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Physical properties of Devonian limestones from selected deposits in the context of frost resistance

Introduction

The use of stone for utility purposes requires extensive knowledge of its structure, mineral composition as well as physico-mechanical properties. The use of carbonate rocks in the building industry as a construction or road material has a long history. However, they are not recommend for use in places exposed to atmospheric factors, such as humidity or frost. This applies to both elements and aggregates for frost-resistant concretes. The problem lies, above all, in significant differentiation of properties of available minerals and the lack of clear criteria for standard classification. According to standards: PN-EN 1341, PN-EN 1342 and PN-EN 1343, water absorption by weight of rocks used for the production of road surface components should not exceed 3%, and adopting the criterion of water absorption by weight below 0.5% is recommended. Using such inaccurate standard recommendations can be the reason for serious mistakes in the evaluation of the suitability of the rock material. The rock tests conducted thus far mainly concerned the displacement and retention of fluids in pores (Coutelieris and Delgado 2012; Besserer and Hilfer 2000), the impact of the conditions in which they arose (Halley and Schmoker 1983) or linear changes under the

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influence of freezing and defrosting (Xuedong et al. 2015), as well as direct and indirect tests of resistance of aggregates to cyclic freezing. We can determine the parameters of the material and, on their basis – the suitability corresponding to the market needs. The increasingly frequent application of the principle of broadly understood sustainable development necessitates the adjustment of products to the market needs and maximum utilization of the obtained raw material. Therefore, carrying out tests aimed at appropriate classification of a material is in line with present economic trends.

1. Materials and testing methods

1.1. Materials

Tests were conducted for a selected located of Devonian limestone, originating from two mines in the Swietokrzyskie region, several kilometers apart.

The subject of the research were the rock samples collected from the raw materials extracted on different levels and walls of the examined mines. Both of them are operated at the moment and they deliver the macroscopically diversified limestones. As shown above four rock blocks were collected from each mine.

Samples with dimensions of φ50 mm and 150 mm in height were drilled using the Hilti drill bit from the collected rock fragments. One of the rocks, marked as "H" in Figure 2, was unsuitable for drilling samples due to its numerous cracks.

Fig. 1. Mine I, located in the western part of Swietokrzyskie region
A, B, C and D – location of places of rock sampling for laboratory tests

Rys. 1. Kopalnia I, zlokalizowana w zachodniej części województwa świętokrzyskiego
A, B, C i D – miejsca pobrania brył skalnych do badań

Fig. 2. Mine II, located in the south-western part of Swietokrzyskie region
E, F, G and H – location of places of rock sampling for laboratory tests

Rys. 2. Kopalnia II, zlokalizowana w południowo zachodniej części województwa świętokrzyskiego
E, F, G i H – miejsca pobrania brył skalnych do badań

Fig. 3. Extracted raw material from which the samples used in the tests were collected

Rys. 3. Surowiec skalny, z którego odwiercano próbki do badań

Fig. 4. Drilled lumps

Rys. 4. Wywiercone bryły skalne

Fig. 5. Cut samples for laboratory tests

Rys. 5. Wycięte próbki do badań laboratoryjnych

1.2. Testing methods

The samples were prepared in accordance with the PN-B-11210 standard. The following tests were carried out:

a) physical properties:
   - density, in compliance with PN EN 1936:2010,
   - volumetric density, in compliance with PN EN 1936:2010,
   - porosity, in compliance with PN-EN 1936:2010,
   - volumetric capillary absorbability, in compliance with PN-EN 1925:2001,
   - absorbability under vacuum in compliance with PN-EN 13755,
   - saturation level, defined, as the proportion of the mass of water absorbed during capillary absorption to the mass of water absorbed under vacuum; according to (Centre... 1957; Rusin and Świercz 2017) we can define the critical level of water saturation, which for capillary and porous materials is 80%,
   - the degree of filling pores with water, defined as a ratio of capillary absorbed water volume to the total pore volume;

b) direct frost resistance, in compliance to PN-EN 12371
   The samples were subjected to 80 freezing and defrosting cycles, during which changes in weight and length of the tested samples were recorded. The standard does not provide for any specific number of cycles to be performed on the tested stone material, but it makes this important parameter dependent on the investor's individual decision. The arbitrariness of such assumptions may raise doubts. The number of 80 cycles, resulting from the experience in performing direct test on frost resistance of rocks was assumed for the test (Rusin and Świercz 2017);

c) tests using the Differential Analysis of Volumetric Strain (DAVS) method
   This method consists of the simultaneous analysis of the volumetric strain of the rock sample saturated with water and a reference sample not containing water. This makes it possible to observe volumetric strain of the rock, which is associated with the phase transition of water into ice during freezing, and to calculate the amount of ice produced (Rusin et al. 2011). This test is carried out with dilatometers, shown in Figure 6:

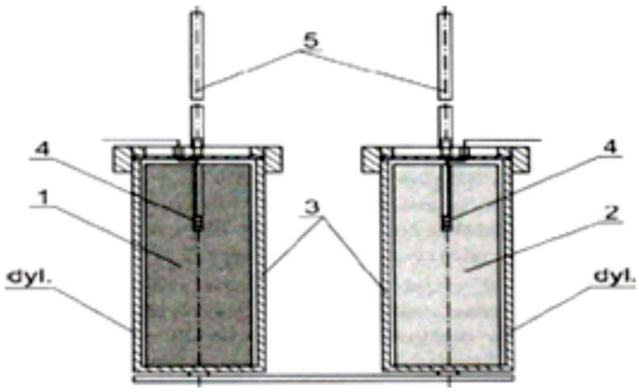

Fig. 6. Dilatometers used in the DAVS method (Rusin et al. 2011)
1 – test sample, 2 – reference sample, 3 – measuring dilatometers, 4 – temperature sensors, 5 – calibrated measuring tubes

Rys. 6. Dylatometry pomiarowe wykorzystywane w metodzie DAVS

The sample saturated with water is placed in one of the dilatometers. The second one contains a reference sample. Dilatometers and calibrated measuring tubes are filled with a liquid which allows the samples to be frozen and their volume changes to be determined. The cover of dilatometers also have temperature sensors that detect its changes inside and outside each sample every minute throughout the cycle.

d) microstructural tests
An electron scanning microscope SEM Quanta FEG 250 was used in the tests and an X-ray microanalysis for the tested rock samples was conducted.

2. Tests results

2.1. Physical properties

The mean values of porosity, density, volumetric density, volumetric capillary absorbability, absorbability under vacuum, saturation level and the degree of filling pores with water are presented in Table 1.

Table 1. Physical properties of the tested rocks

Tabela 1. Zestawienie cech fizycznych badanych skał

ID of samples	Porosity (%)	Density (Mg/m^3)	Bulk density (Mg/m^3)	Volumetric capillary absorbability (%)	Absorbability under vacuum (%)	Saturation level (%)	Pore filling degree (%)
A	1.11	2.71	2.68	0.64	1.02	63	58
B	1.11	2.71	2.68	0.41	0.84	49	37
C	1.10	2.69	2.67	0.50	0.95	53	45
D	1.51	2.73	2.69	0.37	1.43	26	25
E	1.49	2.74	2.70	0.37	0.50	74	25
F	1.11	2.73	2.70	0.39	0.60	65	35
G	1.86	2.76	2.71	1.18	1.23	95	63

2.2. Direct frost resistance

Results of the direct frost resistance tests are presented in Figures 7 and 8.

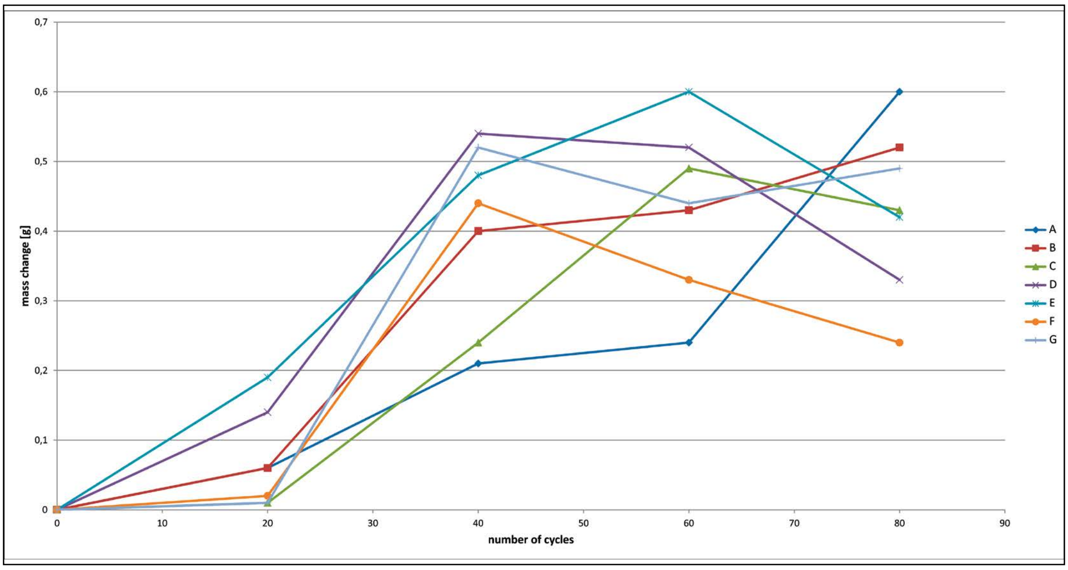

Fig. 7. Change in mass of rock samples during 80 freeze and thaw cycles

Rys. 7. Zmiana masy próbek skał w trakcie 80 cykli zamrażania i rozmrażania

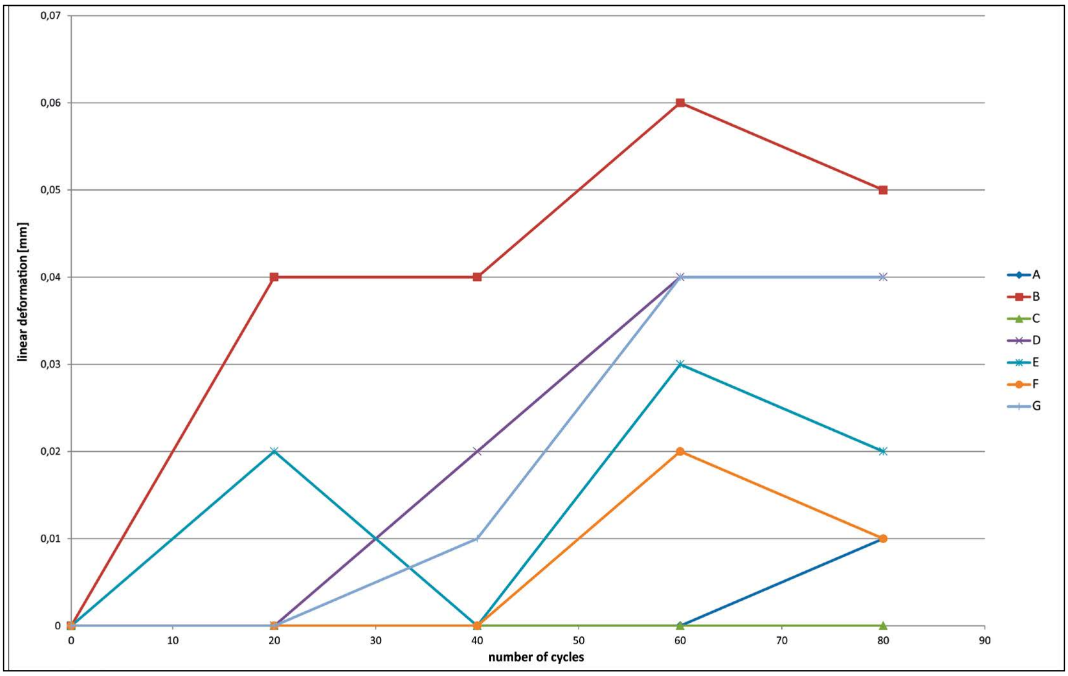

Fig. 8. Linear deformation of rock samples during 80 freeze and thaw cycles

Rys. 8. Odkształcenia liniowe próbek skał w trakcie 80 cykli zamrażania i rozmrażania

Table 2. Mass of the samples before the direct frost resistance test

Tabela 2. Masa próbek przed badaniem mrozoodporności bezpośredniej

ID of samples	Mass (g)
A	668.01
B	663.36
C	664.32
D	648.91
E	651.87
F	657.54
G	655.38

2.3. Differential Analysis of Volumetric Strain

The volumetric absorbability and the results of the freezing water content per unit volume of the rock sample calculated based on DAVS test results are shown in Table 3.

Table 3. DAVS measurement results (in temperature of –10°C)

Tabela 3. Wyniki badań Różnicowej Analizy Odkształceń (w temperaturze –10°C)

ID of samples	Volumetric capillary absorbability (%)	Absorbability under vacuum (%)	m_i/V capillary* (%)	m_i/V vacuum** (%)
A	0.64	1.02	0.16	0.89
B	0.41	0.84	0.08	0.39
C	0.50	0.95	0.42	0.79
D	0.37	1.43	0.28	1.25
E	0.37	0.50	0.25	0.41
F	0.39	0.60	0.24	0.30
G	1.18	1.23	0.50	0.72

* Ice mass in a volume unit of a capillary-saturated sample.

** Ice mass in a volume unit of a vacuum-saturated sample.

2.4. Microstructure

Figures 9 and 10 present two selected rock samples, shown under an electron scanning microscope and their X-ray microanalysis. This samples was chosen due to their biggest macroscopic differentiation.

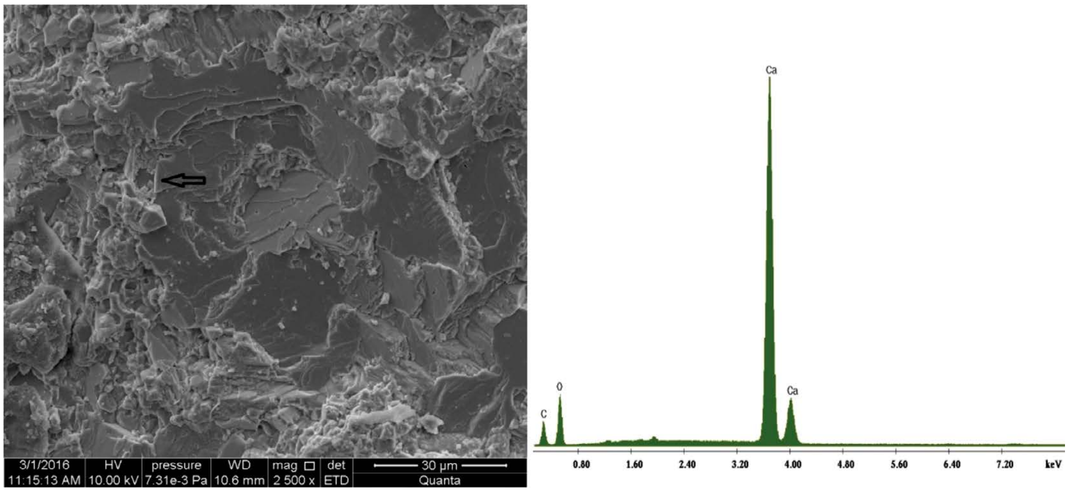

Fig. 9. Microstructure of A rock sample (left) and X-ray microanalysis of the marked point (right)

Rys. 9. Mikrostruktura skały A (po lewej) oraz mikroanaliza zaznaczonego punktu (po prawej)

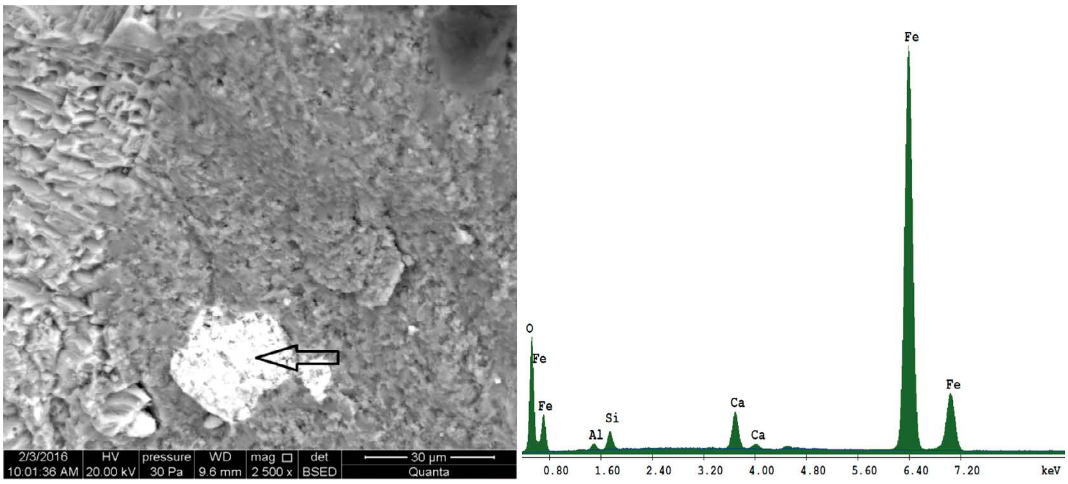

Fig. 10. Microstructure of G rock sample (left) and X-ray microanalysis of the marked point (right)

Rys. 10. Mikrostruktura skały G (po lewej) oraz mikroanaliza zaznaczonego punktu (po prawej)

Discussion of results and conclusions

The porosity of the samples of rocks A, B and C from mine I and rock F from mine II was about 1%. The fourth rock from mine I (rock D) and rock E from mine II had a slightly higher porosity, amounting to approx 1.5%. Rock G from mine II showed the highest porosity among the tested materials, amounting to approx. 1.9%.

Volumetric absorbability, measured under a vacuum, was the lowest for rock E from mine II and amounted to 0.5%. The highest value was recorded for rock D from mine I – approx. 1.5%. According to the binding standards for the suitability of rock material for use in the construction industry, only rock E meets the recommended requirement of absorbability of up to 0.5%. However, as other tests indicate, especially the direct frost resistance test described below, none of the rocks were destroyed.

Rocks D and E showed the lowest value of volumetric absorbability determined after a capillary rise, which amounted to less than 0.4%. The highest value of volumetric capillary absorbability was determined for rock G from mine II, which was slightly below 1.2%.

The saturation level for the samples collected in mine I was on average less than 48%. For samples from mine II it was definitely higher and amounted to 78%. The range of individual results of saturation level is relatively high and ranges from 26%, for rock D from mine I, to 95% for rock G from mine II. The critical saturation level for rock material can be estimated to about 80% (Centre... 1957; Rusin and Świercz 2017). Therefore, rock G should not be resistant to cyclical freezing and defrosting.

The average pore filling degree is the same for the mines and amounts to 41%. On the other hand, values for individual rocks vary widely: from 25% for rocks D and E to about 60% for rocks A from mine I and G from mine II.

By analyzing the content of ice generated in the pores of the material, estimated on the basis of DAVS tests at the temperature of –10°C, we can determine the mass ratio of water undergoing the phase transition to the volume of the sample vacuum-saturated and saturated by capillary action (Table 3). It is evident that at –10°C the weight of ice in the tested rocks represents a maximum of 0.5% of the volume of the sample (Table 3). The lowest values of this coefficient were found in case of rocks A and B from mine I. The values are higher in the case of vacuum-saturated samples. Sample D from mine I showed a maximum value of 1.25%.

The direct frost resistance test is currently the most common indicator of frost resistance of the materials. The performed tests showed that all of the rock samples remained frost-resistant after 80 cycles of freezing and defrosting, despite slight changes in mass and linear deformations, which are shown in Figures 7 and 8. Rock G also remained completely frost resistant, although the degree of water saturation of samples was above the critical level. After 80 freeze and thaw cycles the value of samples mass changed slightly (Figure 7). The same situation was with linear deformation (Figure 8). The samples did not show any damages at the end of this test.

Microstructure tests were performed for the collected samples, as shown in Figures 9 and 10. The authors used this method to check if there is any differentiation in the microstructure of the tested samples. The corrugated surface of the material with irregular edges of rock A is shown in Figure 9. The X-ray microanalysis of this sample, performed at the marked point, showed a high calcium content appropriate for this type of rock. Microstructural analyses of rocks B–F showed no significant differences, nevertheless the tested samples are different based on physical parameters such as: porosity, density and bulk density. A certain amount of iron was shown in rock G from mine II, which was visible in white spots on pictures, as can be seen in the X-ray microanalysis, shown in Figure 10. The presence of this element was also reveled in other fragments of rock G. Influence of the iron content in that sample will be the subject of additional tests.

Differences in the physical characteristics of the tested rocks, such as: porosity, absorbability and the content of water capable of freezing, did not affect the differences in their frost resistance. All samples remained frost resistant. Assuming that aggregates and stone products originating from both mines meet other necessary standard conditions, there is no reason to give up their use, only because they belong to the group of limestone rocks. It is worth noting that these rocks, formed in the Devonian period, are generally characterized by higher volumetric density and lower porosity than limestones from later geological periods (Stępień et al. 2017).

These results are similar with the conclusions from (Skowera 2016). In that publication, authors use limestone from another mine also localized in Swietokrzyskie region and have a similar opinion about them.

The range of variations in the physical properties of the tested rocks, their colors and porosity were not that important so that in the context of frost resistance, one could propose a disqualification of a part of the deposit. Nevertheless, it cannot be excluded that some parts of the mine may contain rocks of insufficient quality.

Further research will concern the determination of the pore size distribution inside the material, as well as the attempt to determine their connections and the impact of these characteristics on frost resistance.

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PHYSICAL PROPERTIES OF DEVONIAN LIMESTONES FROM SELECTED DEPOSITS IN THE CONTEXT OF FROST RESISTANCE

Abstract

Widespread opinion holds that calcareous rocks have limited suitability for use in the production of aggregates and stone products having adequate frost resistance. However, some of the rocks, in particular those from earlier geological periods, provide a promising alternative to silicate rocks.

The paper presents results of the analysis of Devonian carbonate rock originating from two selected mines in the Swietokrzyskie region. The examined mines extract limestone from two different deposits of the same age. The rock samples are collected from beds lying at different depths, distinct in texture and color in macroscopic examination. It was found that despite the changes in bulk density, porosity and absorption, all the examined samples were frost resistant.

Using the Differential Analysis of Volumetric Strain method, the content of ice formed in the pore spaces was determined. In addition, the ratio of the content of water capable of freezing to the total pore volume, and the total amount of water absorbed due to capillary action in rock samples soaked in water, were analyzed. In all cases, it was revealed that the destructive action of freezing water was weakened due to a relatively low content of water capable of freezing and a substantial volume of pores that are not filled with water in capillary absorption.

It is extremely important to be able to classify the available rock material. The generally adopted methods, including absorptivity tests, do not allow for precise categorization. In the investigations, the authors focused on the analysis of the basic factors that are decisive for rock durability, including bulk density, pore filling level and volume absorption. The authors do not correspond compressive strength and resistance to abrasion as this will be the subject of further research.

Keywords: limestone, frost resistance, carbonate rock, DAVS method

ZRÓŻNICOWANIE CECH FIZYCZNYCH WAPIENI DEWOŃSKICH POCHODZĄCYCH Z WYBRANEGO ZŁOŻA W KONTEKŚCIE ICH MROZOODPORNOŚCI

Streszczenie

Powszechnie uważa się, że skały wapienne mają stosunkowo ograniczoną przydatność do stosowania w produkcji kruszyw i wyrobów kamiennych ze względu na ich odporność na działanie mrozu. Jednak niektóre skały, w szczególności pochodzące z wcześniejszych okresów geologicznych, stanowią obiecującą alternatywę dla skał krzemianowych.

W pracy przedstawiono wyniki analizy dewońskich skał węglanowych pochodzących z dwóch wybranych kopalń z regionu świętokrzyskiego. Skały wapienne w obu wybranych kopalniach pochodzą z tego samego okresu geologicznego. Pobrany materiał skalny pochodził z różnych pokładów kopalń i różnił się makroskopowo między sobą teksturą i kolorem. Ostatecznie stwierdzono jednak, że pomimo różnic w nasiąkliwości objętościowej, porowatości i absorpcji kapilarnej, wszystkie skały okazały się być mrozoodporne.

Wykorzystując w badaniach Różnicową Analizę Odkształceń określona została zawartość lodu powstającego w przestrzeni porów. Ponadto określono stosunek zawartości wody zdolnej do zamarzania w odniesieniu do całkowitej objętości porów oraz ilość zaabsorbowanej wody przy podciąganiu kapilarnym. We wszystkich przypadkach okazało się, że destrukcyjne działanie zamarzającej wody zostało osłabione poprzez stosunkowo małą ilość wody zdolnej do zamarzania i znaczną objętość porów niewypełnionych wodą przy podciąganiu kapilarnym.

Bardzo ważne jest, aby móc odpowiednio klasyfikować dostępny materiał skalny. Ogólnie przyjęte metody, takie jak chociażby badania nasiąkliwości, nie pozwalają na precyzyjną diagnostykę. Dlatego też autorzy w swoich badaniach skupiają się na analizie podstawowych czynników decydujących o trwałości skały, takich jak nasiąkliwość objętościowa, stopień wypełnienia porów wodą, czy stopień nasączenia. Autorzy nie odwołują się do badań wytrzymałości na ściskanie i odporności na ścieranie wybranych skał, ponieważ będzie to przedmiotem dalszych badań.

Słowa kluczowe: wapień, mrozoodporność, skały węglanowe, metoda DAVS