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LEITHA LIMESTONES’ PROPERTIES AND THEIR DEGRADATION – CASE STUDY OF BELGRADE FORTRESS

ABSTRACT

The availability and workability of limestones resulted in their extensive use throughout history for the construction or decoration of buildings, while their sensitivity to the aggressive environmental conditions initiated its degradation, leading to a loss of monumental integrity. Belgrade fortress was predominantly built of Badenian autochthonous corallinacean limestones, called “Leitha limestones” or “Lithotamnium limestones”. Since they contain red algae (Lithotamnium ramisissimum) fossils, molluscs, snails, sea urchins, corals, bryozoa and foraminifera, as well as clastic components, they are very heterogenous. This results in an uneven appearance and colour, but also mechanical properties and porosity. The mentioned features of limestones in conjunction with the influence of external factors - environmental and anthropogenic, results in their high degree of degradation. In this paper, the lithological mapping of six fortress gates dating from 15th to 18th century is shown. This determined the dominant existence of microfacies – grainstone and algal rudstone, but also the rare use of impure rudstone. Through field research and later laboratory studies, the petrological, chemical, physical and mechanical properties of these stones were examined. The results were used for the correlation of these features as intrinsic factors of decay with present weathering forms, and environmental influences as extrinsic factors. It enabled us to define the physicochemical degradation processes of limestone microfacies - cyclic dissolution, wetting/drying and freezing/thawing over a long period of time, causing the continuous progression of the intensity of decay and resulting in the present state of the studied limestone, which is in urgent need of conservation.

KEYWORDS: LITHOTAMNIUM (LEITHA) LIMESTONES, BELGRADE FORTRESS, INTRINSIC PROPERTIES, DEGRADATION, WEATHERING.

INTRODUCTION

The use of stone in construction is widespread throughout human history. From the moment of the extraction from the rock mass to the placing of the stone in a building, a long process of adaptation to the new environment begins. Physical-chemical processes that take place on the surface, but also inside the stone, can manifest themselves after a short or a very long time. The durability of the stone is reflected in its ability to resist decay over time and retain its original size, shape, hardness and appearance over a longer period of time (Bell 1993: 187–200).

The term "weathering" denotes changes in the physical-mechanical and chemical properties of stone under the influence of natural atmospheric agents (Vergès-Belmin 2008: 78). Weathering rate, on the one hand, depends on the intrinsic properties of the stone: mineral and chemical composition, structure and physical-mechanical properties. On the other hand, the degree and type of damage depends on the exposure of the stone to numerous extrinsic factors of the environment in which it is located. Within the group of extrinsic factors that aggressively affect the durability of the stone, the environment in which the building is located is of primary importance. The aggressiveness of the environment, regardless of the lithotype of the built-in stone, depends on the parameters that are defined as degradation factors: climatic, i.e., microclimatic parameters and composition of the atmosphere, with an emphasis on the presence of air pollutants, water, flora and fauna in the environment, effects of natural hazards (earthquakes, landslides, floods, etc.), but also equally significant anthropogenic influences. All these factors act synergistically on the stone and, depending on the intrinsic properties of the petrographic type, initiate certain processes of its weathering (McCabe et al. 2007: 77–86).

The manner in which intrinsic factors affect the durability of built-in stone is determined by its petrographic characteristics – mineral and chemical composition and structure, and then by its physical-mechanical properties, which are a reflection of the structure, texture, characteristics of the pore network, etc. The structural and textural heterogeneity of the stone results in its different reactions to extrinsic factors and, thus, also in different forms of decay (Mckinley et al. 2006: 1–12; Mckinley and Warke 2007: 950–969; Esbert et al. 2008: 87–95). The susceptibility of the stone to decay over time depends on all the discontinuities that exist in it, as well as on the heterogeneity in terms of shape, size and manner of interfusion of the constituents (Siegesmund and Torok 2014: 11–96), which are, all together, reflected in the porosity of the stone.

Porosity, as a textural parameter of stone, is the result of depositional and post-depositional processes and, as a physical property, it reflects the volume of pore space in the stone, type of pores (open/closed), pore size distribution, pore surface, and their interconnection and connection with the external environment (Fort 1996: 481–492). Bearing in mind the importance of the mentioned data, as well as the fact that porosity conditions the mechanical properties of the stone and determines its relationship to water, it is considered that porosity is a direct indicator of stone's sensitivity to physical, chemical and biological decay factors, even more significant than the mineral and chemical composition (Ordonez 1996; Esbert et al. 2008: 87–95).

Water, in any form, has a destructive effect on stone, by way of the crystallisation of salt or ice, biological colonisation and/or the process of dissolution of mineral components with a simultaneous decrease of hardness due to the loss of the cohesive bonds between minerals (Benavente 2006; Bell 2000). The degree of roughness of discontinuous stone surfaces (pore walls and microdiscontinuities) directly affects the level of fluid retention and adhesion of all components introduced into the stone by that fluid (soluble salts, aerosol, etc.). Greater roughness of the surface is directly proportional to a greater solution retention and, therefore, greater dissolution intensity, as well as a greater adhesion of all types of plants, from microorganisms to more complex rooted varieties. (Tomaselli et al. 2000: 251–258; Prietro and Silva 2005: 206–215; Scardino et al. 2006: 55–60, 2008: 45–53; Korkanc and Savran 2015: 279–294; Miller et al. 2012: 1–12).

Since the petrographic composition and structure of every type of stone has its own special interaction with the extrinsic factors of the environment in which it is located and, thus, different sensitivity to the physical and chemical decom-

Fig. 1. Position of the gates of Belgrade fortress subject to research (photo from Google Earth version 9.176.0.0 – Web Assembly, *Belgrade, 44°49'30"N 20° 27'40"E, elevation 79 m*, [online] available through: https://earth.google.com/web/, from November 10th, 2022, modified by M. Franković).

position processes, a detailed study of its internal nature is of extreme importance as a prerequisite for a correct selection and planning of the conservation treatment.

Among the numerous petrographic types of stone, limestones are rocks very suitable for exploitation and processing, which is why a significant number of buildings that are protected today as cultural monuments were built precisely from these rocks. While the high level of availability and workability of limestones resulted in them being abundantly used throughout all epochs of the development of civilizational heritage, their sensitivity to the aggressive environmental conditions, on the other hand, would initiate the decay process of the built-in limestone, damaging the integrity of monuments to a greater or lesser extent.

The subject of this research is the limestone used for the construction of Belgrade Fortress, which is categorised as a cultural monument of exceptional importance for the Republic of Serbia. Belgrade Fortress is located in Belgrade's old town, within Kalemegdan Park, forming a spatial cultural and historic ensemble with it. Because of its strategically important position on the border, the tumultuous history of Belgrade Fortress resulted in richness of cultural and historical layers that testify to the development of European military architecture from Antiquity to the end of the 18th century (Popović 2006: 335).

Within the architecture of Belgrade Fortress, its gates are prominent, due to their strategic function in communication routes within the fortress and as links with the main roads outside the fortress. Today, 26 gates have been preserved within Belgrade Fortress, dating from different periods of construction (Vulović 1972: 157–212). Their architecture is conditioned by their position and function within the fortifications, but also by the fortification styles that were current at the time of their construction. Considering the high frequency of circulation and the prominent placement within the fortification, aside from the utilitarian aspect, the gates also have a distinct aesthetic aspect. Special attention was paid to the decorative design of their façades, especially those on main communication routes and entrances into the fortified city. Due to the aforementioned features, the gates of Belgrade Fortress have an exceptional monumental value today and occupy a prominent place within the preserved parts of the fortification. The desire to preserve their authenticity, both stylistically and in terms of the materials they were built with, originated from the need to present them in a manner which would highlight their cultural and historical significance.

The aim of the research was to identify the main degradation processes of the limestone built into the buildings of Belgrade Fortress and to examine the role of the intrinsic properties of limestone on the form and intensity of their degradation. The research included six representative gates from different periods of construction, dating from the 15th up to the 18th century: Zindan Gate, Leopold's Gate, King Gate, Gate of Karl VI, Inner Stambol Gate and Dark Gate (Fig. 1).

In all construction phases of the fortification, mostly Badenian Lithotamnium limestones were used, the so-called *Leitha* limestones1 (Pantić 1988: 91–102). These are carbonate reef formations, deposited on the edges of coral reefs of the warm Pannonian Sea and, as such, represent a transition zone between coral reefs to non-reefal coral communities (Wiedl et al. 2013: 232–246). The former unique reef, which was later divided into smaller blocks by tectonic movements, extends from Tašmajdan to the northwest, emerging on the surface in the Kalemegdan section. These limestones have been exploited since ancient times, first at the site of the construction of the fortress, and later from the quarry of Tašmajdan. Today, the open profiles of *Leitha* limestones are visible at Tašmajdan, where they are massive, on Kalemegdan, under the monument of *The Victor* (*Pobednik*), in the form of banks, and near Belgrade Zoo, above the former Hammam, in the form of slabs or layers (Stevanović 1977: 107–162).

Due to the different nature of building organisms and variable participation of the clastic component, limestones are heterogeneous in composition and structure. This heterogeneity, as well as weak consolidation, are reflected in the physical-mechanical properties of the stone and affect the creation of different weathering forms. According to their spatial distribution and intensity, the most dominant registered weathering forms are crusts, both white calcite and black gypsum, followed by scaling, flaking and granular disintegration, which is especially present on newly exposed surfaces following crust detachment. The weathering processes result in the loss of material in the forms of backweathering and various forms of erosion. Depending on the lithotype, erosion manifests as rounding, loss of matrix, alveolisation or differential disintegration.

METHODOLOGY

The methodology of examining the intrinsic properties of the stone consisted of field surveys of selected gates of Belgrade Fortress with the aim of identifying the type of rocks (*in situ* mapping of the lithology of built-in stone blocks) and laboratory examinations: analyses of petrographic properties, chemical and X-ray analyses, determination of pore structure parameters by mercury intrusion porosimetry (MIP), and testing of physical and mechanical properties.

Considering the fact that the goal of this research is the understanding of the physical-chemical processes that lead to the degradation of limestone, samples for laboratory analyses were selected based on their susceptibility to degradation, i.e. sampling was done on stone blocks which were already affected by degradation processes. This is an important aspect for the interpretation of the results obtained. Samples were taken from the gates themselves, from blocks where the stone material had already detached, in the amount required for the preparation of petrographic thin-sections and a chemical analysis: eight samples of limestones built into the façades of the Dark Gate, four samples from the façade

1 The term "Leitha" comes from the German name *Leitha kalk* for the Vienna Basin rocks. They were named after Leitha Hills, where they were first discovered and studied.

Fig. 2. Location of sampling points on facades: a) Southeast facade of the Dark gate; b) Inner Stambol gate (Franković 2021: 48).

of the King Gate and one sample from both the Leopold's Gate and the Inner Stambol Gate (Fig. 2). For the testing of the physical and mechanical properties, it was necessary to take larger stone blocks from which the test specimens would be obtained, and they were selected from the disposal area for stone blocks at Belgrade Fortress.[2] Initially, a total of 33 stone blocks were sampled. Following identification of their petrographic characteristics, an analogy was made with the limestones built into the façades of the gates, after which seven blocks were selected to form test bodies for the purpose of testing of the physical and mechanical properties.

The mapping of the lithology of the built-in stone blocks was carried out by macroscopic observation of their structural characteristics with the application of Dunham's classification (Dunham 1962: 108–121).

The mineralogical-petrographic analysis included optical examinations of petrographic thin-sections on a *Leica DMLSP* Transmitted Polarizing Light Microscope connected to a *Leica DFC 290HD* digital camera. On the basis of the obtained results of the petrographic analysis, a structural/genetic classification of the type of limestone was carried out using Folk's classification (Folk, 1959: 1–38).

The chemical analyses included complexometric determination of CaO and MgO content by using 1 M-EDTA complex (Ethylene-diaminetetraacetic acid), and separation of the carbonate phase – by using HCl 1:3. For the test, 0.5 g of the test sample was used (if the sample showed a violent reaction with HCl) or 1 g (if the sample did not show a reaction). On the basis of the obtained contents of Ca and Mg oxides, the contents of $CaCO_3$ and $MgCO_3$ were recalculated and the rock type was determined. The content of organic matter was determined colourimetrically, by titrating the solution with $KMnO_4$ (1N), with the addition of oxalic acid.

Rock samples where an elevated MgO content was identified complexometrically, were subjected to X-ray analyses. The determination of the phase composition of the limestone samples was performed by means of an X-ray analysis of the powder, with the use of a *Philips PW-1710* diffractometer. The samples were analysed in the imaging range from 50° to 750° 2θ by using radiation obtained from a copper anticathode CuKa (1.54178 Å). The current was 30 mA and the voltage was 40 kV. Recording was performed at a step of 0.02° 2θ (2.45°/min) and a time delay of 0.5 s. The X-ray analysis of the powder can identify only the phases that occur in the examined material in amounts greater than 2%. The analyses were performed in the Laboratory of Crystallography at the Faculty of Mining and Geology, University of Belgrade.

Examinations of the physical properties of the stone were carried out in accordance with standardised methods (defined by national standards SRPS EN) with a correction of the number of test specimens due to the limited amount of sampled material (tests were performed on four instead of six samples). The following physical properties were determined: bulk and real density, open and total porosity (SRPS EN 1936:2006), water

2 At Belgrade Fortress, which has been subject to continuous renovation for the past few decades, a disposal area for stone blocks used for restoration purposes was formed. The origin of the blocks is twofold: from the ramparts of the fortress that underwent restoration phases or from archaeological excavations at Belgrade Fortress.

absorption at atmospheric pressure – immersion method (SRPS EN 13755:2009) and capillary water absorption (SRPS EN 1925:2009).

In order to determine the parameters of the pore structure of limestone, the mercury intrusion porosimetry (MIP) method was used, carried out on an *AutoPore 9500* device (Micromeritics, USA), with the maximum applied pressure of mercury intrusion of 228 MPa in the range of pore diameter sizes from 150 to 0.005 µm. The measuring was carried out at the Laboratory for Materials in Cultural Heritage of the Faculty of Technology, University of Novi Sad. Due to the limited possibilities of the scope of the research, the examination was only conducted on four samples.

The determination of pulse velocity and ultrasonic elastic constants was performed according to the SRPS B.B8.121:1990 standard. The measurement of pulse velocity of longitudinal and transverse waves – Vp and Vs was performed on two samples, on three cube-shaped test bodies (50 ± 5), with previously known values of bulk density (ρb). Measurements were performed on a *SONIC viewer – MODEL 5210* device (reading accuracy of the smallest time unit 0.10 µs).

The determination of uniaxial compressive strength (SRPS EN 1926:2010) was performed in the Laboratory for Stones and Stone Aggregates of the Highway Institute, Belgrade. The test was carried out on cube-shaped stone samples (50 ± 5 mm) in a dry state, at a constant pressure increase of 1 ± 0.5 MPa/s.

RESULTS

During the field lithological mapping of the façades, a macroscopic differentiation of the rocks was carried out on the basis of structural properties, size of the constituents and dominant type of allochem (Dunham's classification), as well as the colour of the built-in stone. Built-in lithological types were classified into three limestone facies: grainstone (Fig. 3a), algal rudstone (Fig. 3c), and impure rudstone (Fig. 3e). The overall results of the lithological mapping of the gates show an almost equal representation of grainstone and algal rudstone microfacies. Impure rudstone is rarely present, suggesting that it might have been used in the reconstruction phases of the fortress. The precise lithological determination of the examined limestones was carried out by means of an optical analysis of petrographic samples with the application of Folk's classification.

Grainstone is the dominant lithotype built into the façades of the gates of Belgrade Fortress. These are bioclastic limestones of arenitic character, with a medium to densely packed allochem made of fragments of various microfauna, mainly algal fragments, foraminifera, shells, gastropods and other types of organic detritus bound by microsparite and, rarely, sparite orthochem. Aside from bioclasts, ooids and intraclasts occur in this limestone microfacies, and according to their composition, algal biomicrosparites, oobiosparites, biosparites, intrabiosparites, as well as all transitional forms, can be distinguished. In addition to the mentioned allochems, the rocks often contain a terrigenous component in the form of quartz, mica, feldspar and rock fragments. The size of the allochem gives the rocks an arenitic character (Fig. 3b). According to their textural properties, they are characterised by occasionally noticeable thin layering, a pronounced difference in the coarseness of the allochems and regularly present porosity of the type: intergranular, intragranular, or mould-type porosity, but also secondary porosity in the form of cracks and cavities.

Algal rudstone is characterised by a porosity texture with poorly consolidated coarse allochem – algal fossil fragments with round to nodular cross-sections, measuring over 2 mm, which give the rock a rudite character. Bioclasts of other types of macro- and microfauna are usually intergrown with the algal fragments, but they are all poorly consolidated with microsparite to sparite cement, which affects the high porosity of the type of cavities, channels and cracks (Fig. 3d). Additionally, primary inter- and intragranular porosity and porosity linked to skeletal growth are also regularly present. According to the type of allochem present, these rocks are characterised as algal biosparrudites, rarely biolithites.

Impure rudstones are characterised by an increased content of the terrigenous component (> 10%), the size of which varies from arenite to rudite. The identified authigenic constituents, of sandy to gravelly fractions, are quartz, feldspars, muscovites, and rock fragments dominated by quartzites (Fig. 3f).

The results of the chemical characterisation of

Fig. 3. Limestone microfacies: a) grainstone of the northern facade of the King's Gate; b) photomicrograph of grainstone - oval to ellipsoidal forms of algal fragments, with chambers filled with sparry calcite, sample 34 of the southeast facade of the Dark Gate; c) algal rudstone of the southern facade of the Karl VI Gate with visible algal macrofauna; d) photomicrograph of algal rudstone - algal skeleton in weakly consolidated rudstone, sample 41 of the Inner Stambol Gate; e) impure rudstone of the southwest facade of the Dark Gate; f) photomicrograph of coarse lithoclast with bioclasts of impure rudstone - sample 36 of the southern facade of the Dark Gate (Franković 2021: 70, 73, 75, 76).

the examined limestones show that chemically pure limestones, with a carbonate content ($CaCO_3$) of 91.41 % to 96.27 %, dominate among the examined samples. The content of insoluble residue in the four tested samples varies from 11.12 % to 23.75 %, classifying these rocks in the group of sandy limestones (the prefix "sandy" was assigned based on the results of the optical analysis, which confirmed the presence of a terrigenous – sandy component). Only one sample was classified as impure dolomite

Sample	ρ_b (Mg/cm³)	ρ_r (Mg/cm³)	Po (%)	Pt (%)	Ab (%)	C (g/m$^{2\cdot s\text{-}0.5}$)
Grainstone						
S-3	1.88	2.68	/	29.8	11.05	/
34	1.84	2.68	24.30	31.21	11.61	527
37	1.84	2.70	24.69	31.85	13.44	/
42	1.68	2.70	27.84	37.42	16.90	997
43	1.90	2.70	21.17	29.70	11.17	∥ 325 ⊥ 395
44	1.87	2.70	21.85	30.46	11.68	255
	1.83	2.70	23.97	31.74	12.64	500
min	1.68	2.68	21.17	29.70	11.05	255
max	1.90	2.70	27.84	37.42	16.90	997
Stan.Dev.	0.08	0.01	2.64	2.90	2.25	
KV	4.33	0.38	11.03	9.14	17.85	
Algal rudstone						
Z-1	1.95	2.68	/	28.05	7.39	/
Z-2	1.50	2.59	/	41.00	14.11	/
K-4	1.84	2.71	25.17	32.10	13.60	/
K-5	1.81	2.74	23.60	33.90	13.00	/
K-7	1.94	2.75	20.76	29.50	10.70	/
K-9	1.80	2.74	26.97	34.30	15.13	/
38	1.98	2.72	18.42	27.10	9.29	/
S-1	1.75	2.67	/	34.40	12.52	/
S-2	1.82	2.70	/	32.80	11.20	/
41	1.76	2.70	27.96	34.99	15.94	415
8	1.85	2.71	21.90	31.33	11.85	215
11	1.74	2.69	24.08	35.40	13.86	513
15	1.79	2.70	25.83	33.57	14.40	434
23	1.89	2.69	23.57	29.71	12.48	219
	1.82	2.70	23.83	32.73	12.53	359
min	1.50	2.59	18.42	27.10	7.39	215
max	1.98	2.75	27.96	41.00	15.94	513
Stan.Dev.	0.12	0.04	2.89	3.54	2.32	
KV	6.50	1.44	12.14	10.84	18.52	

Key: – mean value; min – minimal measured value; max – maximal measured value; Stand.Dev. – standard deviation; KV – coefficient of the variation.

Table 1. Physical properties of grainstone and algal rudstone samples (according to Franković 2021: 97, 108)

limestone, due to the high presence of MgO, i.e., dolomite mineral (12.72 %). In all the examined samples, the content of organic matter is extremely low and varies from 0.03 % to 0.08 %.

The presence of dolomite was also confirmed by an X-ray analysis. Diffractograms indicate that calcite is the main mineral phase (078-4615; ICDD PDF Standard), and that, aside from the presence

Sample	P_{om} (%)	V_p (ml/g)	PP (m²/g)	D (µm)	D_c (µm)	S_c (%)	D_u (µm)	S_u (%)
Grainstone								
34	33.12 (24.3)	0.189	0.728	1.04	29	31.24	40	9.59
42	35.01	0.205	1.149	0.71	38	20.32	60	7.69
Algal rudstone								
41	32.54	0.184	1.127	0.65	40	36.76	60	20.88
8	29.51	0.162	1.219	0.53	18	27.94	50	5.83

Table 2. Parameters of the pore structure for grainstone and algal rudstone samples (according to Franković 2021: 100)

Sample	**Pore volume (%)**				
	Macro-pores D > 0.05 µm			**Meso-pores D** = 0.05-0.002 µm	
	Large pores 1000-100	Pores 100-10	Large capillaries 10-0.05	Medium capillaries 0.05-0.01	Small capillaries 0.01-0.002
Grainstone					
34	2.52	58.22	38.40	0.85	0.00
42	3.26	62.09	32.98	1.67	0.00
Algal rudstone					
41	6.36	56.81	35.54	1.28	0.00
8	2.92	37.01	58.38	1.68	0.00

Table 3. Volumetric distribution of the pores by their size in the grainstone and algal rudstone samples (according to Franković 2021: 101)

of dolomite (074-7800) in sample 34 and Mg-calcite (089-1304) in sample 37, the rocks regularly contain quartz (087-2096) and feldspar-albite (009-0466). It is important to point out that the presence of a small amount of the gypsum mineral (076-8728) was registered in both samples, which is certainly a secondary product of limestone degradation.

The results of the physical properties (bulk density – ρb, real density – ρr, open porosity – Po, total porosity – Pt and water absorption – Ab) of the examined limestone samples are shown in Table 1.

The results of the testing of parameters of the pore structure using the MIP technique on the grainstone and algal rudstone samples are expressed in the values of open porosity (Pom), total pore surface (PP), mean pore diameter (D), critical pore diameter (Dc), entry pore diameter (Du), volumetric content of pores with diameters larger than the critical diameter (Sc) and larger than the entry pore diameter (Su), and distribution of defined pore size classes (Tables 2 and 3).

The grainstone samples are characterised by close values of Pom (33.12 % and 35.01 %, Table 2), PP shows small variations in the examined samples, i.e., it is slightly higher in sample 42 compared to sample 34, which is consistent with the size ratio of the mean pore diameter. Differences are also evident in the pore size distribution, i.e., the representation of the defined classes of the corresponding range of pore diameters (Table 3). The grainstone samples have a unimodal pore size distribution with a dominant presence of the 10–100 µm pore diameter size class and the almost twice as small presence of the 0.05–10 µm pore diameter size class (Table 3). The content of large pores (100–1000 µm) is extremely small (2–3%), and the content of pores <0.05 µm is almost negligible (0–2%). The range of variation of Dc values also shows uniformity in the examined grainstone

3 The open porosity value of 33.12% is significantly different from the value of 24.3% obtained by the laboratory test procedure using the immersion method according to the SRPS EN 1936:2006 standard (all other samples have close values). The difference is due to the textural heterogeneity of sample 34.

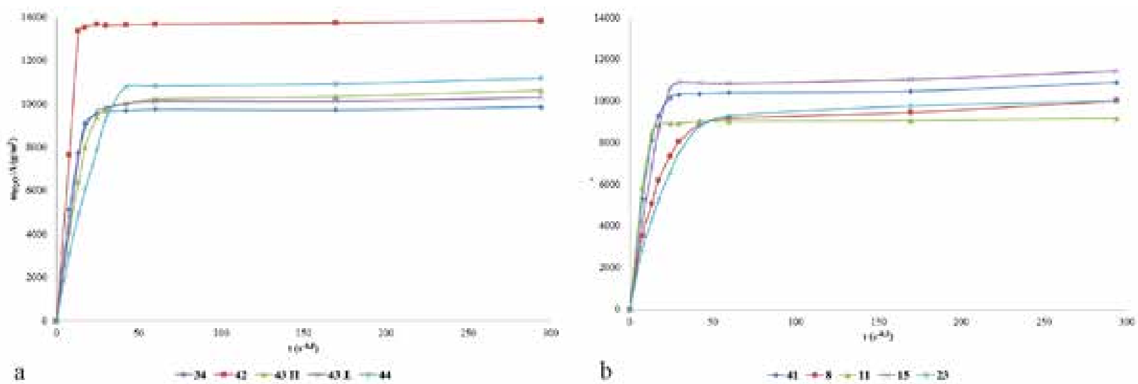

Fig. 4. Curves of capillary water absorption: a) grainstone; b) algal rudstone. (according to Franković 2021: 109, 111)

samples (22–50 μm), with an average value of 34 μm for all analysed samples.

Algal rudstone samples have close Pom values, little difference in PP values, and close mean pore diameter values (Table 2). However, differences are prominent in the pore size distribution (Table 3). Both samples have a unimodal pore distribution, but with different modes. While the dominant population of pores in sample 41 has a size of 100–10 μm (56.81 %), sample 8 is in the 10–0.01 μm size class – 58.38 %. Both samples are characterised by a small presence of medium capillaries and an absence of small capillaries. Despite the similarity in mean pore diameter values, the size of the critical pore diameter varies from 50 μm in sample 41 up to 15 μm in sample 8, indicating a difference in the pore network available for fluid movement.

The mode and trend of capillary water absorption are represented by diagrams of the ratio of the mass of absorbed water per unit area as a function of the square root of time (Fig. 4). In addition to the graphical presentation of capillary absorption curves, the results are also shown by the capillary absorption rate, expressed by the capillary absorption coefficient (C) (Table 1). For the sample with pronounced thin layering (43), test results are shown in parallel, or perpendicular to the anisotropy plane. Capillary absorption curves, of both limestone varieties, initially have asymptotic flow that, after a certain time, passes into a stationary absorption mode. The capillary uptake curves are linear, which indicates that the pore network is homogeneous (Beck et al., 2003: 1151–1162), while the C values indicate different kinetics of capillary absorption. The high value of C – 997 $g/m^{2\cdot s^{-0.5}}$ in sample 42 indicates extremely fast absorption, while the values of the other samples vary from 225 to 527 $g/m^{2\cdot s^{-0.5}}$. In algal rudstone, C varies from 215 to 513 $g/m^{2\cdot s^{-0.5}}$ and the curve shows a slight increase in the last time interval, indicating the process of extrusion of air trapped in the pores (Beck et al., 2003: 1151–1162).

Based on the measurement of the velocity of propagation of longitudinal and transverse waves, the values of the dynamic elasticity module (Edyn) and Poisson's coefficient (μdyn) were calculated as parameters representing the hardness of the porous stone, especially its internal structure. Grainstone has ~26% lower propagation values for both types of waves compared to algal rudstone (Fig. 5). The difference is twice as great if we compare the mean values of the dynamic elasticity module, which is 3.19 GN/m^2 for grainstone, and 6.74 GN/m^2 for algal rudstone, which is in agreement with the porosity results of the examined samples (the open porosity of sample 42 is higher than the open porosity of sample 8 – see Table 1). The volumetric presence and pore size did not affect the value of Poisson's coefficient, which is 0.35 for both the microfacies. Based on the results of compressive strength measurements of the selected representative samples, it is concluded that the grainstone and algal rudstone samples have low, but similar, uniaxial compressive strength values (7.2 MPa grainstone and 6.35 MPa algal rudstone), which is in agreement with the close values of other properties such as, for example, total porosity. It is characteristic for all tested samples that the fractures were subtle, without any special sounds, and the form of destruction was along the cracks that intersect the axis of the sample at an angle.

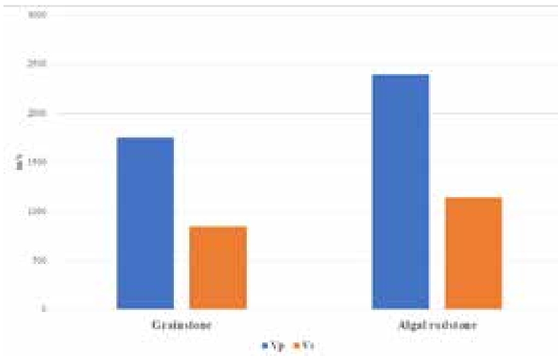

Fig. 5. Histograms of the results of measuring the velocity of longitudinal waves of grainstone and algal rudstone samples

DISCUSSION

Limestones built into the gates of Belgrade Fortress show signs of weathering in various individual decay forms: granular disintegration and scaling, alveolisation, flaking and splintering, the appearance of light and black crusts, biological colonisation and others. The observation of the mentioned decay forms and correlation with petrological and physical-mechanical properties established the influence of intrinsic factors of built-in limestone on the representation of individual decay forms, without major differences in the intensity of degradation.

The results of petrological analyses and lithological mapping of stone blocks built into the façades of the gates at Belgrade Fortress quantitatively showed the distribution of limestone microfacies. From the aspect of the genetic type of rock, i.e., the dominance of limestone as the building lithotype used, the gates of the fortress are petrologically and mineralogically homogeneous. From a chemical point of view, the most common type are pure limestones ($CaCO_3$ content ~95%) and less common impure limestones with variable $CaCO_3$ content (76–89%). Dolomitic limestones were also identified, rather sporadically, in which the dolomite component is prominent (12.72% $MgCO_3$). When it comes to the structure, however, the heterogeneity of the incorporated limestones is notable. These are allochemical sediments, classified into three microfacies according to the ratio, packing and size of allochem: grainstone, algal rudstone and impure rudstone.

Although structurally different, the physical properties of the examined grainstone and algal rudstone are very similar. According to the values of the bulk and real density, both varieties of limestone are medium-heavy rocks, i.e., soft limestones with a coarse-porous texture. The total porosity values classify them as extremely porous rocks. Both limestone lithotypes have almost the same values of open porosity and mean pore diameter (G-0.9 μm, AR-0.6 μm), very close values of critical pore diameter (G-34 μm, AR-29 μm), with the inlet pore diameter in the range of 40–60 μm. The grainstone pore network is homogeneous with a unimodal pore size distribution, a dominant class of pores with the size of 10–100 μm (~60%) and a significant participation of large capillaries (30–40%). Algal rudstone shows heterogeneity in the pore structure, with pores and large capillaries alternating as dominant classes.

According to the pore structure, the examined lithotypes are characterised by high water absorption, with a high capacity for capillary water absorption. Grainstone samples have an average coefficient of capillary water absorption of 376 g/m2·s-0.5,4 while in algal rudstone it is 359 g/m2·s-0.5, which can be defined as a high coefficient of capillary absorption, and at the same time an indicator of the rock's susceptibility to decay (Snethlage 2005; Graue et al. 2011: 1799–1822).

A large amount of capillary pores with a unimodal character of distribution, as well as the small difference between total and open porosity in both lithotypes, indicate a good interconnection of pores, capable of absorbing and retaining water and enabling its transport through the interior of the built-in limestone. Pore size is a crucial parameter that regulates fluid movement through the stone pore system. While pore sizes of 1 mm – 1 μm enable a high degree of water absorption, pore sizes below 1 μm and their interconnections are considered critical for the stone's susceptibility to decay. They enable easy capillary movement of fluids, and when they are additionally well connected, they facilitate the diffuse movement of solutions along with a simultaneous increase in the intensity and surface of stone dissolution. A high content of capillary pores conditions a larger specific surface, which represents, at the same time, the surface available for capillary condensation and moisture retention and, thus, the ag-

4 The extreme value of sample 42 was excluded from the statistical analysis.

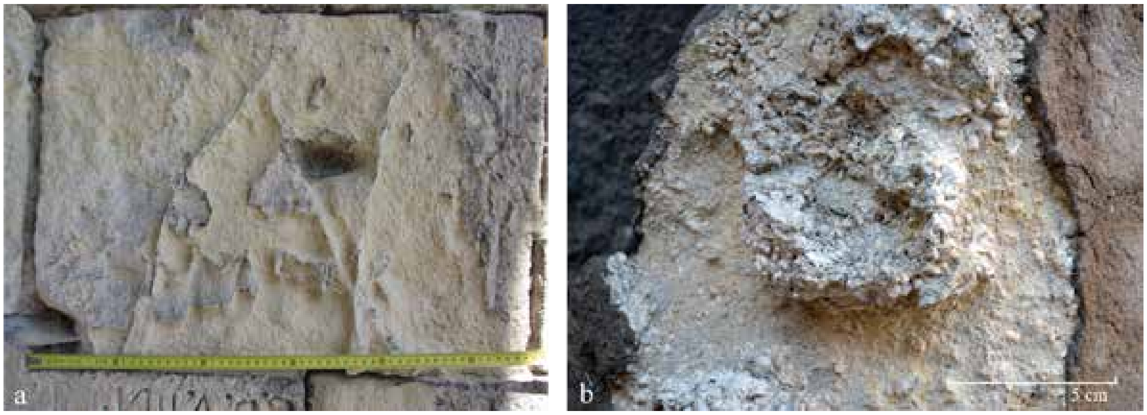

Fig. 6. Differential weathering of the same damage category – manifestation according to structural characteristics of the microfacies: a) grainstone; b) algal rudstone (Franković 2021: 70, 81).

gressive action of all components that enter the stone with the fluids. Additionally, when it comes to pores with sizes of 0.1–1 μm, the crystallisation and hydration pressure of ice and salt represent a regular destructive factor to the stone (Benavente 2006; Bugani et al 2007: 316–320; Benavente 2011: 41–42). High coefficients of capillary water absorption indicate the ability of both lithotypes to absorb water in an amount that enables long-term moisture retention and consequent dissolution and migration of soluble salts (Graue et al. 2011: 1799–1822). The overall pore network of the examined limestones enables unhindered water circulation and consequent chemical dissolution, primarily of the orthochem. Therefore, the pore structure of both lithotypes enables the physical and chemical decomposition processes to take place, which led to the present state of the built-in limestones.

According to their mechanical properties, both varieties of limestone can be characterised as soft rocks with a low propagation velocity of ultrasonic waves and very low to low compressive strength. Since it has been proven that the compressive strength of porous limestone decreases significantly in a water-saturated state compared to the values in a dry state (Vásárhelyi 2005: 69–76; Torok and Vásárhelyi 2010: 237–245), and the pore network of the examined limestones enables long-term water retention, it can be considered that the mechanical resistance of the limestones built into the gates of Belgrade Fortress is very weak, which makes them sensitive to all types of physical destruction.

When considering the morphology of the degradation in relation to the lithotype, the petrological (structural-textural) influence on the decay forms is evident in the manifestation of individual decay forms. Cavities and the presence of coarse allochem in algal rudstone favours biological colonisation, as well as the formation of deposits on surfaces. The higher content of the limonite component in grainstone, under the influence of high temperature, causes chromatic changes. The textural characteristics of the grainstone cause the detachment of centimetre-thick scales, which has not been observed in the algal rudstone. The thickness of the crust corresponds to the difference in the size and packing of the allochem, the position of structurally different layers, which further affects the movement of the drying and wetting fronts, and the generation of hydration and crystallisation pressures of salt or ice. All of the above leads to scaling. Backweathering of grainstone occurs with greater intensity precisely due to scaling, compared to algal rudstone, where it is a consequence of the crust detachment or splintering. Erosion, in the form of alveolisation and differential weathering, is a more common characteristic of grainstone. Differential weathering is a consequence of the existence of areas with harder, firmer and more compact constituents, which are, thus, more resistant to decay over time. While this form occurs in grainstone due to the existence of structurally different layers and/or locally deposited secondary calcite, when it comes to algal rudstone, especially biolithite, Lithotamnium algae remain prominent due to the granular disintegration of softer parts of the limestone (Fig. 6).

Granular disintegration and flaking mostly occur with equal intensity and, therefore, in the same damage categories in both lithotypes. The different intensity that can occur even within one block of stone is, on the one hand, a consequence of the heterogeneous microstructure of the examined limestone blocks, and on the other, the intensity of the degradation processes. Granular disintegration is intense in those parts where the cement binder has been washed away or mechanical microdamage has occurred due to the action of hydration and crystallisation pressure, on newly opened surfaces after the detachment of the surface crust/ scale. In the zones of surface crusts, this weathering form has not been registered, due to the compaction of intergranular spaces with dissolved calcite and/or gypsum.

In contrast, significant differences in the intensity of individual weathering forms in relation to the lithotype have not been recorded. The presence of all damage categories on both lithotypes, with great similarity of physical-mechanical properties, generally indicate their equal susceptibility to weathering processes, while the degree of damage on individual stone blocks is related to their exposure to extrinsic decay factors.

CONCLUSIONS

Based on everything presented previously, in the complex mechanism of weathering of the limestone at Belgrade Fortress, key intrinsic factors have been identified that enable the physical-chemical weathering processes to take place. The carbonate composition, i.e., the presence of mineral calcite, which is soluble in water and weak acids, enables the chemical dissolution of limestone. The diagenesis of the studied limestones caused weak cementation, which results in low mechanical strength and high porosity. The pore network allows for an unhindered circulation of water and the consequent chemical dissolution of poorly cemented algal rudstone and sparite grainstone cement, weakening the stone from within. Dissolved calcite recrystallises on the surface in the form of a thin white crust, while black gypsum crusts form on protected stone blocks, created by the chemical reaction of calcite with atmospheric pollution. The porosity of the limestone, and the type and distribution of the pores also allow for unhindered freeze/thaw cycles, which result in physical damage in all forms of detachment. The repeating of dissolution, wetting/drying and freezing/thawing cycles over a long period of time causes a continuous progression of the intensity of decay and the appearance of very prominent damage in various forms of loss of the stone material. The simultaneous action of the mentioned principal decay mechanisms on built-in limestones, otherwise susceptible to decay, results in the present condition and is a clear indicator of the urgent need for conservation.

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REZIME

SVOJSTVA LAJTOVAČKIH KREČNJAKA I NJIHOVA DEGRADACIJA – STUDIJA SLUČAJA BEOGRADSKE TVRĐAVE

KLJUČNE REČI: LITOTAMNIJSKI (LAJTOVAČKI) KREČNJACI, BEOGRADSKA TVRĐAVA, INTRINZIČNA SVOJSTVA, DEGRADACIJA, ATMOSFERSKO RASPADANJE.

Predmet ovog istraživanja su litotamnijski (lajtovački) krečnjaci korišćeni za izgradnju Beogradske tvrđave, koja je kategorisana kao spomenik kulture od izuzetnog značaja za Republiku Srbiju. Istraživanje je imalo za cilj identifikaciju glavnih procesa raspadanja ugrađenih krečnjaka i ispitivanje uloge intrinzičnih svojstava krečnjaka na formu i intenzitet njihovog raspadanja. Istraživanjem je obuhvaćeno šest reprezentativnih kapija iz različitih perioda gradnje, datovanih od XV do XVIII veka: Zindan, Leopoldove, Kralj kapije, kapije Karla VI, unutrašnje Stambol kapije i Mračne kapije.

Metodologija ispitivanja intrinzičnih svojstava kamena sastojala se od terenskog rekognosciranja odabranih kapija Beogradske tvrđave sa ciljem identifikacije vrste stena (*in situ* mapiranja litologije ugrađenih kamenih blokova) i laboratorijskih ispitivanja: ispitivanja petrografskih karakteristika, hemijskih i rendgenskih ispitivanja, određivanja parametara porne strukture živinim porozimetrom (MIP), te ispitivanja fizičkih i mehaničkih svojstava.

Rezultati petroloških analiza i litološkog mapiranja kamenih blokova ugrađenih u fasade kapija Beogradske tvrđave, kvantitativno su pokazali distribuciju izdvojenih mikrofacija krečnjaka. Sa aspekta genetske vrste stene, odnosno dominacije krečnjaka kao ugrađenog litotipa, kapije tvrđave su petrološki i mineraloški homogene. Hemijski posmatrano, najzastupljeniji su čisti krečnjaci i manje prisutni nečisti krečnjaci sa varijabilnim sadržajem $CaCO_3$ (76-89 %). Sasvim sporadično su identifikovani i dolomitski krečnjaci u kojima je markantno učešće dolomitske komponente. Strukturno posmatrano, međutim, izražena je

heterogenost ugrađenih krečnjaka. To su alohemijski sedimenti koji su prema odnosu, pakovanju i veličini alohema svrstani u tri mikrofacije: *grainstone*, algalni *rudstone* i nečisti *rudstone.*

Iako strukturno različiti, fizička svojstva ispitivanih *grainstone* i algalnog *rudstone* su veoma slična. Prema vrednostima prividne i stvarne zapreminske mase oba varijeteta krečnjaka su srednje teške stene, odnosno mekani krečnjaci gruboporozne teksture. Vrednosti ukupne poroznosti svrstavaju ih u ekstremno porozne stene. Porna mreža *grainstone* je homogena sa unimodalnom distribucijom veličine pora, dominantnom klasom pora veličine 10-100 μm (~60 %) i značajnim učešćem velikih kapilara (30-40 %), dok algalni *rudstone* pokazuje heterogenost u pornoj strukturi gde se kao dominantne klase smenjuju pore i velike kapilare. Saglasno pornoj strukturi, ispitivane litotipove karakteriše veliko upijanje vode, sa velikom sposobnošću kapilarne apsorpcije vode. Prema mehaničkim svojstvima, oba varijeteta krečnjaka se mogu okarakterisati kao meke stene sa niskom brzinom prostiranja ultrazvučnih talasa i vrlo niske do niske čvrstoće na pritisak.

U složenom mehanizmu raspadanja krečnjaka Beogradske tvrđave, identifikovani su ključni intrinzični faktori koji omogućavaju odvijanje fizičko-hemijskih procesa raspadanja. Karbonatni sastav, odnosno prisustvo minerala kalcita koji je rastvorljiv u vodi i slabim kiselinama, omogućava hemijsko rastvaranje krečnjaka. Dijageneza ispitivanih krečnjaka uzrokovala je slabu cementaciju, što za posledicu ima nisku čvrstoću i veliku poroznost. Porna mreža omogućava nesmetanu cirkulaciju vode i posledično hemijsko rastvaranje slabo cementovanog algalnog *rudstone* i sparitnog cementa *grainstone*, slabeći kamen iznutra. Rastvoreni kalcit rekristališe na površini u formi tanke bele kore, dok se na zaštićenim kamenim blokovima formiraju crne gipsane kore, nastale hemijskom reakcijom kalcita sa atmosferskim zagađenjem. Poroznost krečnjaka, tip i distribucija pora omogućavaju i nesmetano odvijanje ciklusa mržnjenja/otapanja koje rezultira fizičkim *oštećenj*ima u svim oblicima odvajanja. Ponavljanje ciklusa rastvaranja, vlaženja/sušenja i mržnjenja/otapanja tokom dužeg vremenskog perioda, izaziva kontinuiranu progresiju intenziteta raspadanja i pojavu veoma jakih oštećenja u različitim formama gubitka kamenog materijala. Simultano delovanje navedenih glavnih mehanizama raspadanja na ugrađene krečnjake, inače podložne raspadanju, rezultira današnjim stanjem i jasnim indikatorima urgentne potrebe za konzervacijom.

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