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ANALYSIS OF FROST RESISTANCE AND PHYSICAL PROPERTIES OF DEVONIAN COMPACT LIMESTONES DERIVING FROM ONE DEPOSIT

Abstract
The use of carbonate rocks in building industry as a raw material for the production of construction elements and aggregates has a long history. Yet, a stereotype approach to this group of materials orders to avoid using them in constructions exposed to moisture and frost. It applies to both elements and aggregates for frost-resistant concretes. The problem lies, above all, in significant differentiation of physical properties of available minerals and the lack of clear criteria for standard classification. The article focuses on the differentiation analysis of physical properties of rocks originating from two singled out mines of Devonian compact limestone, located in the region of Świętokrzyskie.

Keywords: frost resistance, rocks, limestones

1. Introduction

Over decades the fact has been confirmed that frost resistance and durability of rock products and concretes with carbonate aggregate can be high. However, many works and performed research have not contributed to the increase of direct use of this type of rocks in the building industry. Deposits from sedimentary rocks for the needs of production of stone construction elements are not fully exploited. The main problems in this group include: frost resistance and methods of testing it, high heterogeneity (even within one deposit) arising from the genesis of rocks and alkali-aggregate reaction. The article analyzes the rock material originating from two mines that exploit the deposit of Devonian compact limestone similar in geological terms.

The assumption is that it is worth using carbonate rocks in the building industry more efficiently. They can be used more widely for production of facade elements and in some cases pavement surfaces. However, one should consider recommendations of applicable standards in Poland in terms of frost resistance. Freezing and defrosting is a commonly adopted and generally resolving method of establishing frost resistance, despite the fact that discrepancy of conditions of these tests with the real exploitation conditions raises doubts. For example, standard PN-EN 12371 does not specify the number of required cycles of freezing and defrosting for rock materials. It is dependent on the investor's opinion, and it has been recommended to perform even 240 cycles of freezing and defrosting, if necessary. The adoption of such assumptions is quite arguable and puzzling. The arbitrariness of the adopted number of cycles in the test does not support a positive evaluation. On the other hand, the performance of a great number of cycles of freezing extends the testing time considerably. The standard criteria also raise doubts in case of water absorption by weight of rocks.

According to standards PN-EN 1341, PN-EN 1342, PN-EN 1343, water absorption by weight of rocks used for production of road surface components should not exceed 3%, but it is recommended to adopt the water absorption by weight below 0.5%. The tests [1] have demonstrated that rocks are entirely frost resistant, the volumetric absorbability of which when rising damp is not greater than 0.6%, which approximately corresponds to 0.25% of water absorption by weight. Using inaccurate standard recommendations can be the reason for serious errors in the evaluation of usefulness of the rock material. One has suggested guidelines for the classification of rock materials in terms of their frost resistance in the project final report [1]. A measurable effect in the form of volumetric strain of the sample has been adopted as the classification index (determined using the method of Differential Analysis of Volumetric Strain – DAVS) – ΔVu/0.083. The estimated value ΔVu/0.083 approximately corresponding to the mass of ice being formed in a volume unit of the rock should not exceed 0.7% in case of frost resistant products exploited in moderately harsh conditions (long-term contact with water, without access of defrosting agents, without access of salt water). It should be emphasized that the aforementioned condition applies to the samples of rocks absorbed using a vacuum method.

As a result of further analyses [2] it has been stated that frost resistance of rocks should be evaluated not using samples absorbed at the highest level (vacuum method) but as a result of capillary saturation. The following two indicators are used as an evaluation tool of frost resistance: ΔVu/0.083 and volumetric capillary absorbability. It is acknowledged that:
– rocks with capillary volumetric absorbability below 0.6% are frost resistant without exception;
– rocks with capillary volumetric absorbability over 1.5% are not resistant to cyclic freezing and defrosting;
– within the range of absorbability of 0.6–1.5% the indicator ΔVu/0.083 determines durability: frost resistant rocks ΔVu/0.083 < 0.5%, dubious rocks or non-frost resistant rocks ΔVu/0.083 > 0.6%.

2. Methodology

Rock samples taken from 2 mines of Devonian limestones have been tested. It has been stated that rock genesis in both mines is the same. The aim of the tests was to determine the changeability of physical parameters and their comparison with frost resistance of rocks tested directly through freezing and defrosting as well as based on the parameters mentioned previously: ΔVu/0.083 and volumetric capillary absorbability. In both mines it was possible to remove rocks from deposits located at various depths. Nine rock fragments different from one another in terms of color and localization with a mass of 30 to 70 kg each were finally taken based on inspections and a geologist's opinion. Four samples were taken from mine No. 1, three samples were taken from mine No. 2. One of the samples from mine no. 2 (2b) was destroyed while drilling and it was not taken into consideration during the tests of frost resistance and strain using the DAVS method.

From the material taken in the mines, samples were drilled out with the following dimensions 50 mm and 30 mm in diameter and height h = 150 mm and h = 100 mm, respectively. The samples were used for the performance of the following markings:
– density,
– volumetric density,
– porosity,
– volumetric capillary absorbability,
– direct frost resistance (measurements of mass and length of the samples and a macroscopic evaluation during 80 cycles of freezing and defrosting),
– coefficient ΔVu/0.083 according to the DAVS procedure [2]

Density was marked using Le Chatelier flask. Volumetric density was determined using a hydrostatic method. Porosity was calculated from the difference of density and volumetric density.

Capillary absorbability was marked on the samples with dimensions of 50 mm in diameter and h = 150 mm. The samples were immersed at the depth of 10 mm in a covered container. Changes in the mass were recorded in minutes 1, 3, 5, 10, 15, 30, 60, 180, 420, and then every 24 hours until a constant mass was obtained.

The test of direct frost resistance was also performed on the rock samples with dimensions of 50 mm in diameter and h = 150 mm. Holes were drilled in each sample on both sides that allowed to equip the samples with benchmarks that made it possible to record changes in length in the Graf-Kaufman apparatus. The test program included 80 cycles of freezing and defrosting. They were frozen in the air up to the temperature of –20°C, and then were defrosted in water. Changes in the samples' mass, their linear strains and damages visible on the surface were recorded.

Coefficient ΔVu/0.083 was determined using the DAVS procedure. DAVS method through simultaneous analysis of volumetric strain of the rock samples saturated with water and a comparative sample that did not contain water allowed to observe volumetric strain of the rock related only to the water phase change into ice while freezing. The entire procedure has been described in the study [3].

3. Test results and their analysis

Table 1 presents the results of basic physical features of the rocks studied.

Table 1. Physical properties of rock samples

	Sample No.	Porosity [%]	Volumetric density [g/cm^3]	Volumetric capillary density [%]	Evaluation of frost resistance
Mine 1	1a	1.13	2.68	0.64	+
	1b	0.98	2.68	0.41	+
	1c	0.77	2.67	0.50	+
	1d	1.68	2.69	0.37	+
Mine 2	2a	1.61	2.70	0.37	+
	2b	1.37	2.70	-	-
	2c	1.96	2.71	1.18	+

+ means total frost resistance after 80 cycles of freezing

The tested samples were macroscopically different from one another. The samples from mine 1 are rocks of grey color with few interlayers. Significantly darker rocks, and in the case of sample 2c – rust-colored, with numerous visible interlayers came from mine No. 2.

Figure 1 presents the percentage increase of volumetric absorbability of the tested rock samples during capillary saturation.

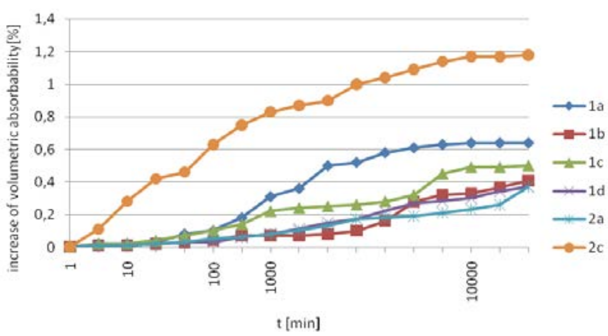

Fig. 1. Damp rising of rock samples

Changes in the samples' mass, their linear strains and damages visible on the surface were recorded during the test of direct frost resistance. Figure 2 presents the changes in linear strains of rock samples.

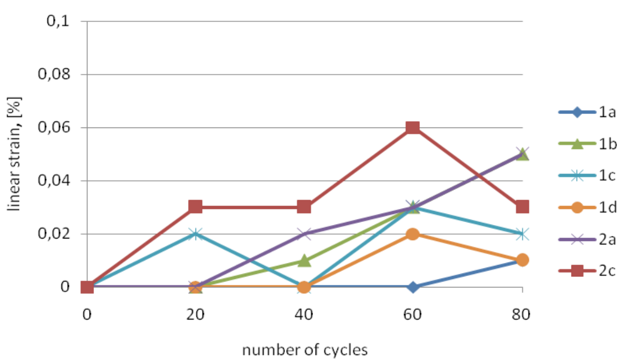

Fig. 2. Linear strain of rock samples

All tested samples were considered to be entirely frost resistant after 80 cycles of freezing and defrosting. None of the tested rock samples demonstrated a significant mass increase. The sample marked with symbol 1a was the most stable – both in linear strains and mass increase.

Table 2 presents the results of maximum values of capillary absorbability and ΔVu/0.083 values which correspond to capillary absorbability of a given rock.

Table 2. List of ΔVu/0.083 indicators and capillary absorbabilities

Sample No.	Maximum value capillary absorbability [%]	ΔVu/0.083 value corresponding to capillary absorbability [%]
1a	0.64	0.36
1b	0.41	0.36
1c	0.50	0.36
1d	0.37	0.35
2a	0.37	0.37
2c	1.18	1.08

Rocks 1d, 2a and 1b are characterized by similar very low volumetric capillary absorbability at the level of about 0.4%, which classifies them into the group of frost resistant rocks according to standard criteria and DAVS tests. Slightly higher value of capillary saturation of rock 1c is also within the group of the results characteristic for frost resistant rocks. The rock marked 1a has capillary volumetric absorbability at the level of 0.64% and the value of ΔVu/0.083 indicator should determine its classification according to DAVS. For sample 1a ΔVu/0.083 is 0.36% which is characteristic of frost resistant rocks. Rock 2c with capillary volumetric absorbability being 1.18% and the value of ΔVu/0.083 indicator equaling 1.08% is classified in the group of rocks with dubious durability. However, the rock remained frost resistant like all other samples during the conducted direct frost resistance tests using 80 cycles of freezing and defrosting. In order to obtain additional information on sample 2c, a chemical analysis of the material was performed and it was examined under an electron microscope.

SEM image of the fracture surface of sample 2c has been presented below and for comparison an image of sample 1b (Fig. 3).

Pictures taken in thousandfold magnification. They present the fracture surface of the sample and a "shining" mineral clearly marked out on the left in the picture of sample 2c.

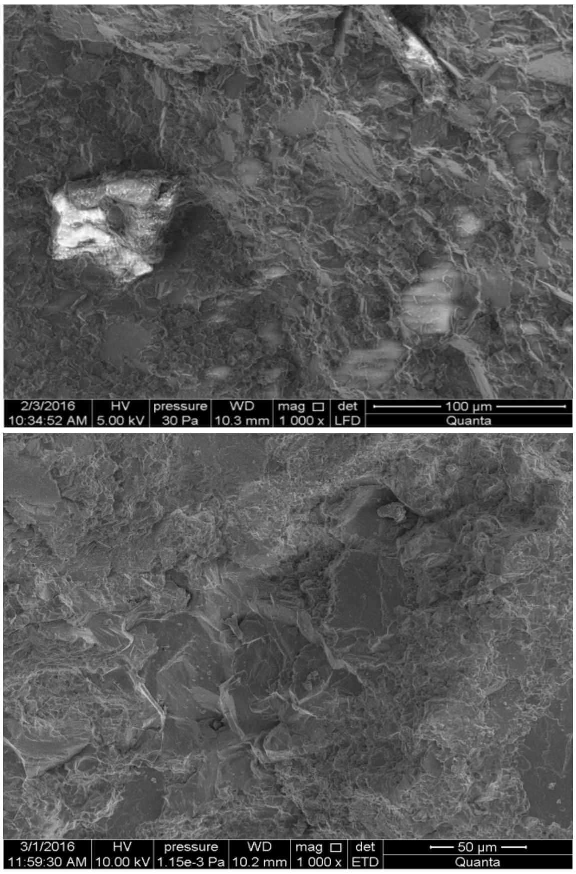

Fig. 3. Fracture surface of sample 2c (on the up) and 1b (on the down) magnified a thousand times

The chemical analysis presented below has shown that it is iron. Other fragments of the sample confirmed the high content of iron in the studied material. No presence of iron has been detected in the remaining samples used during the tests.

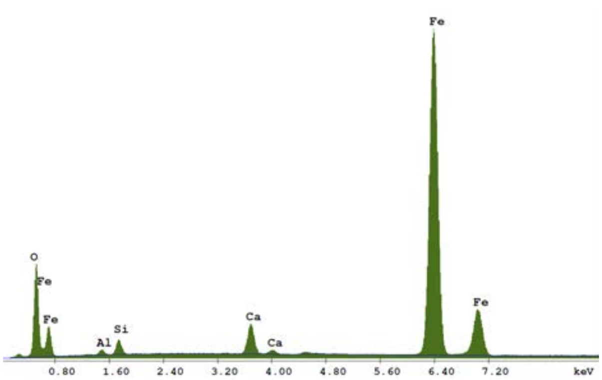

Fig. 4. Chemical analysis of the "shining" fragment of sample 2c

According to the adopted assumptions, it has been stated that all rocks besides sample 2c could have been classified in the group of frost resistant materials. The direct test of cyclic freezing and defrosting has confirmed correctness of the opinion based on the DAVS test.

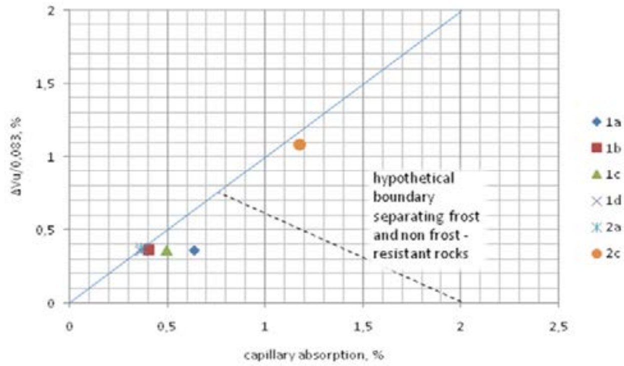

Fig. 5. Assessment of the test results ΔVu/0.083 and capillary absorbability in the context of the anticipated frost resistance according to [2]

Rock sample 2c was disqualified as a result of the DAVS test. Nevertheless, no destructive impact of frost on the rock was found during the test of cyclic freezing. There is an issue of the number of freezing cycles the rock samples undergo. It is possible that rock 2c, when subjected to an increased number of cycles, would be significantly damaged. The content of iron in the rock composition could have affected the test results, but possible relations seem to be unclear at this stage of material identification.

4. Conclusions

The test results show that the tested rocks deriving from various spots of both mines are characterized by high frost resistance. Their differentiation in terms of changeability of physical parameters is small – except for rock 2c which differs from the other ones significantly. Macroscopic differences in the color of the material were observed which seem to have no effect on the physical properties (except for rock 2c). Low absorbability and good frost resistance of the rocks are reasons to use them more efficiently, e.g. to produce facades made of stone slabs.

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Analiza mrozoodporności i właściwości fizycznych dewońskich wapieni zbitych pochodzących z jednego złoża

1. Wprowadzenie

Przez dziesiątki lat potwierdzony został fakt, iż mrozoodporność i trwałość wyrobów skalnych i betonów z kruszywem węglanowym może być wysoka. Wiele prac i wykonanych badań nie przyczyniło się jednak do wzrostu bezpośredniego wykorzystania tego typu skał w przemyśle budowlanym. Nie wykorzystuje się w pełni możliwości eksploatacji złóż ze skał osadowych na potrzeby produkcji kamiennych elementów budowlanych. Do głównych problemów w tej grupie należą: mrozoodporność i sposoby jej badania, duża niejednorodność (nawet w obrębie jednego złoża) wynikająca z genezy skał oraz reakcja alkalia-kruszywo. W artykule poddano analizie materiał skalny pochodzący z dwóch kopalń eksploatujących podobne pod względem geologicznym złoże dewońskiego wapienia zbitego.

Założeniem jest, iż warto racjonalniej wykorzystywać skały węglanowe w przemyśle budowlanym. W sprawozdaniu końcowym projektu [1] zaproponowano wytyczne do klasyfikacji materiałów skalnych pod kątem ich mrozoodporności. Za wskaźnik klasyfikacyjny przyjęto mierzalny efekt w postaci odkształcenia objętościowego próbki (określonego metodą Differential Analysis of Volumetric Strain – DAVS) – $\Delta Vu/0{,}083$. Szacowana wartość $\Delta Vu/0{,}083$, odpowiadająca w przybliżeniu masie powstającego lodu w jednostce objętości skały, nie powinna przekraczać 0,7% w przypadku wyrobów mrozoodpornych eksploatowanych w umiarkowanie trudnych warunkach (długotrwały kontakt z wodą, bez dostępu środków rozmrażających, bez dostępu wody morskiej). Należy podkreślić, że powyższy warunek dotyczy próbek skał nasączanych metodą próżniową.

W wyniku dalszych analiz [2] stwierdzono, że mrozoodporność skał powinna być oceniana nie na próbkach nasączanych w stopniu najwyższym (metodą próżniową), lecz w wyniku nasycenia kapilarnego. Jako narzędzie oceny mrozoodporności wykorzystuje się wówczas dwa wskaźniki: $\Delta Vu/0{,}083$ oraz objętościową nasiąkliwość kapilarną. Uznano, że:

– skały o kapilarnej nasiąkliwości objętościowej poniżej 0,6% są bez wyjątku mrozoodporne;
– skały o kapilarnej nasiąkliwości objętościowej powyżej 1,5% nie są odporne na cykliczne zamrażanie i rozmrażanie;
– w przedziale nasiąkliwości 0,6–1,5% o trwałości decyduje wskaźnik $\Delta Vu/0{,}083$: skały mrozoodporne $\Delta Vu/0{,}083 < 0{,}5\%$, skały wątpliwe lub niemrozoodporne $\Delta Vu/0{,}083 > 0{,}6\%$.

2. Metodologia

Badaniom poddano próbki skalne, pobrane z dwóch kopalń wapieni dewońskich. Stwierdzono, że geneza skał w obu kopalniach jest ta sama. Celem badań było określenie zmienności parametrów fizycznych i porównanie ich z mrozoodpornością skał, badanej bezpośrednio przez zamrażanie i odmrażanie, a także na podstawie wcześniej wspomnianych parametrów: $\Delta Vu/0{,}083$ oraz objętościowej nasiąkliwości kapilarnej. Z pobranego w kopalniach materiału wywiercono próbki o wymiarach Ø50 mm i Ø30 mm oraz wysokości odpowiednio h = 150 mm i h = 100 mm. Wykonane próbki posłużyły do przeprowadzenia następujących oznaczeń:

– gęstości,
– gęstości objętościowej,
– porowatości,
– objętościowej nasiąkliwości kapilarnej,
– mrozoodporności bezpośredniej (pomiary masy i długości próbek oraz ocena makroskopowa podczas 80 cykli zamrażania i odmrażania),
– współczynnika $\Delta Vu/0{,}083$ zgodnie z procedurą DAVS [2].

3. Wyniki badań i ich analiza

Wszystkie przebadane próbki uznano za całkowicie mrozoodporne po 80 cyklach zamrażania i rozmrażania. Żadna z przebadanych próbek skał nie wykazała istotnego przyrostu masy. Najbardziej stabilnie zachowywała się próbka oznaczona symbolem 1a – zarówno w odkształceniach liniowych, jak i przyroście masy.

Zgodnie z przyjętymi założeniami stwierdzono, że wszystkie skały poza próbką 2c można było zakwalifikować do grupy materiałów mrozoodpornych. Bezpośredni test cyklicznego zamrażania i odmrażania potwierdził poprawność opinii opartej na teście DAVS. Próbka skały 2c została w wyniku testu DAVS zdyskwalifikowana. Pomimo to w teście zamrażania cyklicznego nie stwierdzono destrukcyjnego wpływu mrozu na tę skałę. Otwarty pozostaje problem liczby cykli zamrażania, którym poddaje się próbki skał. Nie jest wykluczone, że skała 2c poddana zwiększonej liczbie cykli uległaby istotnym uszkodzeniom. Zawartość żelaza w składzie tej skały mogła mieć wpływ na wyniki badań, lecz ewentualne związki wydają się na tym etapie rozpoznania materiału niejasne.

4. Wnioski

Z przeprowadzonych badań wynika, że przebadane skały pochodzące z różnych miejsc obu kopalni charakteryzują się wysoką mrozoodpornością. Ich zróżnicowanie pod kątem zmienności parametrów fizycznych jest niewielkie – za wyjątkiem skały 2c, znacznie odróżniającej się od pozostałych. Zaobserwowano różnice makroskopowe w barwie materiału, które wydają się nie mieć wpływu na właściwości fizyczne (poza skałą 2c). Niska nasiąkliwość i dobra mrozoodporność tych skał są przesłankami do bardziej racjonalnego ich wykorzystania, np. do produkcji elewacji z płyt kamiennych.