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THE INFLUENCE OF THE SALT MIST ON THE DETERIORATION OF ROCK MATERIALS

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Abstract: The paper is focused on changes of geomechanical properties with regard to loss of long-term resistance in studies on the influence of salt spray on the structure of selected rocks from Poland. The investigation has shown that the analyzed rock material shows variable susceptibility to this corrosive factor. The most susceptible to ageing by salt mist were Śmiłów sandstones, whose progressive deterioration was observed in subsequent cycles. Analysis of resistance parameters has shown decreased resistance to uniaxial compression exceeding 30% also in the case of the Józefów limestones. Limestones from Raciszyn have revealed high resistance to ageing by salt mist.

Key words: *salt mist, resistance, deterioration, susceptibility*

1. INTRODUCTION

Crystallization of salts in the stone elements of buildings and monuments often leads to partial or complete deterioration of the rock material. The sources of salts in such objects include air pollution, particulates, soil, precipitation, de-icing agents, as well as sea water. There are numerous reports devoted to the influence of salts of various origin on natural stones used as building material in Polish constructions [1]–[7], so far, however, there are no studies on the susceptibility of local stone material to the crystallization of sea salts. This paper presents such studies for selected sedimentary rocks used as building material in Poland.

Emission of salt sea spray is linked with wind velocity, in particular with breaking waves. Sea waves breaking along the coast emit fine water particles with sea salt into the atmosphere. Water drops dispersed above the sea evaporate fast while salt crystals remain in the air. Sea salt particles are then subject to wet or dry deposition, which contributes to the enrichment of buildings in salt thus causing their deterioration.

The paper is devoted to structural and resistance alteration taking place under the influence of salt spray. The studies were conducted with application of cyclic ageing tests in a salt chamber. The velocity of longitudinal wave propagation, weight changes and sample appearance were recorded during the test; this allowed the rock behavior to be evaluated in succeeding test stages. After the test, the rock samples were subject to a uniaxial compression test, which allowed one to determine their susceptibility to the corrosive factor under study.

2. CHARACTERISTICS OF THE ROCK MATERIAL

The research material comprised sedimentary rocks commonly used in historical and contemporary building material. Carbonate rocks, i.e., limestones from Józefów and Raciszyn, as well as clastic rocks, i.e. sandstones from Śmiłów and Żerkowice were selected for the study. For ages there has been a lot of interest in these materials in Poland and other countries, due to their aesthetic, usability as well as tractable values.

The Józefów limestones, derived from a closed-down quarry in the Roztocze area, represent a poorly sorted carbonate rock with numerous grains bonded with a micritic-sparitic cement. The grains comprise well-preserved bioclasts of algae and large foraminifers, echinoderm plates, echinoid spines, fragments of bivalve shells and bryozoans. Non-skeletal grains include rounded, oval ooids and fine quartz grains (Fig. 1a). Microcaverns are present in the rock, as well as large voids between the grains, within the grains and between the crystals. The rock represents packstone with bioclasts.

The Raciszyn limestones, exploited in the Polish Jura Chain represent a very poorly sorted carbonate deposit with numerous ooids, bioclasts and concentrations of crystalline anhydrite bonded with a mixture of micrite and calcite sparite of different size. The skeletal grains are rare and occur as poorly preserved fragments of thin-shelled bivalves, echinoderm plates and multi-chambered foraminifer tests (Fig. 1b). In turn, non-skeletal grains are very numerous, usually they are oval or elliptical ooids, as well as irregular grain aggregates (intraclasts) and fine grains of detritic quartz. The rock contains numerous caverns and wide pores between the grains, within the grains and between the crystals. The rock represents ooid packstone with bioclasts.

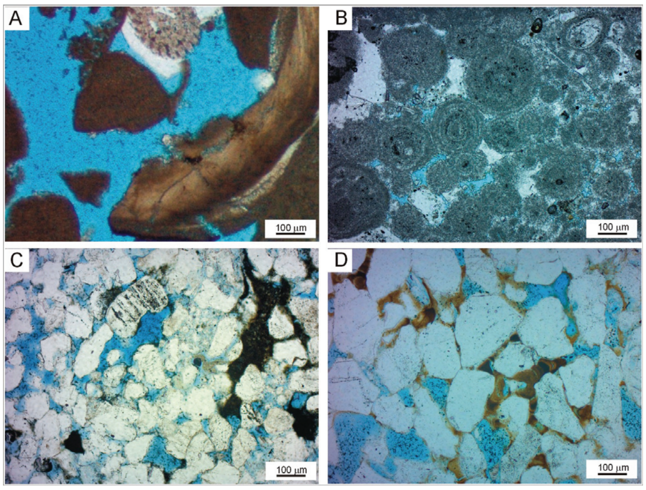

Fig. 1. Microscopic images of thin-sections of the analyzed rocks, under normal transmitted light: (a) Józefów limestone, (b) Raciszyn limestone, (c) Śmiłów sandstone, (d) Żerkowice sandstone

Sandstones from Śmiłów, exploited in the Holy Cross Mountains area, are fine-grained and have a massive texture. The mineral composition includes well-sorted, poorly and medium rounded detritic quartz grains with an irregular or isometric habit. The grains are usually partly regenerated and covered by more or less complete regeneration rims. Subordinately there also occur polycrystalline quartz grains, fragments of quartz rocks, elongated mica flakes and feldspar grains. The detritic grains are bound with a sparse siliceous-clayey cement, only partly filling the voids between the grains; in effect, the rock has very large porosity. Clay cement occurs locally as irregular aggregates of kaolinite and a dark-brown iron-clay matter (Fig. 1c). The sandstones represent quartz arenites.

Sandstones from Żerkowice, exploited in the North Sudetic Depression, are also fine-grained and have a sparse siliceous-clay cement (Fig. 1d). The detritic material is dominated by mono-mineral quartz with secondary regeneration rims. Polycrystalline quartz, fragments of quartz rocks, muscovite plates and grains of partly altered feldspars occur in smaller amounts. The cement fills only part of the voids between the grains, resulting in high porosity of the rock. There occur locally small aggregates of kaolinite and a yellow-brown iron-clay matter. The sandstones have also been assigned to quartz arenites.

Table 1 presents the variability of physical and ultrasonic properties of the analyzed rocks.

3. METHODS

The test of determination of resistance to ageing by salt mist has been conducted based on Polish standard PN-EN 14147: 2004 [8] according to the scheme presented in Fig. 2. The test was carried out on 5 samples from every type of the stone (5 × 4). After drying to a constant weight at 70 °C and cooling to room temperature, the samples were inserted in a salt chamber and exposed to the activity of salt mist for 4 h ± 15 min at 35 ± 5 °C. After this stage, the samples were dried in a chamber for 8 h ± 15 min at the same temperature. These actions comprised one test cycle

Table 1

Physical and ultrasonic properties of the rocks under study

Type of the stone	Bulk density* [kg/m^3]	Effective porosity* [%]	Longitudinal wave velocity [m/s]
Limestone from Józefów	1850	23.4	2833–2910
Limestone from Raciszyn	2360	12.8	4755–5059
Sandstone from Śmiłów	2070	20.8	2598–2894
Sandstone from Żerkowice	1960	25.7	3694–3808

* result of the mercury intrusion porosimetry

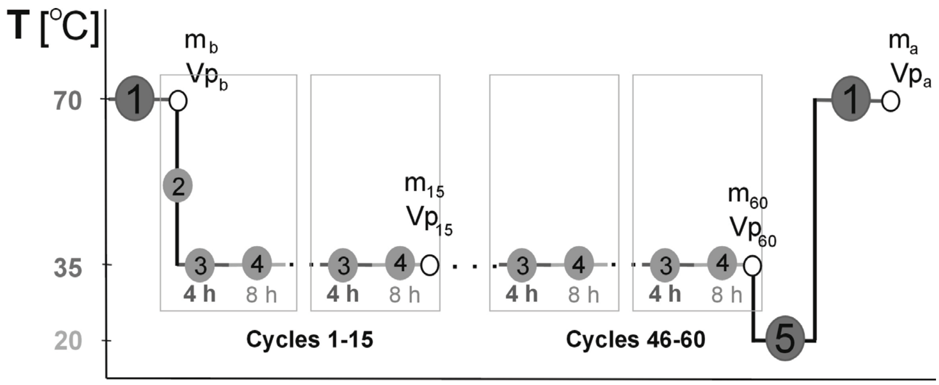

Fig. 2. Test scheme: 1 – drying to a constant weight; 2 – cooling to room temperature; 3 – salt mist test; 4 – drying, 5 – immersion in distilled water

with a total duration of 12 h. The entire test encompassed 60 cycles; after every 15 cycles, the samples were taken out of the chamber for a visual evaluation and for measurements of weight and longitudinal wave velocity. After the test, the samples were taken out of the chamber and immersed in distilled water in order to remove all the precipitated soils. The process was conducted till all the salts were removed, i.e., the electrical conductivity of the solution in contact with the samples did not exceed the double value of the primarily used water. Next, the samples were dried to a constant weight at 70 °C. The results were presented as (relative) percentage values of the weight loss in relation to the initial weight of the dry sample, according to the following formula

$$\Delta m = \frac{(m_a - m_b)}{m_b} * 100\% \tag{1}$$

where

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

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

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

$$\Delta Vp = \frac{Vp_x - Vp_b}{Vp_b} * 100 \tag{2}$$

where

Vp_b – longitudinal wave velocity of a dry sample before the test (in the air-dry state) [m/s],

Vp_x – longitudinal wave velocity of a sample during the test [m/s].

The changes in the rock properties under the influence of salt mist in the test were described by the integrity index (I_{MS}), which determines the degree of rock deterioration. This index describes the change of the longitudinal wave velocity recorded for the material after the salt mist test in reference to the longitudinal wave velocity measured in an air-dry state and is designated by the following formula

$$I_{\mathrm{MS}} = \frac{(Vp_a)^2}{(Vp_b)^2} \tag{3}$$

where

I_{MS} – integrity index of the longitudinal wave velocity change after the salt mist test [–],

Vp_a – longitudinal wave propagation velocity after the salt mist test [m/s],

Vp_b – longitudinal wave propagation velocity before the test (in an air-dry state) [m/s].

After the salt mist test, the samples were subjected to an uniaxial compressive strength test. The test was performed in a stiff loading machine MTS-815 in reference to the Polish standard PN-EN 1926: 2007 [9] and suggestions of ISRM [10]. Based on the deformation curves obtained from the tests (Fig. 3) the following values have been determined: uniaxial compression strength (R_c), critical axial strain (ε_a) and Young's modulus (E). These values have been compared to values obtained in natural conditions and their percentage change has been determined according to the following formulas

$$\Delta Rc = \frac{Rc_a - Rc_b}{Rc_b} * 100 \tag{4}$$

where

Rc_a – uniaxial compressive strength of sample after completing the test of resistance to salt mist [MPa],

Rc_b – uniaxial compressive strength of a sample before the test in an air-dry state [MPa].

$$\Delta \varepsilon_a = \frac{\varepsilon_{aa} - \varepsilon_{ab}}{\varepsilon_{ab}} * 100 \tag{5}$$

where

$\varepsilon_{a\,a}$ – critical axial strain of sample after completing the test of resistance to salt mist [MPa],

$\varepsilon_{a\,b}$ – critical axial strain of sample before the test in an air-dry state [MPa].

$$\Delta E = \frac{E_a - E_b}{E_b} * 100 \tag{6}$$

where

E_a – Young's modulus of sample after completing the test of resistance to salt mist [MPa],

E_b – Young's modulus of sample before the test in an air-dry state [MPa].

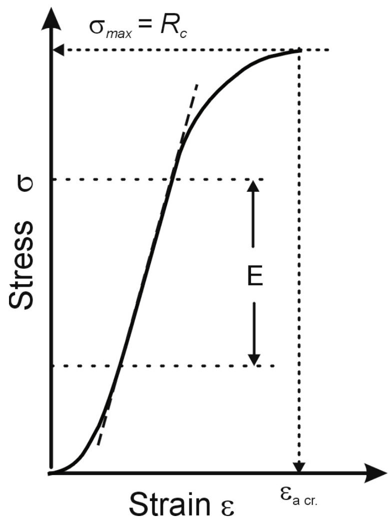

Fig. 3. Scheme of determining the resistance parameters

Additionally, the study included observations in a scanning electron microscope, which enabled monitoring of the microstructural changes after completing the tests as well as identification of the newly formed minerals.

4. RESULTS

Macroscopic observations conducted after every 15 test cycles have indicated that the rock material has variably reacted to the alternate action of salt mist and air drying. The first symptoms of ageing have been observed after 30 cycles of spraying with NaCl solutions, when samples became covered with thick fluffy deposits (Raciszyn limestones) and thin, dense salt crusts (Śmiłów and Żerkowice sandstones). After the next 15 cycles, the amount of salt crusts distinctly increased; however, at the same time, in the case of the Śmiłów sandstones, small blisters began to form below the sample surface, which in consequence led to flaking of thin subsurface layers parallel to the surface. Deterioration was displayed also in the falling off of smaller fragments and rounding of primarily sharp edges. During subsequent cycles, till the end of the test (60th cycle), the ageing process proceeded further with consecutive signs of deterioration. The state of sample preservation after 60 cycles is presented in Fig. 4. The test ended with soaking the rock samples in water for several days, which resulted in removal of most salt crusts accumulated on the surface of the rock samples during the test, as well as loose fragments detached from the surface due to structure destruction.

SEM images conducted after the test, i.e., after soaking in water, have shown strong disintegration of the space between the grains in every case either on

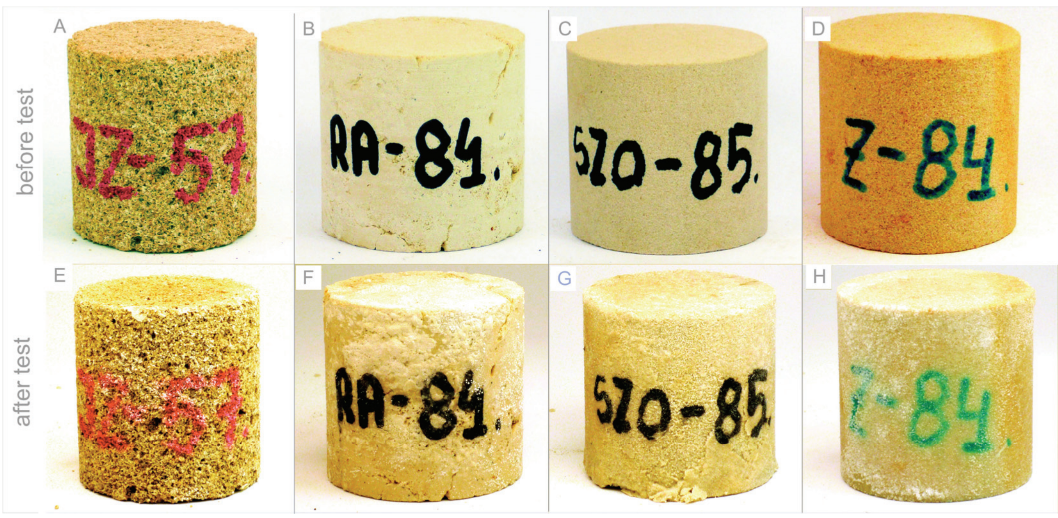

Fig. 4. Samples after completing the salt mist test: (a)–(d) reference samples (before the test); (e)–(h) samples after the test

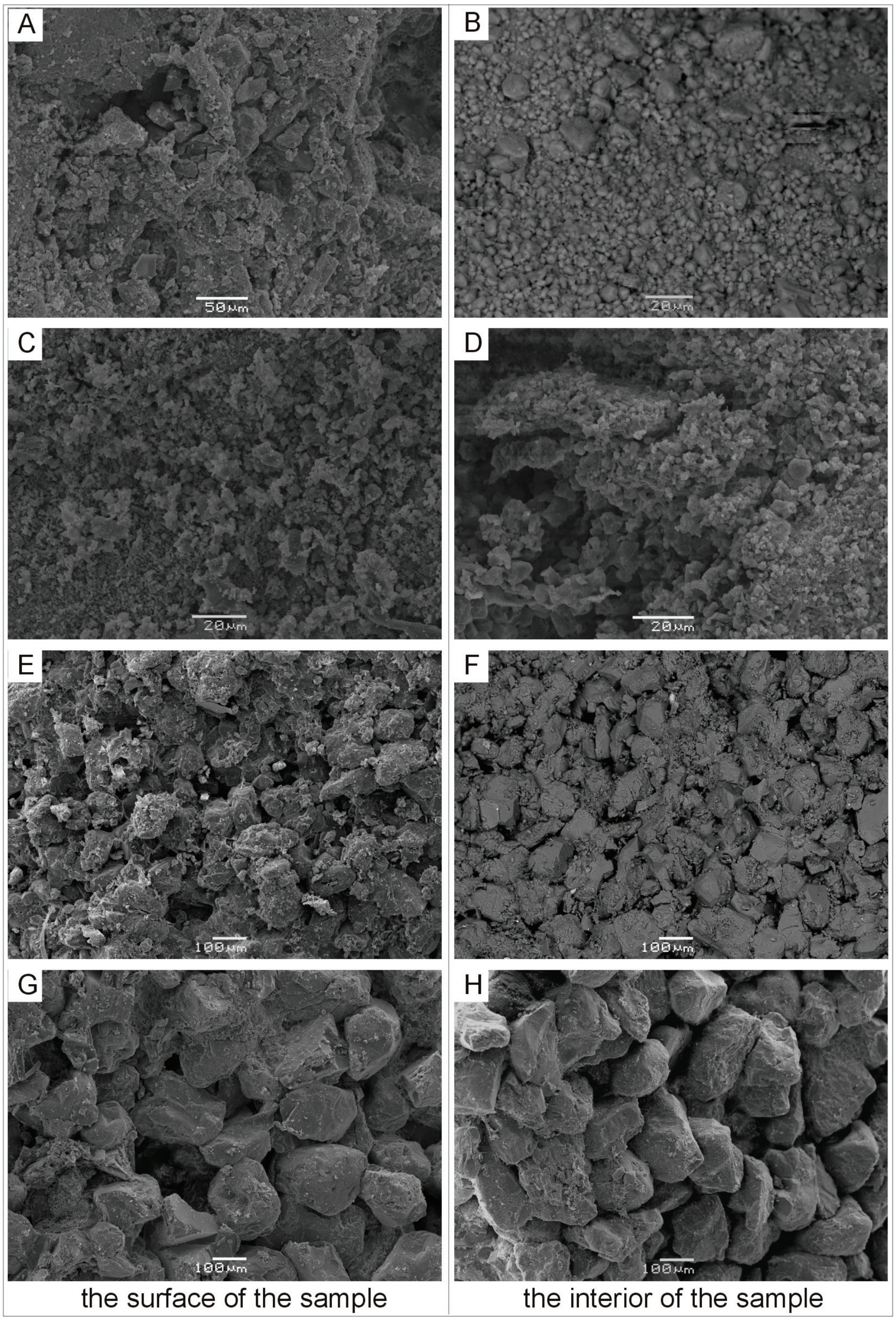

Fig. 5. SEM images of the pore space structure after completing the test of resistance to salt mist:
(a)–(b) Józefów limestone; (c)–(d) Raciszyn limestone; (e)–(f) Śmiłów sandstone; (g)–(h) Żerkowice sandstone

the surface or within the samples (Fig. 5). Loose rock fragments and cement fragments were noted in the entire rock weight, while the cement was occasionally impoverished (Śmiłów and Żerkowice sandstones) or dissolved (Józefów and Raciszyn limestones). The presence of trace amounts of salts have been registered only on the surface of the Józefów limestones (Fig. 6). In the remaining cases the salt was washed out leaving a strongly degraded structure.

Weight measurements conducted after every 15 test cycles have shown a distinct weight increase due to the appearance of salt crusts on the sample surfaces. The largest weight increase reaching 8–10% was observed in the sandstones from Śmiłów and Żerkowice after 45 test cycles, and in limestones from Józefów after 60 test cycles. In the Raciszyn limestones the weight increase did not exceed 4%. After soaking in distilled water and drying to a constant weight, a weight

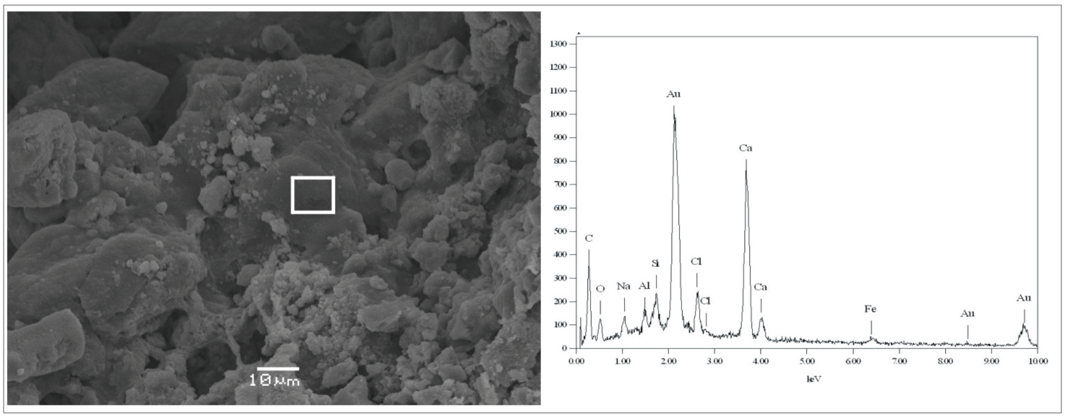

Fig. 6. Energy dispersive spectrum (EDS) on the surface of the Józefów limestone

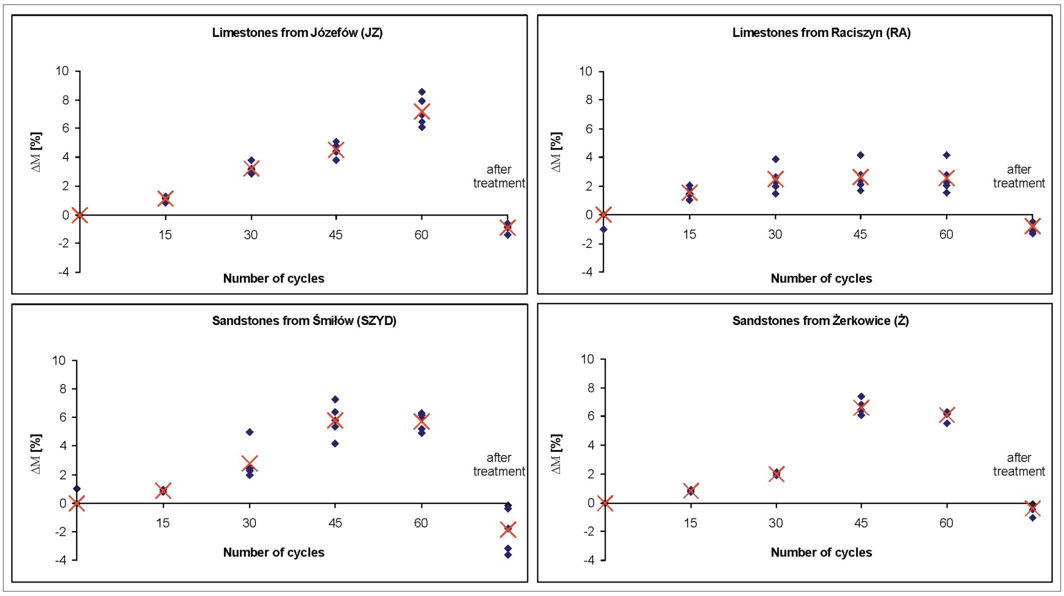

Fig. 7. Changes of weight during the test

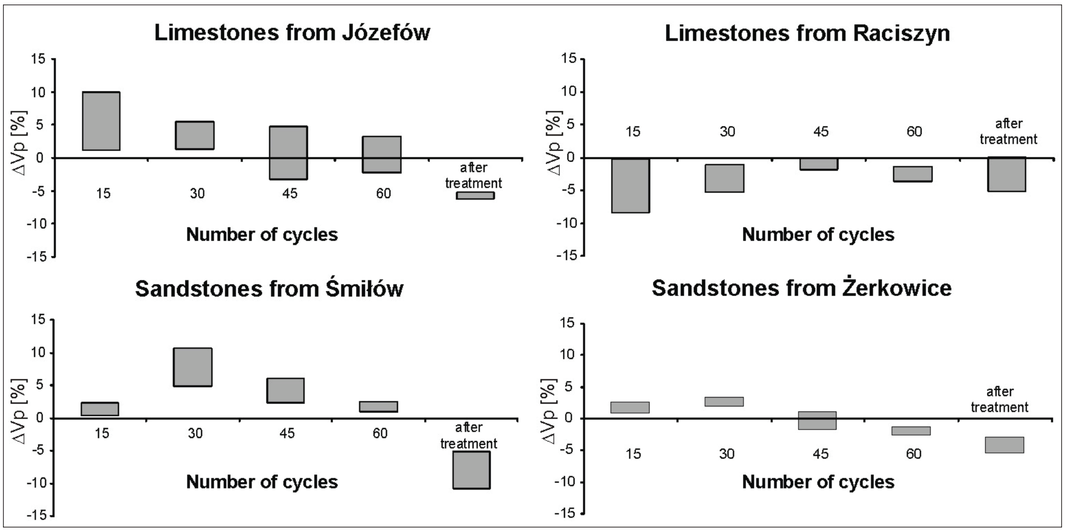

Fig. 8. Changes of longitudinal wave velocity during the test

decrease reaching an average of almost 2% in Śmiłów sandstones, below 1% for Józefów and Raciszyn limestones and 0.5% in Żerkowice sandstones has been noted in all samples subject to the salt mist tests.

Generally, the sample weight gradually increased during subsequent test cycles, whereas soaking in water that ended the test significantly influenced the variable character of the changes. Removal of sediments accumulated on the surface caused weight reduction of the analyzed samples (Fig. 7).

Ultrasonic tests carried out after subsequent test cycles have indicated the increase of the longitudinal wave velocity maximally by 10% in the case of the Józefów limestones after the 15th cycle and in the Śmiłów sandstones after the 30th cycle. In the Żerkowice sandstones, the increase of the longitudinal wave velocity was also observed, but maximally by 5%, whereas in the Raciszyn limestones a decrease of the longitudinal wave velocity by 8% was observed from the beginning of the cyclic tests. Ultrasonic tests conducted after the end of the ageing tests, i.e., soaking for several days and drying to a constant weight have shown that salt mist causes the decrease of the longitudinal wave velocity with regard to the initial state in all analyzed rock samples. The changes reach from 3 to 9% on average (Fig. 8).

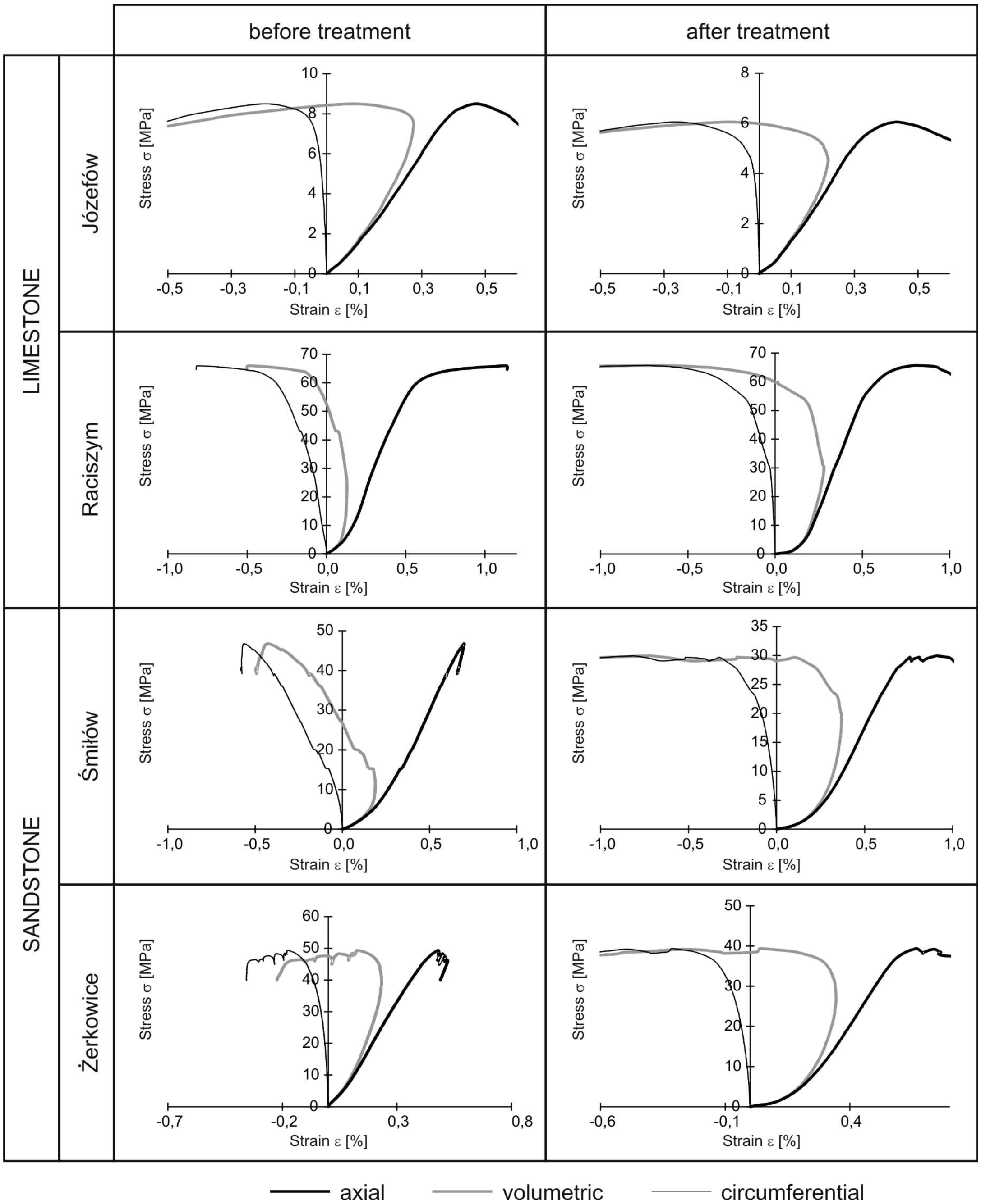

Fig. 9. Stress–strain characteristic of limestone from Józefów and from Raciszyn, sandstone from Śmiłów and from Żerkowice before and after the salt mist test

Table 2

Geomechanical properties before and after the salt mist test

Type of the stone	Before the treatment (air-dry state)			After the salt mist test		
	uniaxial compressive strength Rc [MPa]	axial strain ε_a cr. [%]	Young's modulus E [GPa]	uniaxial compressive strength Rc [MPa]	axial strain ε_a cr. [%]	Young's modulus E [GPa]
Limestone from Józefów	6.2–8.9 (7.8)	0.44–0.56 (0.50)	1.5–2.5 (2.1)	4.7–6.5 (5.4)	0.28–0.70 (0.44)	1.2–3.9 (2.3)
Limestone from Raciszyn	36.0–72.9 (53.0)	0.54–1.14 (0.74)	10.5–18.8 (15.2)	37.6–81.1 (56.3)	0.59–0.94 (0.74)	9.0–18.7 (13.8)
Sandstone from Śmiłów	33.4–68.6 (49.1)	0.62–0.70 (0.67)	5.8–8.9 (7.2)	23.0–44.9 (33.8)	0.64–1.17 (0.94)	2.2–9.8 (5.7)
Sandstone from Żerkowice	49.1–51.5 (50.3)	0.46–0.50 (0.48)	12.3–14.2 (13.0)	39.3–49.8 (45.6)	0.40–0.71 (0.58)	9.3–13.7 (12.1)

The decrease of the longitudinal wave velocity points to structure destruction and formation of internal defects.

Values of acoustic deterioration (I_{MS}) calculated for each rock sample based on longitudinal wave velocity were in the range 0.79–0.94. The highest indicator was noted for the Raciszyn limestones and the smallest in the Śmiłów sandstones. Indicators close to 1 (0.94 for Raciszyn limestones, 0.91 for Żerkowice sandstones) indicate high resistance of the analyzed rock material to salt mist, whereas the two remaining, 0.88 (Józefów limestones) and 0.79 (Śmiłów sandstones) point to the low resistance of these rocks to the corrosive agent.

Susceptibility of the analyzed samples to salt mist was evaluated also by strength tests. The results of uniaxial compressive strength tests before and after salt mist test on limestones (Józefów and Raciszyn) and sandstones (Śmiłów and Żerkowice) are shown on stress–strain curves (Fig. 9). The following values were compared: uniaxial compressive strength R_c, critical axial strain (ε_a) and Young's modulus (E) obtained for samples after the ageing tests and in natural conditions (Table 2). Salt mist caused decrease of uniaxial compressive strength values in samples of both sandstones and the Józefów limestones, and the increase of strength in samples of the Raciszyn limestones (Table 3). This factor caused also an increase of critical axial strain values and decrease of Young's modulus in samples of the Śmiłów and Żerkowice sandstones (Table 3). An opposite trend, i.e., a decrease of critical axial strain values and increase of Young's modulus, has been observed in the case of the Józefów limestones. Generally, similar values of the parameters described have been noted for the Raciszyn limestones.

Analysis of the results of strength tests on samples subjected to salt mist has shown a decreased resistance of the Józefów limestones and both sandstones to this factor and high resistance of the Raciszyn limestones to salt mist.

Table 3

Changes of the geomechanical properties after the salt mist test

Type of the stone	ΔR_c [%]	$\Delta\varepsilon_{a\text{ cr.}}$ [%]	ΔE [%]
Limestone from Józefów	–31	–12	10
Limestone from Raciszyn	6	0	–9
Sandstone from Śmiłów	–31	40	–21
Sandstone from Żerkowice	–9	21	–7

5. CONCLUSIONS

Laboratory tests, based on complex microstructural and geomechanical analyses have shown qualitative and quantitative changes in the rock material under study. The cyclic action of salt mist significantly decreases the appearance of the rock material used as building material and resulting in "deterioration patterns" (efflorescence, granular disintegration, blistering, rounding, roughening and contour scaling). The process results also in structure disintegration (loosening of microstructural bonds, cement dissolution and impoverishing), which has been confirmed by decreased longitudinal wave velocity values. Moreover, the obtained lower values of acoustic deterioration indicators for the Śmiłów sandstones and the Józefów limestones suggest a higher susceptibility of these rocks to the activity of sea water. This factor also influences weight reduction and decrease of strength parameters even by 30% in the case of the Śmiłów sandstones and the Józefów limestones. Therefore, the Śmiłów sandstones and Józefów limestones show higher susceptibility to the activity of salt mist in comparison to the Żerkowice sandstones and Raciszyn limestones.

The reason for such different responses to the action of salt mist within the same lithological type (e.g., clastic rocks) may be the pore size distribution. As the porosimetry studies have shown, both sandstones are rocks with a high effective porosity of about 21–26% (Table 1). However, the sizes of hysteresis of the curves of the increasing and the decreasing pressures are significantly different in the two types of rocks. The research shows that the sandstone from Żerkowice has a very low hysteresis (5%), reflecting the cylindrical shape of the pores in the rock. This model allows the free flow of water in the rock, reducing the probability of the salt crystallization in the pores [11].

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