Durability evaluation of some Slovenian building limestones

Vrednotenje obstojnosti izbranih slovenskih apnencev kot naravnega kamna

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Abstract This study deals with the characterisation of two limestones widely used in the construction of Slovenian historical monuments as well as modern buildings. In order to estimate their durability, samples of the selected limestones were subjected to salt crystallisation and frost resistance tests. Changes in the structure of the limestones after these ageing tests were determined using SEM-EDS and USV measurements. In addition, their splitting tensile strength was also determined. Results showed that despite having good mechanical characteristics, the limestones exhibited several forms of deterioration when exposed to the deleterious agents.

Izvleček V prispevku sta obravnavana dva slovenska apnenca, ki sta bila široko uporabljena pri gradnji številnih objektov kulturne dediščine, eden od njiju je še vedno aktualen pri gradnji modernih objektov. Za oceno obstojnostne lastnosti so bili vzorci izbranih apnencev izpostavljeni preizkusom odpornosti proti kristalizaciji soli in odpornosti proti zmrzovanju. Spremembe v strukturi kamnine po preizkusih staranja so bile preverjene z uporabo SEM-EDS-metode in z USV-meritvami. Določena je bila tudi natezna razcepna trdnost preiskovanih apnencev. Rezultati kažejo, da kjub dobrim mehan-

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Original scientific paper

skim karakteristikam preiskovanih apnencev le-ti propadajo, ko so izpostavljeni škodljivim dejavnikom.

Key words: limestone, durability, deterioration, salt crystallisation, natural stone

Ključne besede: apnenec, obstojnost, propadanje, kristalizacija soli, naravni kamen

INTRODUCTION

Since prehistoric times, limestone has been one of the most popular types of building stone and is today used in both the construction of modern buildings and in conservation as a replacement material for the reconstruction of monuments. All stone used in these applications eventually changes due to their interaction with the various environmental conditions to which they are subjected. Although limestone consists mainly of calcite, it can show significant variation in composition in terms of minor minerals, as well as structure and texture, resulting in complex and contrasting weathering behaviours (Warke et al., 2006). Among the decay factors, soluble salt crystallisation is considered to be one of the most powerful affecting the weathering of carbonate stone (Charola, 2000; Doehne, 2002). These salts are known to cause damage to porous materials through a variety of mechanisms, such as the production of physical stress resulting from their crystallisation in the pores, differential thermal expansion, hydration pressure and enhanced wet/dry cycling caused by deliquescent salts (Charola, 2000; Doehne, 2002).

As many Slovenian monuments and modern buildings are built of limestones, estimation of their durability is necessary for their successful maintenance, protection and proper restoration/conservation. Two Slovenian limestones were selected for study: Lesno Brdo and Drenov Grič. Lesno Brdo limestone is characterised by a variety of colours: red, pink and numerous shades of light to dark grey. It has been frequently employed in the construction of Slovenian historical monuments (Mirtič et al., 1999; Ramovš, 2000; Jarc, 2000), as well as in modern buildings. In the past, the limestone was also used in many churches in Ljubljana, for portals or fountains (Ramovš, 2000). In modern buildings it is used for cladding and flooring, or as a replacement material in the conservation and restoration of historical monuments. Drenov Grič limestone on the other hand, is dense and as such can produce a highly polished finish. As a result it was considered as popular as marble, being widely used particularly in baroque architecture not only in Ljubljana, but also in other regions of Slovenia. Many interior and exterior architectural elements and monuments, especially the portals of houses and altars, were made of this limestone (Ramovš, 2000). However, both limestones are at risk when exposed to certain climatic conditions, with chromatic and salt weathering recognised as the phenomena most responsible for their deterioration (Kramar et al., 2010a; Kramar et al., 2010b).

In order to estimate the weathering behaviour of the selected limestones, samples were subjected to the salt crystallisation test and freeze/thaw cycles. Changes in the mechanical-physical properties of the limestones after these ageing tests were estimated via ultrasonic velocity measurements and SEM examination. In addition, the splitting tensile strength of the fresh limestones was also determined.

Materials and methods

Materials

For the study, two Slovenian limestones were selected; Lesno Brdo and Drenov Grič. Samples of Drenov Grič limestone (DG) were collected from the main quarry in Drenov Grič near Ljubljana (Figure 1a), which historically had a leading role in supplying building material to central parts of Slovenia (Ramovš, 2000). This Triassic well-stratified limestone occurs in 10–80 cm thick beds, which alternate with thin sheets of marls. The Drenov Grič limestone is considered one of the most beautiful Slovenian natural stones due to its typical black colour interwoven with white veins (Figure 1b). Fragments of fossil bivalvia, gastropoda, algae, foraminifera, ostracods and corals are also occasionally found (Ramovš, 2000). Samples of Lesno Brdo limestone were taken from the still active local quarry of Lesno Brdo near Ljubljana (Figure 2a). Two lithotypes of this Triassic reef limestone were selected: the dark grey lithotype – SLB (Figure 2b) and the light red lithotype - PLB (Figure 2c). Lesno Brdo limestone is heterogeneous, composed of intraclasts, pellets and fossil fragments. Coloured (violet, red, green and white) veins and styloliths filled with phyllosilicates or iron oxides/hydroxides are also present, along with large yellow or violet dolomite crystals (Ramovš, 2000).

Analytical methods

Analysis of the limestones' splitting tensile strength was performed according to SIST EN 12390-6, using a ZWICK apparatus b24, type Z 400 E. Samples took the form of (50 × 50 × 50) mm cubes,

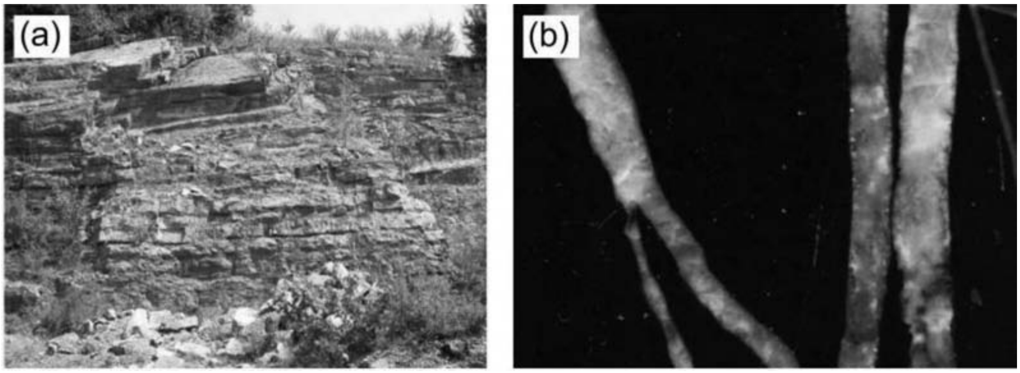

Figure 1. a) Historical Drenov Grič limestone quarry. b) Polished surface of Drenov Grič limestone. Image is about 4 cm in size.

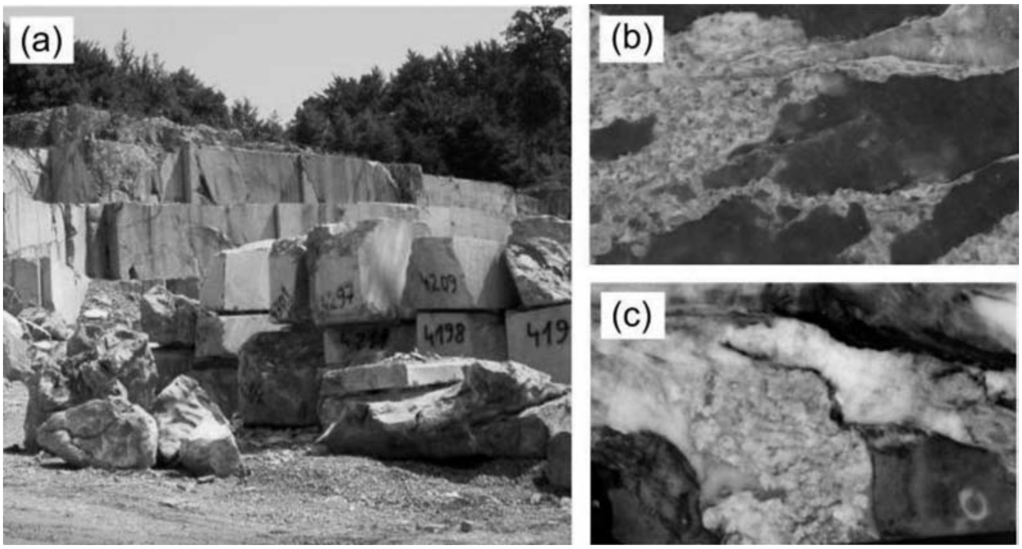

Figure 2. a) Active Lesno Brdo limestone quarry. b) Polished surface of the grey lithotype of Lesno Brdo limestone. Image is about 4 cm in size. c) Polished surface of the red lithotype of Lesno Brdo limestone. Image is about 4 cm in size.

with three taken from each limestone lithotype. Measurements were performed on dry as well as water-saturated samples (water immersion undertaken according to SIST EN 1936).

The salt crystallisation test (SIST EN 12370) and the determination of frost resistance (SIST EN 12371) were carried out on (50 × 50 × 50) mm cubes in order to provide information as to their damaging effect. After the frost resistance test, limestone loss of mass Vb48 was determined. Changes in microstructure were observed using SEM-EDX and USV after 15 immersions in Na-sulphate and 48 freeze-thaw cycles.

Cross-sections of the weathered limestone samples were examined under a Scanning Electron Microscope (JEOL 5600 LV), using the low vacuum back-scattered electrons (BSE) imaging mode. Some areas of the samples were analysed for chemical composition using the energy dispersive X-ray technique (EDS).

In order to determine changes in the mechanical-physical properties of the samples after the ageing procedures were carried out, ultrasonic velocity measurements were performed in three directions using an AU 2000 Ultrasonic Tester (CEBTP) with a transmission frequency of 60 kHz. Speed of sound wave propagation was undertaken according to standard procedure EN 14579. Three measurements were performed in each of the three orthogonal directions. Additionally, the total structural anisotropy coefficient ΔM/% and relative anisotropy coefficient Δm/% of the samples were obtained from the mathematical relationship between the ultrasonic propagation velocities, following the equations of Guydader & Denis (1986):

a) total anisotropy:

$$\Delta M/\% = 100\ [1 - (2\ V_{L1}/V_{L2} + V_{L3})] \qquad (1)$$

b) relative anisotropy:

$$\Delta\, m\% = 100\ [2\ (V_{L2} - V_{L3})/V_{L2} + V_{L3}] \qquad (2)$$

where V_{L1} is the lowest and V_{L2} the highest measured velocity.

The degree of weathering can be calculated through the reduction of longitudinal wave velocity (Zezza & Veinale, 1988) from unweathered (V_0) to weathered (V_w) stone samples:

$$K = (V_0 - V_w)/V_0 \text{ or } \Delta V(\mathrm{L})\% = 100\ (V_0 - V_w)/V_0 \qquad (3)$$

USV measurements were carried out both before and after the salt crystallisation (on unwashed and washed specimens) and frost resistance tests.

Results and discussion

Splitting tensile strength

As can be seen from Table 1, all three limestones exhibited high values of splitting tensile strength, although levels slightly differed between each one. The highest strength was observed in the grey lithotype of the Lesno Brdo limestone, followed by Drenov Grič limestone and the red Lesno Brdo lithotype. There were no significant differences observed between the different orientations of bedding planes

Table 1. Splitting tensile strength of the investigated limestones. Results represent three sample mean values ± standard deviation.

Sample	Splitting tensile strength (MPa)	
Drenov Grič limestone (DG)	dry	water-saturated
⊥ bedding	11.70 ± 4.72	11.13 ± 3.91
// bedding	13.43 ± 3.12	
Lesno Brdo limestone		
Grey lithotype		
(SLB)	14.22 ± 1.85	14.40 ± 4.85
Red lithotype		
(PLB)	11.62 ± 4.57	12.72 ± 5.63

in Drenov Grič limestone. Using the system of BELL (1992), all three investigated limestones can be classified as very high (3–10 MPa) to extremely high strength rock (>10 MPa). There was also no difference in splitting tensile strength between the corresponding dry and water-saturated samples of each of the limestones.

Analysis of the results suggests that the higher the content of clay mineral-filled discontinuities, as observed in the red Lesno Brdo lithotype (Kramar et al., 2010a) and the higher the porosity, the lower the splitting tensile strength of the limestone. In addition, the results also reveal that splitting tensile strength values are much lower than those of the salt crystallisation or ice formation pressures. Salt crystallisation is accompanied by an increase in pressure due to the formation of new mineral phases. Whereas the splitting tensile strength of the investigated limestones does not exceed 20 MPa, the crystallisation pressures of the most soluble salts range from more than 100 MPa (Goudie & Viles, 1997). As a result, the occurrence of crystallisation or hydration within these rocks would lead to the disruption of the material.

USV measurements

Results of the ultrasonic velocity analysis are presented in Table 2. The fresh SLB samples revealed faster ultrasonic wave propagation, suggesting a greater compactness and higher mechanical resistance with respect to the PLB and DG samples. In contrast, total structural anisotropy - ΔM and relative structural anisotropy - Δm values are lower in SLB than PLB samples. The large difference between the total and relative anisotropy in the DG samples is due to the presence of bedding planes within the limestone. As ultrasound velocity increases with density, compressive strength and water saturation, but decreases with porosity (Bouineau, 1978), the results indicate the higher compactness and homogeneity of the SLB samples, followed by PLB and DG.

Durability

Limestone samples were subjected to salt crystallisation and frost resistance tests, before subsequently being observed by SEM and undergoing sound wave propagation (USV) measurements. After these ageing tests were carried out, some changes in microstructure were observed.

SEM examination of samples revealed that post-ageing test limestone deterioration was expressed as granular disintegration, fissuring or flaking. These features were observed in both lithotypes of the Lesno Brdo limestone

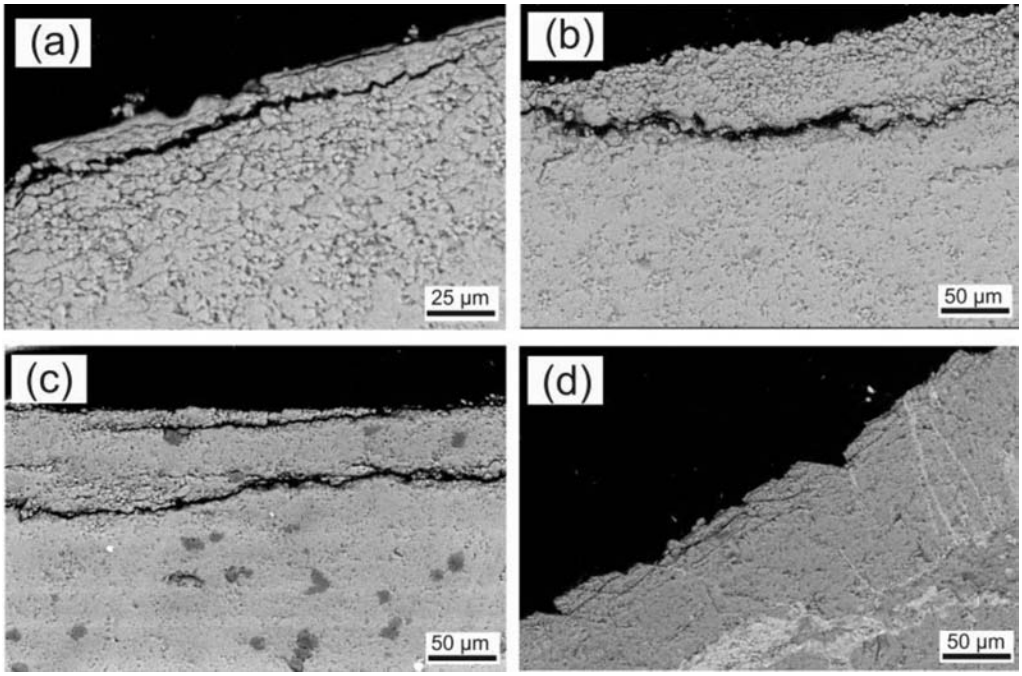

Figure 3. SEM-BSE images of investigated limestones after the ageing tests. a) Flaking of the grey Lesno Brdo limestone lithotype after salt crystallisation. b) Flaking of the red Lesno Brdo limestone lithotype after salt crystallisation is associated with the presence of phyllosilicate-filled discontinuities. Granular disintegration can also be observed at the surface. c) Flaking of the Drenov Grič limestone after salt crystallisation. d) Deterioration along cleavage planes of the grey Lesno Brdo limestone lithotype after the frost resistance test.

after salt crystallisation (Figure 3a). Fissuring and granular disintegration were limited to the upper 50 μm or so beyond the limestone surface, whereas flakes occurred up to a depth of around 25 μm. Flaking was in some cases related to the presence of phyllosilicate-filled discontinuities, as can be seen in Figure 3b. Some samples also displayed an etched surface, probably the result of dissolution caused by the salt solutions. The coarse grained dolomite was deteriorated along cleavage planes. The area of deterioration in Drenov Grič limestone after salt crystallisation was rather deeper than that observed in both Lesno Brdo lithotypes. Flaking (Figure 3c) was observed to a depth of 50 μm to 100 μm from the surface, in some areas up to 200 μm. Granular disintegration was restricted to the upper 20 μm of the samples.

Analysis of the frost resistance test results revealed no measurable loss of limestone mass, except in one DGb sample, where a small loss was observed (V_{b48} = –0.06). Thus according to the general criteria, the limestones can be considered to be highly resistant to frost action. In contrast however, SEM examination of samples revealed several deterioration phenomena. Both lithotypes of Lesno Brdo limestone were affected, with granular disintegration observed 25–80 μm under the surface, although in most cases decohesion was restricted to a depth of about 50 μm. Coarse-grained dolomite degraded along cleavage planes up to 25 μm below the surface (Figure 3d). In addition, Drenov Grič limestone showed a system of fissures occurring parallel to the surface at depths of up to 200 μm. Decohesion between grains was observed at depths of up to 50 μm, while sparitic vein decohesion occurred even deeper, up to 200 μm below the sample surface.

As seen from Table 2, there were measurable reductions in ultrasound velocity in the majority of samples before and after the crystallisation (15 immersions in Na_2SO_4) and frost resistance tests (48 cycles). A decrease in ultrasound velocity indicates the occurrence of deterioration, corroborating the observations made by SEM examination. It is also widely known that a decrease in ultrasound velocity suggests the presence of discontinuities or other obstacles within stone (Fassina et al., 1993).

An increase in total structural anisotropy after the salt crystallisation and frost resistance tests was observed for all investigated limestones. Furthermore, the total structural anisotropy was always lower in unwashed compared with washed samples, suggesting that salt crystals filled the discontinuities and pores in the limestone, resulting in a temporary reduction in anisotropy (Papida et al., 2000). In general, the samples' relative anisotropy increased after undergoing the ageing tests. In PLB and DG samples, a decrease in relative structural anisotropy was observed in unwashed samples, probably for the same reason as described above for total structural anisotropy. These results correlate with the findings of other studies (Cultrone et al., 2008; Cardell et al., 2008), who have also reported an increase in velocity and structural anisotropy after the salt crystallisation test. The degree of weathering *V*/% of the samples was always higher after the salt crystallisation test compared to the frost resistance test for all investigated limestones. This is in agreement with SEM observations, where the samples always demonstrated higher damage after salt crystallisation. In terms of the salt crystallisation test alone, the degree of weathering was always higher in washed than unwashed samples.

Table 2. Results of USV measurements: v1-3 = average values± standard deviation of ultrasound velocities in all three orthogonal directions of the investigated limestones, ΔM (%) = total anisotropy, Δm (%) =relative anisotropy, ΔV_L (%) = degree of weathering.

Samples		Salt crystallisation SIST EN 12370			Frost resistance SIST EN 12371	
Drenov Grič limestone		unweathered	weathered		unweathered	weathered
			unwashed	washed		
DG	v1 (km/s)	4.76 ± 0.36	4.76 ± 0.46	4.77 ± 0.46	4.78 ± 0.22	4.67 ± 0.42
	v2 (km/s)	4.63 ± 0.54	4.58 ± 0.51	4.11 ± 0.77	4.69 ± 0.27	4.61 ± 0.26
	v3 (km/s)	4.22 ± 0.82	4.77 ± 0.69	4.09 ± 1.19	4.49 ± 0.06	4.54 ± 0.11
	ΔM_p/%	10.29 ± 8.45	10.27 ± 6.91	14.09 ± 12.32	5.05 ± 3.00	6.17 ± 1.98
	Δm_p/%	2.42 ± 3.68	7.16 ± 4.12	12.33 ± 12.33	2.08 ± 2.25	3.75 ± 2.58
	ΔV_L/%		(-) 3.98 ± 7.86	4.70 ± 5.85		0.96 ± 1.82
Lesno Brdo limestone						
Grey lithotype						
SLB	v1 (km/s)	5.23 ± 0.29	4.71 ± 0.49	4.73 ± 0.53	5.21±0.21	4.95 ± 0.17
	v2 (km/s)	5.16 ± 0.33	4.89 ± 0.55	4.98 ± 0.78	5.04±0.17	4.99 ± 0.12
	v3 (km/s)	5.04 ± 0.33	4.84 ± 0.27	4.69 ± 0.57	4.99±0.08	4.74 ± 0.12
	ΔM_p/%	3.19 ± 1.96	4.71 ± 3.00	4.10 ± 2.59	2.57 ± 2.29	4.65 ± 4.27
	Δm_p/%	1.39 ± 1.28	5.03 ± 2.17	7.26 ± 6.18	3.22 ± 2.45	2.93 ±1.52
	ΔV_L/%		6.38 ± 3.15	6.65 ± 3.05		3.66 ± 2.31
Red lithotype						
PLB	v1 (km/s)	5.19 ± 0.21	4.42 ± 0.35	4.74 ± 0.13	4.82±0.25	4.65 ± 0.14
	v2 (km/s)	4.88 ± 0.39	4.73 ± 0.57	4.76 ± 0.36	4.61±0.22	4.51 ± 0.28
	v3 (km/s)	4.53 ± 0.64	4.66 ± 0.13	4.11 ± 0.56	4.35±0.03	4.35 ± 0.04
	ΔM_p/%	10.29 ± 8.80	7.02 ± 5.90	15.55 ± 7.58	6.67 ± 4.93	7.18 ± 2.36
	Δm_p/%	6.32 ± 6.80	1.42 ± 0.82	3.19 ± 2.47	4.61 ± 3.70	9.98 ± 1.17
	ΔV_L/%		5.01 ± 9.01	6.80 ± 3.77		1.90 ± 1.78

A negative trend was observed in the Drenov Grič limestone, suggesting that salt filled the pores and resulted in increased limestone compactness. In general, USV data reveal that the DG samples experienced the least amount of change after undergoing ageing.

Sodium sulphate is one of the most important salts responsible for the damage of natural stone (Goudie and Viles, 1997). At room temperature, sodium sulphate has two stable phases: thenardite (Na_2SO_4) and mirabilite (Na_2SO_4x-$10H_2O$), with a metastable phase represented by sodium sulphate heptahydrate ($Na_2SO_4x7H_2O$). The high damage potential of sodium sulphate has been studied by several authors (SCHAFFER, 1932; EVANS, 1970; MARSCHNER, 1978; SPERLING & COOKE, 1985; GOUDIE & VILES, 1997), with the salt also contributing to tests studying the durability of building materials (ASTM C88-90, RILEM PEM/25, SIST EN 12370). Tests involving sodium sulphate were first carried out by Brard (1828), who used a saturated solution of sodium sulphate for simulation of the frost resistance of natural stone. Since then, a similar procedure has been used in several types of accelerated ageing test, with the aim of simulating the deterioration of natural stone, concrete and other building materials (SPERLING & COOKE, 1985; KWAAD, 1970; FAHEY, 1986; RODRÍGUEZ-NAVARRO et al., 2000; BENAVENTE et al., 1999; BENAVENTE et al., 2001; FLATT, 2002; BENAVENTE et al., 2004; BENAVENTE et al., 2007; RUIZ-AGUDO et al., 2007; ROTHERT et al., 2007; CARDELL et al., 2008). The choice of sodium sulphate is based mainly on two factors: (i) its frequent occurrence in objects or environments (ARNOLD & ZEHNDER, 1988; TUNCOKU et al., 1993; BROMBLET, 1993; FASSINA et al., 1996; LAUE et al., 1996) and (ii) its high damage potential.

RUIZ–AGUDO et al. (2007) described the occurrence of Na-sulphate crystallisation up to 3 mm under the surface of samples, resulting in flaking. A decrease in stone porosity was also reported. However, it should be emphasised that the stones analysed in that study were highly porous, with levels of more than 30 %. In this investigation on the other hand, deterioration of the Slovenian limestones was restricted to a much smaller area. This fact could be ascribed to their extremely low porosity of less than 5 % (KRAMAR et al., 2010a). In addition, due to their high compactness, deterioration was observed only to a depth of around 200 μm below the surface. Deterioration of these limestones could be a result of the crystallisation pressure of thenardite, which ranges from 29.2 to 196.5 MPa (WINKLER & SINGER, 1972) and exceeds the splitting tensile strengths of the investigated limestones which are not higher than 15 MPa. With repeated cycles of salt crystallisation, hydration pressure also develops. The crystallisation pressure of thenardite is higher than that of mirabilite (Winker & Singer, 1972), resulting in greater damage. The transition of mirabilite to thenardite is also accompanied by an increase in volume of 300 % (Price & Brimblecombe, 1994).

One factor which could have influenced the smaller amount of stone deterioration caused by the frost resistance test could be the lower pressures which occur during ice formation with respect to salt crystallisation. Pressure caused by the former ranges from 14 to 138 MPa with a decrease in temperature of between –1.1 and –12.5 °C (Goudie & Viles, 1997). During the ageing test performed in this study, the temperature fell by up to –10 °C. The temperature range considered critical for the deterioration of natural stone is from about –4 to –15 °C (Goudie & Viles, 1997). Stone with a higher quantity of smaller pores is more prone to frost deterioration as well as salt crystallisation, although stone damage is more specifically influenced by nanopores in the case of salt crystallisation and by micropores in the case of frost damage (Lindquist et al., 2007). Since the investigated limestones have low capillary kinetics (Kramar et al., 2010a), they can be considered as more prone to frost damage, as slow water transfer may prevent water movement, resulting in higher pressures (Thomachot & Matsouka, 2007).

Conclusions

The limestones investigated in this study were recognised as high strength rocks. The highest strength was observed in the grey lithotype of the Lesno Brdo limestone, followed by Drenov Grič limestone and the red Lesno Brdo lithotype, which suggests that the higher the content of phillosilicate-filled discontinuities, the lower the splitting tensile strength. There were no significant differences observed between the bedding planes of different orientations in the Drenov Grič limestone. Furthermore, there was also no difference in observed tensile strength between the dry and water-saturated samples.

There were, however, measurable differences in USV values between the studied limestones. Faster ultrasonic wave propagation was seen in fresh SLB samples, suggesting a greater compactness and mechanical resistance than the PLB and DG samples. In contrast, total structural anisotropy (ΔM) and relative structural anisotropy (Δm) were lower in SLB than PLB samples.

After ageing tests were carried out, some changes in microstructure occurred, as observed via SEM-EDS examination and USV measurement. Deterioration of the studied limestones took place in the form of granular disintegration, fissuring and flaking. A much higher level of damage was apparent after the salt crystallisation test than the frost resistance test, with the area damaged area also larger. Deterioration was slightly higher in the Drenov Grič and thus this limestone can be considered as more prone to deterioration than either Lesno Brdo lithotype. Of the two lithotypes of Lesno Brdo limestone, the grey lithotype possessed better durability characteristics. In general, the durability of the studied limestones is mostly affected by their porosity and the presence of phyllosilicate-filled discontinuities.

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