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Resistance to salt crystallization of thin-bedded or platy limestone from the town of Benkovac in Croatia

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Abstract

Purpose. This paper aims to show the petrographic microstructural properties of natural stone as a building material from Benkovac, which is exposed to the influence of sea salt crystallization on the Croatian Adriatic coast.

Methods. The research is based on the graphical and statistical analysis of the results of polarization and electron microscopy, resistance to salt crystallization, ultrasound propagation velocity and uniaxial compressive strength testing. Three different lithotypes of limestone – grainy, micritic and laminated are analyzed to evaluate their important petrographic properties that have impact on the durability when material is exposed to the salt crystallization.

Findings. In the petrographic analysis, different characteristics are highlighted, especially those relevant to anisotropy of the structural features as lamination or layering. Besides determination of resistance to the salt crystallization, propagation of ultrasound direct P waves and uniaxial compressive strength are also tested. It is of scientific importance that a change in the internal structure of all samples, especially the laminated lithotype, is observed during the testing. The decrease of ultrasonic propagation velocity, decrease in compressive strength, and durability due to the action of crystallization pressure is a result of increase of the pore space and the fracturing along natural discontinuities such as lamination and layering.

Originality. This paper is the first to deal with the resistance to salt crystallization of the Benkovac stone, especially from the point of view of its petrographic properties. It also deals with the new aspect of interpreting the durability results by combining different methods of evaluating properties that are related to each other.

Practical implications. The knowledge gained in a specific area of the thin-bedded limestone of Benkovac can also be utilized in other places for better and effective protection and preservation of buildings, for which the same type of stone is quarried and used in construction.

Keywords: *Benkovac limestone, thin-bedded or platy limestone, durability, salt crystallization, stone properties, structural anisotropy*

1. Introduction

Stone as a building material has numerous architectural applications [1], [2] depending on its decorative effect and its physical-mechanical properties. After quarrying, natural stone is molded into slabs that are used in construction [3]. That is why it is important to test its properties. In most cases, the construction industry requires a series of tests, including the results of resistance to salt crystallization. Durability is a resistance of the stone towards the simultaneous action of physical, mechanical, chemical and biological factors at the construction site [1]. Probably, the most important factor of the physical deterioration of stone is the influence of the crystallization pressure during the crystallization of salt and/or ice. The pressures during the crystallization of various salts in the pores have a similar physical effect on the stone as the crystallization of ice. Damage to the samples and weight variation begin at the moment when the pressure on the pore walls, due to the crystallization of salt, overcomes the tensile strength of the stone [4]. Over time, stone can physically break down in the form of granular disintegration, flaking and chipping of entire crusts. In this regard, before using any variety of stone material in construction, it is necessary to test its resistance to salt crystallization, especially if it will be used in the exterior, where sea salt aerosol or salt defrosting is possible.

Dissolved salts can appear on the stone element surface in the form of efflorescence, and inside the pores – as a subflorescence. The salt that has crystallized on the subsurface can cause greater stress and increased damage to the material in relation to the salt that has crystallized on its surface. In addition, if salt crystallizes in one predominant direction or is not uniformly distributed inside of the stone material pores, it can create greater stress and damage than the uniformly distributed salt in any type of stone material [5].

The origin of dissolved salts in the stone material structures can vary from sea aerosols to air pollution, or from soil and cement or even de-icing salt. The natrite and thermonatrite can originate from the cement or the ground, while thenardite and mirabilite can be concentrated in the stone material from its origin. Carbonates and sulphates are com-

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mon in urban areas. Salts of different origins and salt mixtures with different physical and chemical properties can be identified in stone structures and in the many cultural heritage objects [6]. Thus, the composition of the salts can have a significant impact on the damage of the stone material [4], [7], [8]. Sodium sulphate is one of the most destructive salts that affect the durability of a stone. Therefore, it is used in a laboratory method which tests the effect of salt crystallization pressure in the pores of the stone material [9]. The dissolution and crystallization, but also hydration and dehydration reaction, can occur in the water – sodium sulphate system. Dissolution and crystallization depend on the degree of supersaturation or concentration of the salt and the temperature, while hydration and dehydration of the salt depend on the relative humidity and temperature [10]. Volume can be increased by as much as four times during the transformation of thenardite to mirabilite [11]. Under normal atmospheric conditions, this transformation can happen several times in one day. Alternating crystallization and/or hydration pressures on the pore walls can affect the disintegration of samples, especially in the weakest places. At a temperature of 50°C, sodium chloride can cause a crystallization pressure of 66.3 MPa. This pressure can cause significant damage especially in the structure of a weaker stone variety [1]. In addition to sodium sulphate or chloride, other salts can be used for durability testing, such as magnesium sulphate [12]. Damage to stone elements caused by crystallization pressure during salt crystallization significantly depends on the physical property such as porosity [13], [14] and on mechanical property such as material strength [15]. It also depends on the environmental conditions [14], salt concentration [16], saturation of the solution, the place of salt crystallization [5] and on the temperature change [17].

The old stone cities and monuments along the Mediterranean Sea coast are constantly exposed to sea salts, particularly sodium chloride [18], [19]. Many valuable monuments built of limestone in the traditional way were damaged, due to the sea salt. The importance of stone desalination on buildings is especially noted [20]. Stone facades, structures and monuments can be desalinated by the effect of the rainfall. However, stone elements that are not exposed to rain can be intensely destroyed. The life of stone buildings and monuments can be prolonged by occasionally washing of salt from the surfaces with pure water, especially after intense winds.

Croatia has several natural stone deposits that have been and are still used in construction [21]. However, the natural stone from Benkovac should be presented separately due to its specific characteristics, which is also the main purpose of this research. The Benkovac limestone is quarried in the vicinity of the small town of Benkovac near Zadar (Fig. 1).

This stone is traditionally used in Croatian construction industry due to its decorative effect, platy structure, physical and mechanical properties. Today it represents the brand in the stone industry [22]. It is commonly used in areas of increased salinity due to the proximity of the sea. Recently, it has been increasingly used in the continental part of Croatia for pavements, where de-icing salt is used in winter. Therefore, it is necessary to test samples for influence of salt crystallization pressures according to the recommendations on the mode and the area of its use.

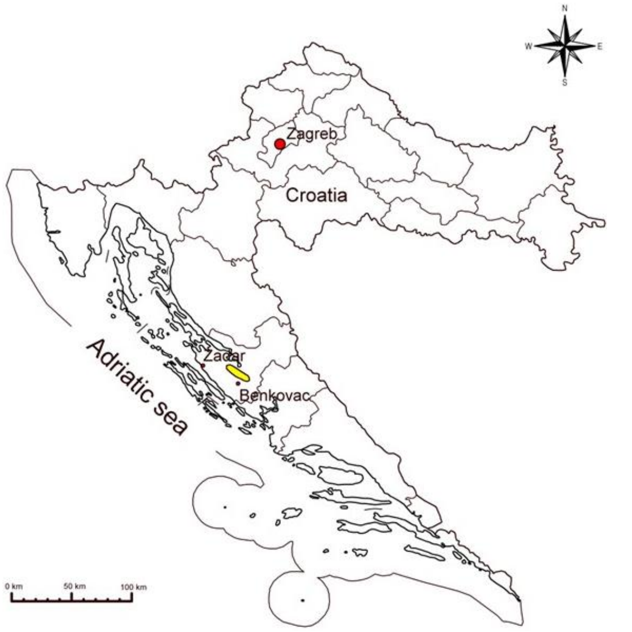

Figure 1. Geographic location of Benkovac thin-bedded limestone deposits, marked in yellow

Recently, scientific research has focused on the study of rock fracture mechanisms after heating and cooling with liquid nitrogen [23], then on the mode-I fracture toughness and damage mechanism of sandstone under different conditions [24], [25]. The influence of microwave irradiation and cooling with water on fracture behavior has also been investigated [26]. In contrast, this paper will present the results of resistance to salt crystallization of three different limestone lithotypes from Benkovac, focusing on the physical effect of salt on the samples.

2. Methods

Properties were determined on three lithologically different sets of Benkovac stone samples: grainy, micritic, and laminated lithotype, as described in [22], [27]. Samples of Benkovac limestone were subjected to the determination of resistance to the action of crystallization pressure during salt crystallization in its pores, according to the recommendations in [28]. Also, a non-invasive method of measuring the ultrasound propagation velocity (P-wave velocity) through the samples was used with purpose to evaluate the resistance to salt crystallization and damage of the stone [28]-[30]. The anisotropy coefficient of samples was calculated based on the P-wave velocity oriented parallel and perpendicular to the planes of layers and lamination [14], [17], [31], [32]. The changes of the stone anisotropy coefficient were monitored during the 15 cycles of resistance to the action of salt crystallization according to the recommendations in [14], [32].

Before and after the durability test, the uniaxial compressive strength (UCS) of samples was determined [2], [29]. The reduction in compressive strength after the test is an indirect indicator of durability and damage to the stone. Optical and electron microscopy, resistance to salt crystallization, ultrasonic propagation velocity and uniaxial compressive strength tests were carried out on the Benkovac natural stone samples. The results were then analyzed graphically and statistically.

2.1. Method of polarization and electron microscopy

Petrographic microscope OPTIKA B-1000 was used for petrographic analysis to classify samples according to the appropriate lithotypes. In addition, petrographic features that may affect the resistance of stone to salt crystallization were determined. Petrographic classifications [33]-[36] were used for petrographical analysis of the samples.

A scanning electron microscope (SEM) JEOL JSM-6510 LV with Oxford INCA X-act EDS detector was also used to photograph the salt crystallized on the sample surfaces. After 15 cycles of salt crystallization, the samples with a surface of 0.5 cm^2 were steamed with gold in a vacuum station. Such samples were photographed with magnification of 500×.

2.2. Resistance to salt crystallization

The determination of resistance to salt crystallization [9] was conducted on 30 cubic samples 4 cm long, for 15 cycles (Fig. 2). The dimensions of samples differed from those recommended by the standard, as stone slabs were a few centimeters thick. The samples were immersed in a saturated solution with respect to sodium sulphate (14% Na_2SO_4). The complete saturation of the sample was checked by weighing, as a fully saturated sample no longer increases its mass.

Figure 2. Samples immersed in a saturated solution of sodium sulphate

Afterward, samples were dried 17 hours at 110°C and cooled 3 hours at room temperature in a desiccator. During the test, weight variation was measured. Weight variation ΔM (wt. %) after the test was calculated according to Formula (1):

$$\Delta M = \frac{M_f - M_d}{M_d} \cdot 100, \quad (1)$$

where:

M_f – mass of dried samples after the 15th cycle, g;

M_d – mass of dried samples before the testing, g.

2.3. Ultrasound propagation velocity

Ultrasound propagation velocity of direct longitudinal (P) waves [37] was measured using CNS-Farnell Pundit 6 equipment with 54 kHZ transducers on the non-degraded dry samples. It was measured in three different directions (X, Y and Z) after every second cycle of durability testing. The Z direction was perpendicular to the planes of layers / lamination, while the X and Y directions were parallel to them. Based on the results gained, the anisotropy coefficient of structural features of samples (K_a) in% was calculated according to Equation (2):

$$K_a = \frac{V_{pa} - V_{per}}{V_{per}} \cdot 100, \quad (2)$$

where:

V_{pa} – P-wave velocity directed parallel to the layers / lamination; m/s;

V_{per} – P-wave velocity directed perpendicular to the layers / lamination, m/s.

2.4. Uniaxial compressive strength

After the crystallization test, the non-degraded samples were subjected to uniaxial compressive strength determination [38] using an ADR 2000 type press, which has sufficient capacity for compressive failure of the samples. Decrease in compressive strength of samples after the salt crystallization in relation to the dry samples was calculated. In this way, strength coefficient – the ratio between strength of dry samples and the ones after testing crystallization cycles – was calculated. Samples with structural anisotropy in the form of layers / lamination were oriented in two different positions: when the force is perpendicular and parallel to the layers / lamination. Uniaxial compressive strength (σ) in MPa is expressed by Equation (3):

$$\sigma = \frac{F}{A}, \quad (3)$$

where:

F – failure force N;

A – surface of the sample, mm^2.

2.5. Graphic and statistical analysis of the results

For basic charts, the software package Microsoft Excel 2010 was used. For statistical analysis of the results, STATISTICA (data analysis software system, version 8.0) was used. Variability between sets of samples, median, grouping values of 25-75% and range of values were graphically presented using the Box-Whiskes application. For comparing the results of successive measurements of resistance to salt crystallization, the Spearman rank correlation coefficient (R_s) with a significance level of 5% was used.

3. Results

3.1. Mineralogical and petrographical properties

The result of the field investigation, during which the sample was taken, is the confirmation that the Benkovac stone is a platy or thin-bedded limestone with a layer thickness of 2 to 45 cm with sharp and uneven surfaces. Beds show visible alteration of bright and dark laminas (Fig. 3). Bright yellowish laminas range in thickness from 2 to 6 cm, and light brown to bright grey laminas from 1 to 4 cm.

Thin sections show that Benkovac limestone consists of alternating layers/laminas of different composition, called grainy and micritic lithotype. Grainy lithotype microscopically consists of very well-sorted carbonate intraclasts bounded with coarsely crystalline sparicalcite cement (Fig. 4a). The color of grainy laminas is light brown to bright grey (Fig. 3). It is mainly composed of calcite with subordinate dolomite. The main diagenetic process evident is cementation. Also traces of dolomitization and dedolomitization are evident. The crystals of secondary formed dolomite are observed in the grainy lithotype.

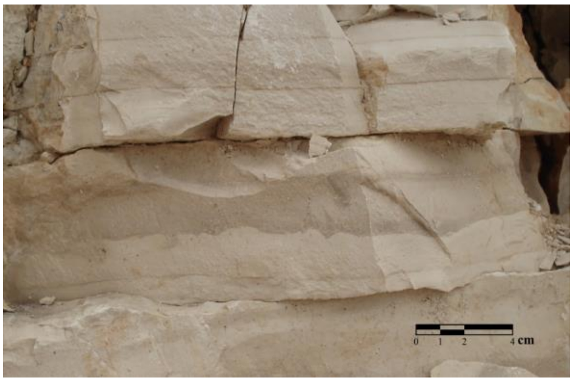

Figure 3. Benkovac platy or thin-bedded limestone with alteration of darker and brighter laminas

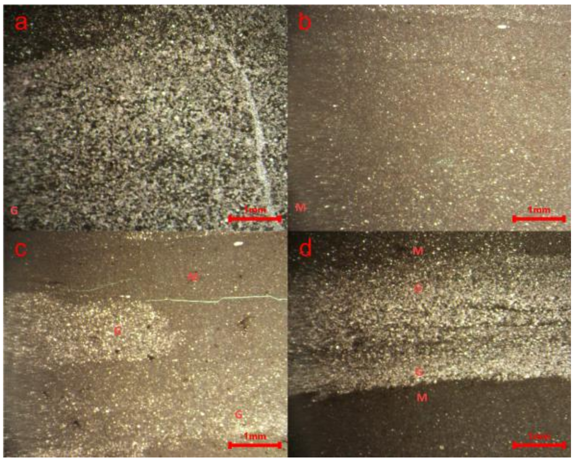

Figure 4. Microphotography of different lithotypes: (a) grainy (G) lithotype is defined as grainstone / intrasparite; (b) micritic (M) lithotype is defined as mudstone / micrite; (c) bioturbation is visible in micritic (M) lithotype where grainy lithotype in micritic lithotype; (d) contact between micritic and grainy lithotype is sharp

Rhomboidal-shaped calcite crystals are also present, indicating a dedolomitization process. This lithotype does not show anisotropy or signs of lamination [22] and is defined as grainstone / intrasparite [33]-[36]. The micritic lithotype microscopically is characterized by dense homogeneous micritic structure (Fig. 4b). The color of micritic laminas is yellowish. It is mainly composed of calcite and small amount of clay minerals with no signs of dolomite. Bioturbations (Fig. 4c) and signs of recrystallization of carbonate mud are common in the micritic lithotype. Recrystallization and bioturbation likely influence increase in intercrystal porosity in the micritic lithotype. Lamination as anisotropy in structure is manifested in this lithotype. Boundary (contact) between grainy and micritic lithotype is evident and in most cases is sharp (Fig. 4d) [22]. Micritic lithotype is defined as mudstone / micrite [33]-[36].

Since layers of different compositions are exchanged in stone slabs, the Benkovac stone is defined as laminated lithotype with exchange of grainy and micritic laminas [22], [39].

3.2. Resistance to salt crystallization

During the testing of resistance to salt crystallization (Na_2SO_4) after 15 cycles, five out of thirty samples broke by the end of the test. Fifteen samples showed a weight increase, while ten samples showed a weight decrease (Table 1). Results of water absorption, open porosity and real density for laminated lithotype were obtained from [22], [27].

Table 1. Mean values of the weight variation ΔM (wt. %) during the test, as well as water absorption Ab (%), open porosity (p_o) and real density (ρ_r)

Sample	No. of samples	ΔM, wt. %	Ab	p_o	ρ_r
Grainy lithotype	2	0.314	0.264	0.704	2.744
	4	-0.088			
Laminated lithotype	6	0.032	0.782	2.039	2.717
	1	-0.006			
Micritic lithotype	7	0.049	1.391	3.604	2.719
	5	-0.088			

The samples of laminated lithotype showed narrow range of weight variation, while the samples of grainy and micritic lithotypes – wide range (Fig. 5). For eleven samples of micritic lithotypes, the values of mass variation in the range from -0.125 to +0.120 wt. % were recorded.

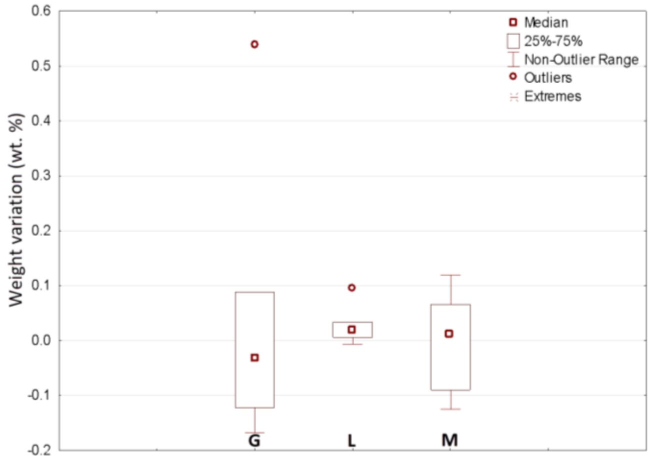

Figure 5. Box plot chart of weight variation (wt. %) of the samples during the salt crystallization: G – grainy lithotype; L – laminated lithotype; M – micritic lithotype

A weight variation of samples during 15 cycles was monitored according to recommendations from [28]. Samples of all three lithotypes (Fig. 5 and 6) showed a weight increase until the 15^{th} cycle of the crystallization test. The weight of samples increased due to the salt that crystallized in the pores. The micritic lithotype samples showed the largest weight increase (0.049 mas. %) (Fig. 5 and 6). Unlike other lithotypes, micritic lithotypes has the highest open porosity value (3.604%), and therefore has increased water absorption (1.391 wt. %). Grainy lithotype has low values of open porosity (0.704%) and water absorption (0.264 wt. %), thereby showing no major change in the weight (Fig. 5 and 6). Intact samples of laminated lithotype, showed an increase in weight of 0.032 wt. % (Table 1; Fig. 5 and 6). The value of open porosity (2.039%) of the laminated lithotype is between the values of grainy and micritic one. The water absorption of the laminated lithotype (0.782 wt. %) significantly depends on the grainy and micritic lithotypes and their share and position in the samples.

Out of 30 samples (Fig. 7a), five samples, all of the laminated lithotype, broke before the end of the test (Fig. 7b). The occurrence of salt efflorescence was noticed on the laminated lithotype samples after the second cycle. Change in color, from yellow to pale yellowish hue, was also observed. Expansion of existing discontinuities in the fabric of samples (micro cracks) was observed after the 4^{th} cycle.

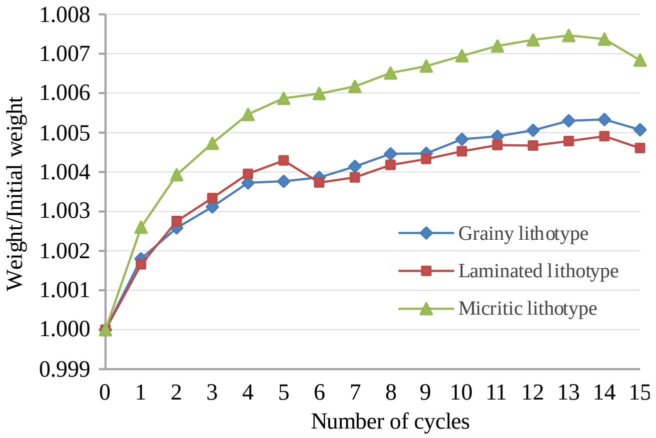

Figure 6. Graphical representation of weight variation of samples during the 15 cycles of salt crystallization

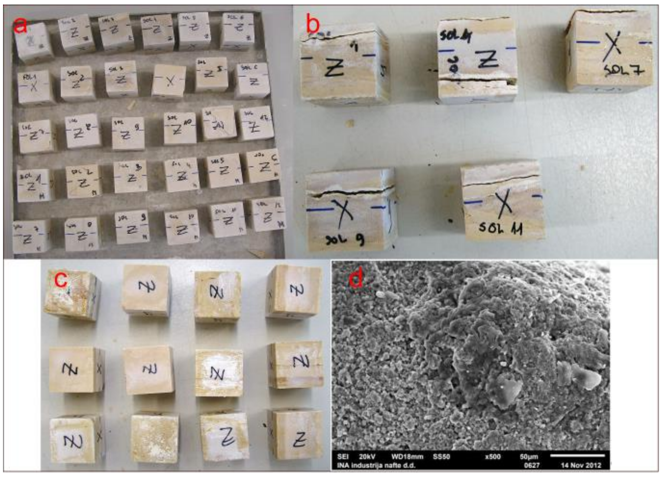

Figure 7. Samples of stone after test: (a) cubic samples with dimension of 4 cm; (b) five samples of laminated lithotype broke before the end of the test; (c) salt efflorescence and surface flaking is visible on the micritic samples; (d) SEM microphotograph of a salt crystallized on laminated lithotype

During the 5th cycle, the two samples broke. The other three samples fractured after the 9th cycle. All samples showed color change after the 15th cycle. Salt efflorescence was clearly visible on the bottom base of all samples, causing surface damage in the form of flaking (Fig. 7c). The salt was crystallized on the surface and at the edge of the laminated lithotype samples (Fig. 7d). Micritic lithotype was not disintegrated (Fig. 7c), although it has maximum open porosity and water absorption values.

3.3. P-wave velocity through the samples

After the 15th cycle of salt crystallization, the expected decrease in P-wave velocity through the samples of all lithotypes was recorded (Table 2, Fig. 8). Velocity decrease, up to 7% relative to the initial, was recorded in the grainy lithotype samples (Table 2).

The decreasing trend of the P-wave velocity for all lithotypes from initial to final cycle of salt crystallization is almost identical (Fig. 9). This is confirmed by a high value of Spearman's rank correlation coefficient (R) after certain cycles $R = 0.766$-0.933; $p < 0.05$. A wide range of velocity before and after the cycles of salt crystallization is found in all samples.

Table 2. Mean values of P-wave propagation velocity through the samples before and after the salt crystallization test

Sample	No. of samples	Velocity before testing, m/s	Velocity after testing, m/s	Decrease in velocity, %
Grainy lithotype	6	5880	5430	-7.65
Laminated lithotype – perpendicular	7	5363	5226	-7.28
Laminated lithotype – parallel	7	5736	5499	-4.13
Micritic lithotype – perpendicular	11	5487	5211	-5.02
Micritic lithotype – parallel	11	5580	5374	-3.69

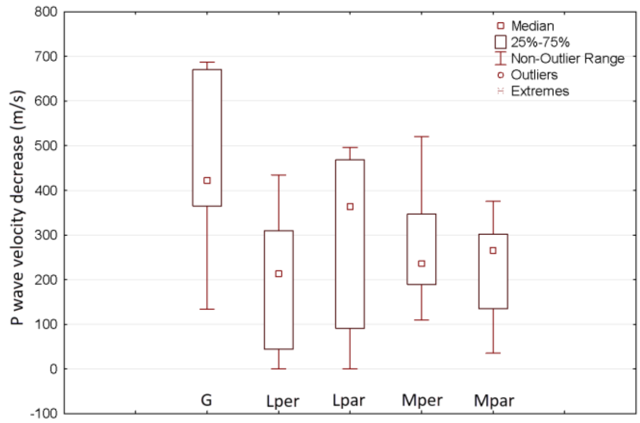

Figure 8. Box plot chart of P-wave velocity decrease after the salt crystallization test: G – grainy lithotype; L – laminated lithotype; M – micritic lithotype, per – perpendicular orientation, par – parallel orientation

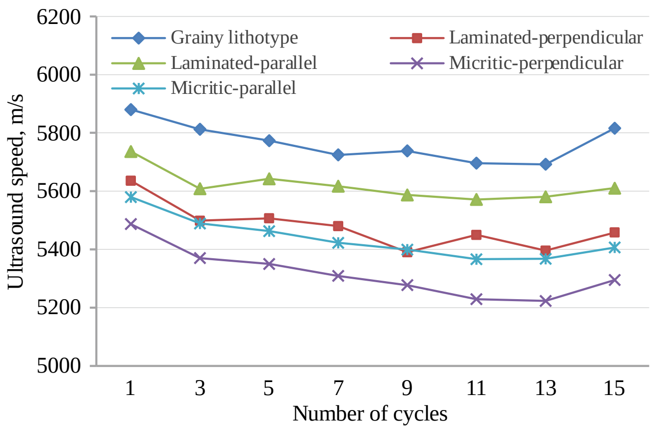

Figure 9. The P-wave velocity (m/s) measured during the cycles of salt crystallization

Besides the decrease in ultrasound velocity (Fig. 9), the change in anisotropy coefficient was also measured during the 15 salt crystallization cycles (Fig. 10), according to recommendations in [14], [32].

3.4. Uniaxial compressive strength

Uniaxial compressive strength (UCS) was determined on the intact samples after the durability test (Table 3), as recommended in [2], [29]. The grainy lithotype samples show a wide range of UCS values, from 98 to 217 MPa. Seven samples of laminated lithotypes after salt crystallization recorded a narrow range of compressive strength values from 206 to 247 MPa.

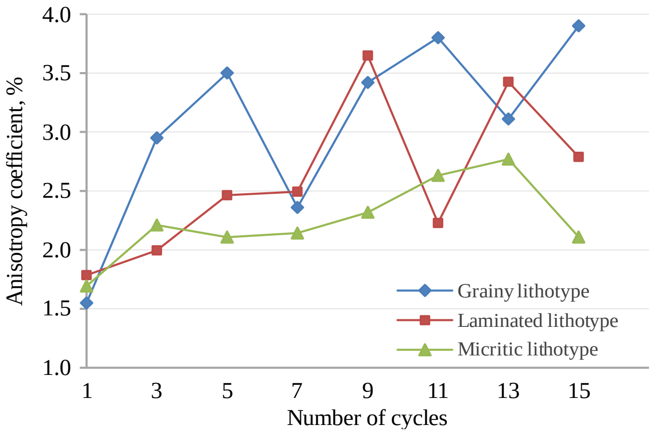

Figure 10. The anisotropy coefficient (%) of samples during the 15 cycles of salt crystallization

Table 3. Mean values of uniaxial compressive strength and strength coefficient of samples after the salt crystallization

Samples	No. of samples	UCS, MPa	Strength coefficient
Grainy lithotype	6	164	0.79
Laminated lithotype force is perpendicular	3	226	1.09
Laminated lithotype force is parallel	4	229	1.01
Micritic lithotype force is perpendicular	6	205	1.03
Micritic lithotype force is parallel	6	184	0.92

Micritic lithotype has values of 127 to 239 MPa (Fig. 11). At the end of the test, only grainy lithotype showed a decrease in compressive strength value with strength coefficient of 0.79 (Table 3).

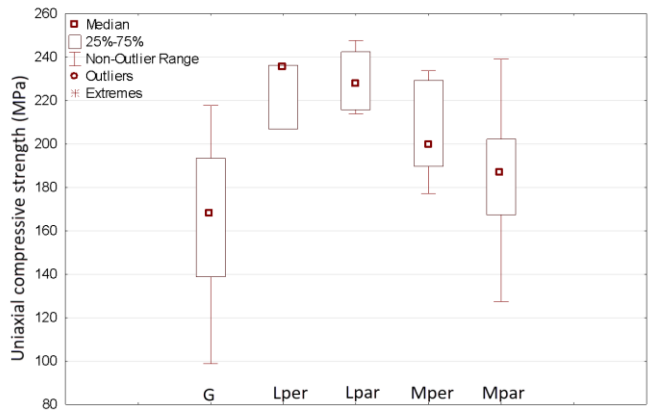

Figure 11. Box plot chart of uniaxial compressive strength after the salt crystallization test: G – grainy lithotype; L – laminated lithotype; M – micritic lithotype, per – perpendicular orientation, par – parallel orientation

In comparison with the strength of dry samples, the compressive strength decreased by about 21%. Unlike grainy lithotypes, micritic and laminated lithotypes after test showed no major changes compared to the compressive strength of dry samples (Table 3).

Only the micritic lithotype showed difference in strength of 21 MPa in two different directions, considering the structural anisotropy.

4. Discussion

The Benkovac thin-bedded limestone is excavated in the form of thin slabs or plates. Layers and lamination are the main structural anisotropy features, which can be used to distinguish individual naturally thicker or thinner layers or plates (Fig. 12). In majority of stone structures, such plates are oriented as naturally bedded or face bedded [39].

Figure 12. Main visible feature of Benkovac stone is layering and lamination, along which slabs or plates can be exploited

The area where, as known in the market, Benkovac stone of Eocene age is exploited geologically corresponds to the informal lithostratigraphic unit called Benkovac stone unit [40]-[42]. Based on the detailed lithostratigraphic and structural investigation, it is determined that this stone unit consists of alternating, sheet-like calcareous sandstone and mudstone layers deposited in shallow-marine sublittoral environment. The sandstone layers are considered to be tempestites (storm deposits), embedded in a "background" mudstone beds (fair-weather deposits). The terms carbonate sandstone and mudstone are used for deposits containing considerable amount of calcareous grains dominantly composed of sand and mud fractions, regardless of the proportion of calciclastic and siliciclastic components [40]-[42].

Changes in different petrographic laminas, caused by sedimentation, mark its appearance and decorative effect. Structurally and petrographically, the Benkovac stone is a limestone defined as a laminated lithotype [27]. The laminated lithotype is the main excavated and commercially used variety of the Benkovac stone (Fig. 12). It is composed of two different lithotypes with thinner laminas, called grainy and micritic. The grainy and micritic lithotypes can be distinguished by color, mineral and chemical composition, by structural and textural characteristics, as well as by physical and mechanical properties. The properties of laminated lithotype depend on the properties of the grainy and micritic lithotype and on their position and proportion in the structure [22]. Lamination and the boundary (contact) between grainy and micritic lithotypes (Fig. 12) caused structural anisotropy (heterogeneity) of the laminated lithotype samples.

Anisotropy in structural characteristics such as layers and lamination was considered when testing the Benkovac stone samples. Anisotropy is a weakened place in the samples [32]. Layers and lamination can greatly enhance stone damage during salt crystallization [22]. This research takes into account the fundamental structural lithotypes, grainy and micritic lithotypes, when they can be distinguished, as well as the case when both primary lithotypes are closely related, as in laminated lithotype. Laminas of different compositions, which change in the laminated lithotype, were of equal thickness. Accordingly, resistance to the action of salt crystallization on samples of grainy, micritic and laminated lithotypes was determined. It is interesting that both the micritic and laminated lithotype samples show anisotropy in their structure. Unlike these samples, grainy lithotype does not show lamination and is visually homogeneous.

According to the results, the grainy and micritic lithotypes are generally resistant to the crystallization pressure during salt crystallization. Samples of grainy and micritic lithotypes did not show any significant change in weight and were not damaged during 15 test cycles (Table 1). Nonetheless, five of twelve laminated lithotype samples broke before the end of the test (Fig. 7b). The samples broke along natural discontinuities (micro cracks) or on the contact between grainy and micritic lithotypes. All discontinuities in laminated lithotypes can be determined as weakened places where samples can potentially break. Thus, laminated lithotype is not resistant to salt crystallization and should not be used in conditions in which it may be exposed to salt. That was expected, because stone with structural anisotropy is susceptible to the damage by action of crystallization pressures and it can cause serious damage [32]. During the test of resistance to the action of salt, pore space can increase, existing discontinuities can expand, or even new cracks can develop [5], [7], [10], [39]. But on the other seven samples of laminated lithotypes, there was no significant damage or a weight decrease. It is considered that the samples with greater open porosity and increased water absorption are less resistant to salt crystallization than those having a lower open porosity [14], as in the case of laminated lithotype.

During the salt crystallization, porosity, micro and macro cracks can increase, as well as damage to the stone can increase. With the occurrence of micro cracks and, thus, the damage to the stone, the P-wave velocity through the sample during cycles of salt crystallization generally decreases [28], [29]. In general, stone samples with higher density and lower porosity have a greater P-wave velocity [43]. Similar results were obtained by testing the Benkovac stone samples. Grainy lithotype, due to increased density and lower porosity (Table 1), as expected, has increased P-wave velocity than the laminated and micritic lithotypes (Table 2), in which the higher porosity, as well as lamination, such as discontinuities, is observed. In addition, regarding structural anisotropy, the higher P-wave velocity was recorded in the samples of the laminated and micritic lithotype in a direction parallel to the lamination with respect to the perpendicular direction (Table 2). As with other varieties of stone with structural anisotropy [29], the P-wave velocity in the direction perpendicular to the lamination was significantly reduced, up to 7% (Table 2, Fig. 9). Although grainy lithotype is homogenous, the difference in P-wave velocity in all three directions is also observed (Fig. 10). This result indicates the existence of structural anisotropy in lithotypes where it is visible, but also in grainy lithotype that appear to be homogeneous. It is therefore very important to conduct a detailed examination of samples depending on the anisotropy of structural features. In general, the anisotropy coefficient of the samples (Fig. 10), as expected, varies with a slight increase with increasing the number of cycles towards the end of the test. According to the results, it is evident that samples that have a higher velocity rate change or reduction also have lower compressive strength (Fig. 13). The greatest reduction in the P-wave velocity and a decrease of about 20% in compressive strength compared to the strength of dry samples are observed in grainy lithotype samples. Accordingly, grainy lithotype has inferior properties compared to micritic lithotype, and it is recommended to use the micritic lithotype, if it is possible to separate them.

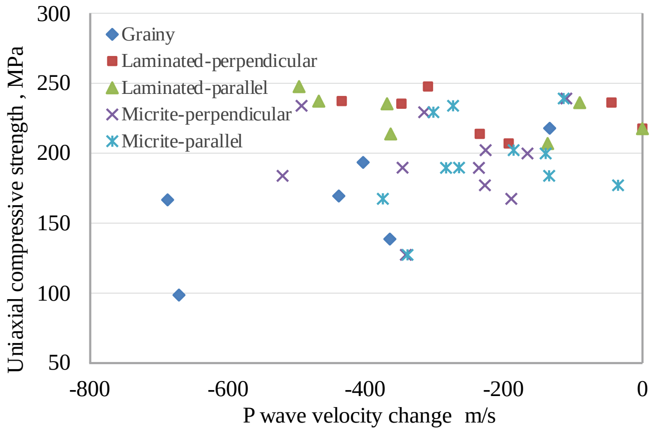

Figure 13. Graphical correlation between the compressive strength (MPa) after 15 cycles of salt crystallization and the ultrasound velocity change (m/s)

Some results were not expected, but they could be explained by the lack of a method for assessing the resistance to salt crystallization. Samples were immediately immersed in a saturated solution of sodium sulphate. In this way, the solution cannot enter in all the pores, especially not into the micro pores which are lagging air bubbles. The samples with smaller cross section pores should be gradually immersed in Na_2SO_4 solution. However, for samples of stone with pores larger than 1 μm, solution can fill all pores [10]. In addition, the recommendation [2] to change the proposed test method so that the samples can be dried at 40ºC instead of 105ºC could be applied, so that the test conditions are more realistic to natural ones. This is important knowledge for this type of stone material, which differs from the dried method for granite and sandstone [8], [26], [30].

In comparison to a previously published study [30], in which six groups of granite samples were treated at different temperatures, the P and S wave velocities of these samples were analyzed at different frequencies. This research represents a scientific contribution as it investigates a different type of geological material, namely layered limestone, in which a clearly visible and expressed structural anisotropy is confirmed by the results after testing the P-wave velocity and uniaxial compression strength.

This research was carried out on thin-bedded or platy limestone and therefore differs from previously published studies focusing on granite and sandstone [8], [23]-[26], [30]. However, the focus of this research is on tests relevant to the use of stone material in construction for cladding buildings, rather than the quarrying of stone. The tests relevant to quarrying are Mode I fracture toughness [24], [25] and indirect Brazilian tensile strength [23], so future studies of thin-bedded or platy limestone from Benkovac may go in this direction.

It should be emphasized that when Benkovac stone is used as a natural facing stone, its surface is not polished due to the construction tradition in Croatia. For this reason, treatments with impregnating agents are probably not fully applicable, as is the case with some other types of stone. Therefore, research on the best protection for Benkovac stone facades still needs to be continued.

5. Conclusions

In conclusion, the scientific novelty in the study of thin-bedded or platy limestone from Benkovac can be summarized as follows.

All three lithotypes of thin-bedded or platy Benkovac limestone (grainy, micritic and laminated) show differences in their physical-mechanical properties and resistance to salt crystallization. The differences are the result of petrographical and structural characteristics of the stone, especially the influence of structural anisotropy. Crystallization pressures caused changes in the microstructure of the samples and weakened the bond between the individual grains and increased pore space. During testing, salt crystallization pressures created new and expanded old, weakened places in the laminated lithotype samples, along the discontinuities (micro cracks) or on the contact between two lithotypes (grainy and micritic).

Five samples of laminated lithotype broke along the discontinuities. All this contributed to the reduction of P-wave velocity and compressive strength of samples, an increase in the anisotropy coefficient and a decrease in the resistance to salt crystallization pressure. The contacts between different lithotypes along the laminas in laminated lithotype represent the largest discontinuity, which is necessary to consider when using laminated lithotype. Natural rocks with layers and lamination exhibit high sensitivity during the water saturation and salt crystallization. The results obtained confirmed that the Benkovac platy stone can be used with caution in conditions of increased humidity, the salts crystallization and possible frost action.

The knowledge gained in a specific area of thin-bedded Benkovac limestone can also be used in other places where the same type of stone is quarried and used in construction.

Author contributions

Conceptualization: AM, ZB, UB; Data curation: AM; Formal analysis: AM; Funding acquisition: AM; Investigation: AM; Methodology: AM, ZB; Project administration: AM; Resources: AM; Software: AM, ZB; Supervision: AM, ZB, UB; Validation: AM, ZB, UB; Visualization: AM, ZB; Writing – original draft: AM, ZB; Writing – review & editing: AM, ZB, UB. All authors have read and agreed to the published version of the manuscript.

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Conflicts of interests

The authors declare no conflict of interest.

Data availability statement

The original contributions presented in the study are included in the article, further inquiries can be directed to the corresponding author.

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Стійкість до сольової кристалізації тонкошарового або пластинчастого вапняку з міста Бенковац у Хорватії

А. Марічич, З. Брішевац, У. Баруджія

Мета. Дослідження петрографічних і мікроструктурних властивостей природного каменю як будівельного матеріалу з Бенковаца, який піддається впливу кристалізації морської солі на хорватському узбережжі Адріатики.

Методика. Дослідження базується на графічному і статистичному аналізі результатів поляризаційної та електронної мікроскопії, стійкості до кристалізації солей, швидкості поширення ультразвуку й випробувань на міцність при одновісному стиску. Три різні літотипи вапняку – зернистий, мікритовий і шаруватий – були проаналізовані для оцінки їх важливих петрографічних властивостей, які впливають на довговічність, коли матеріал піддається впливу кристалізації солей.

Результати. Виділено за допомогою петрографічного аналізу різноманіття характеристик, зокрема ті, що мають відношення до анізотропії структурних особливостей, таких як пластування або розшарування. Проведено випробування зразків вапняку на поширення ультразвукових прямих P-хвиль і міцність на одновісний стиск. Виявлено, що під час тестування спостерігалася зміна внутрішньої структури всіх зразків, особливо пластинчастого літотипу. Встановлено, що зменшення швидкості поширення ультразвуку, зниження міцності на стиск і довговічності внаслідок дії тиску кристалізації є наслідком збільшення порового простору та тріщинуватості вздовж природних розривів, таких як пластування й розшарування.

Наукова новизна. Вперше розглядається стійкість до кристалізації солі каменю з міста Бенковац, особливо з точки зору його петрографічних властивостей, та інтерпретація результатів довговічності шляхом поєднання різних методів оцінки властивостей, які пов'язані між собою.

Практична значимість. Знання, отримані на конкретній ділянці тонкошарового вапняку з Бенковаца, можуть бути використані і в інших місцях для кращого та ефективнішого захисту та збереження будівель, для яких видобувають і використовують у будівництві той самий тип каменю.

Ключові слова: *бенковацький вапняк, тонкошаруватий або пластинчастий вапняк, міцність, кристалізація солей, властивості каменю, структурна анізотропія*

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