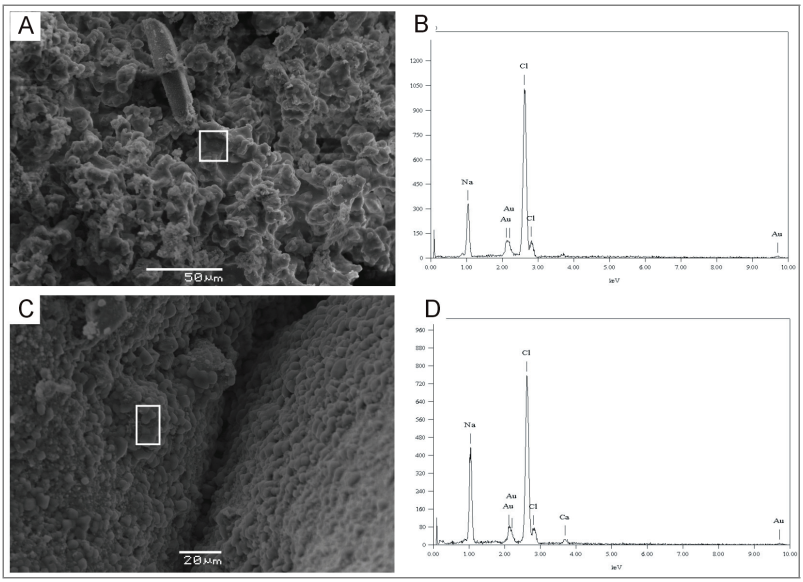

Fig. 7. The sample of limestones from Józefów after completing the test of resistance to the action of de-icing salt: (a) SEM images of the surface of the sample, (b) energy dispersive spectrum (EDS) of halite, (c) SEM images of the interior of the sample, (d) energy dispersive spectrum (EDS) of halite

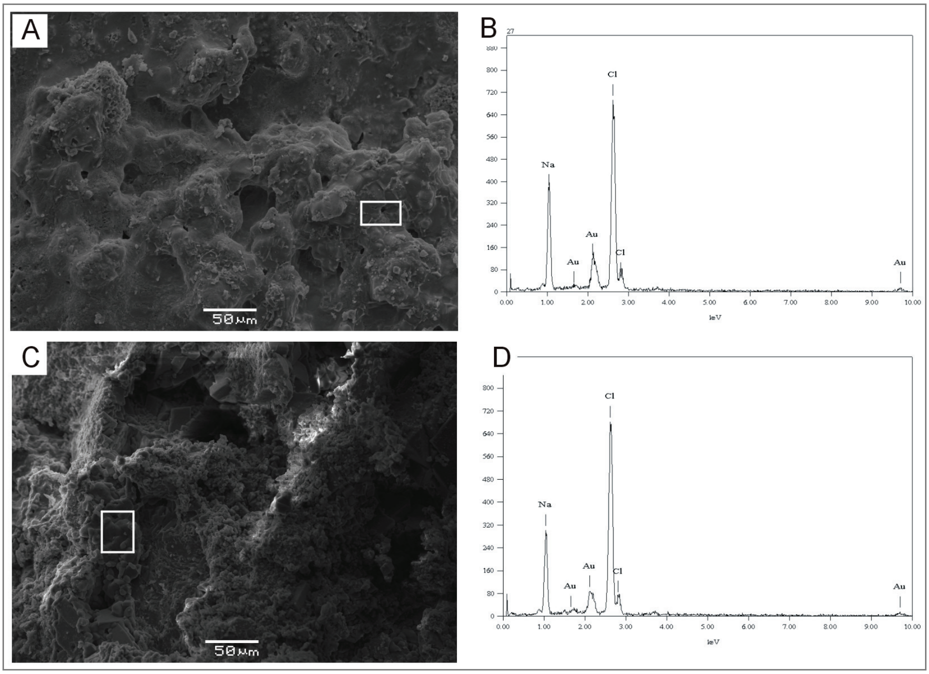

Fig. 8. The sample of limestones from Raciszyn after completing the test of resistance to the action of de-icing salt: (a) SEM images of the surface of the sample, (b) energy dispersive spectrum (EDS) of halite, (c) SEM images of the interior of the sample, (d) energy dispersive spectrum (EDS) of halite

After washing with water and drying to a constant weight, for all samples exposed to the de-icing salt solution the weight increase was noted. It was relatively small and ranged from 0,44 to 1%. The highest average weight increase was observed for the sandstone samples from Śmiłów (1%) and the smallest for the limestone samples from Raciszyn (0,44%). Table 2 shows the average values of weight changes but in Fig. 9 the weight evolution during subsequent test cycles is presented.

Table 2

Average weight changes after the action of de-icing salt

Type of the stone	Mass change Δm [%]
sandstone from Śmiłów	1
sandstone from Żerkowice	0.95
limestone from Józefów	0.94
limestone from Raciszyn	0.44

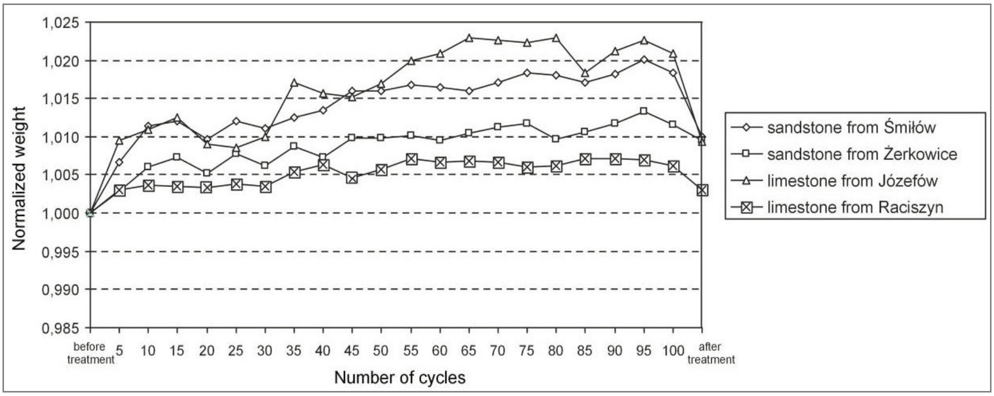

Fig. 9. Weight evolution during subsequent test cycles

The ultrasonic measurements carried out during modeling tests indicate that the action of the de-icing salt at negative temperatures results in the increase of the longitudinal wave velocity in the case of the sandstones from Śmiłów and the limestones from Józefów and Raciszyn, as well as the decrease in the case of the sandstones from Żerkowice (Fig. 10).

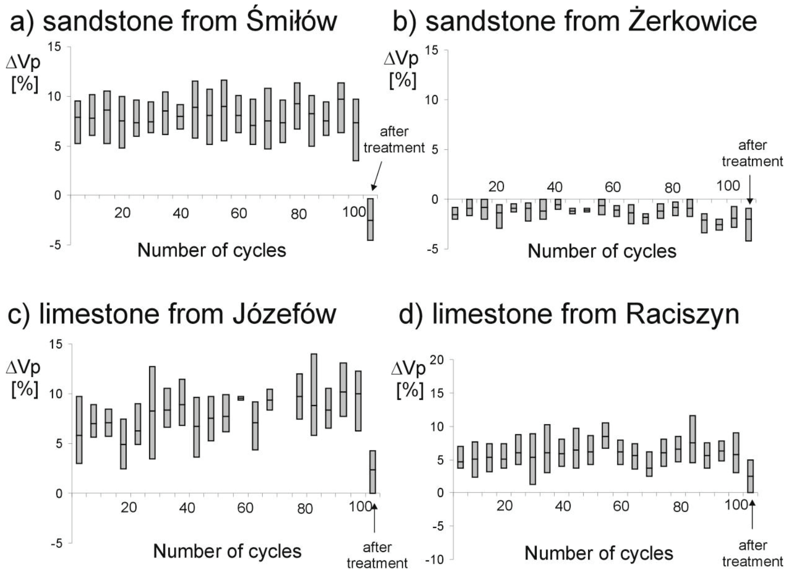

Fig. 10. Changes of the longitudinal wave velocity during the test

The values of the acoustic integrity index (I_{DS}) calculated for each rock on the basis of the longitudinal wave velocity (Fig. 11) were in the range 0.95–1.05 (Table 3). This indicates a high resistance of the analyzed rock material to the action of the de-icing salt at negative temperatures. Furthermore, it was found from the tests that the crystallization pressure of halite at negative temperature only slightly relaxed the structure and caused small internal defects of the rock material. Most probably this was due to the low concentration of the prepared salt solution as well as a relatively high freezing temperature. As emphasized by Williams and Robinson [11], the effectiveness of different salts depends not only on the concentration and type of salt, but also on the intensity of the freeze–thaw regime [4], [5]. However, this process leads to a decrease of uniaxial compressive strength in relation to the strength of these rocks in the air-dry state, as evidenced by the values of the coefficients of resistance to the action of de-icing salt (Table 3).

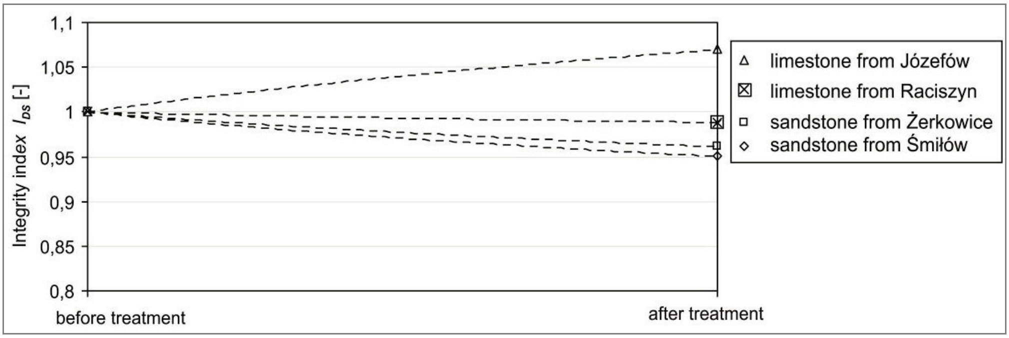

Fig. 11. Average values of the integrity index after the action of the de-icing salt

Table 3

Average values of the deterioration coefficient after the action of de-icing salt

Type of the stone	Integrity index I_{DS} [–]	Coefficient of resistance w_{DS} [–]
sandstone from Śmiłów	0.95	0.95
sandstone from Żerkowice	0.96	0.84
limestone from Józefów	1.07	0.90
limestone from Raciszyn	0.99	0.71

5. CONCLUSION

In the article, the influence of the action of de-icing salt at negative temperatures was presented, based on the authors' own research methodology. The proposed, non-standard method involves 100 cycles of freezing and thawing in a 10% solution of de-icing salt. The number of cycles and the adapted range of values of negative temperature refers to the model of the Polish winter.

The tests performed showed that despite 100 cycles none of the test samples of the sandstones and limestones was destroyed. It must be emphasized that the samples of the limestone from Józefów subjected to standardized tests of 25 cycles of freezing and thawing were destroyed.

Based on the tests performed, the following observations were made:

- weight increase of maximum 1% of both the sandstone and limestone samples,
- high values of the acoustic integrity index determined on the basis of the longitudinal wave velocity providing high resistance of the analyzed sandstones and limestones as well as relatively high values of the coefficient of resistance to the action of de-icing salt providing small decrease of uniaxial compressive strength – only in the case of the limestone from Raciszyn the decrease of the uniaxial compressive strength reached 30%,
- a decrease in aesthetic values of the analyzed rocks due to visible white spots and efflorescences of salt,
- new mineral phases both inside and on the surface of the samples in the form of amorphous crystals and discontinued coatings.

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