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Effect of microstructure on frost durability of rock in the context of diagnostic needs

Zbigniew Rusin[a,*], Przemysław Świercz[a], Zdzisława Owsiak[a]

[a]*Kielce University of Technology, Faculty of Civil Engineering and Architecture, Aleja Tysiąclecia Państwa Polskiego 7, 25-314 Kielce, Poland*

Abstract

Problematic rock classification criteria used in civil engineering require correction. Particular attention should be paid to frost resistance test methods and criteria of acceptable absorption levels. The classification of frost resistance levels may be incorrect due to insufficient number of freeze-thaw cycles, and the criterion of rock absorption is inaccurate. Based on the results of research completed to date, the authors conclude that all rocks with capillary volumetric absorption below 0.6% are highly frost resistant, regardless of their origin. All rocks with capillary volumetric absorption above 1.5% are not frost resistant to a greater or lesser degree. Rocks with capillary volumetric absorption between 0.6% and 1.5% may show both low and high frost resistance. This group of rocks is characterized in this article. The structural features compared include mineralogical composition (derivatography and X-ray analysis), appearance and size of crystallite (analysis with an optical microscope, and SEM). The texture features evaluated include total porosity, pore size distribution MIP, capillary water absorption, vacuum absorption, and the degree of filling the pores with water. It has been found that increasing the number of freeze-thaw cycles allows better assessment of the rock's potential durability. The capillary water absorption in combination with the degree of filling the pores can be an effective durability indicator for use in the classification of rock construction products.

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Keywords: frost resistance; rocks; diagnostics; classification; tests

*Coresponding author. Tel. +48-413-424-398, fax +48-413-424-398.
E-mail address: zbigniew.rusin@tu.kielce.pl

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1. Introduction

Standard tests conducted on rock materials used for the manufacture of building elements exposed to freezing evaluate primarily the water absorption by weight and the resistance to freeze-thaw cycles. According to the requirements set forth in the standards PN-EN 1341, PN-EN 1342 and PN-EN 1343 (slabs, setts and kerbs of natural stone for external paving), the absorption by weight for rocks should not exceed 3%, with a recommended absorption criterion of less than 0.5%. In the range of densities from 2.65 to 3.00 g/cm3 for typical rocks, this corresponds to the values of absorption by volume ranging from 1.25% to 1.5%. The authors' own research results indicate that rocks are frost resistant when at the capillary action the absorption by volume is lower than 0.6% - Rusin at al. [1]. Above this value, frost resistance is dependent on the extent to which the pores are filled with water as well as on the ratio of water capable of nucleation to the water strongly adsorbed which does not freeze under the test conditions. This means that the 0.5% absorption by weight may not be sufficient to provide the rock with appropriate durability. In addition to absorption tests, the standard (PN-EN 12371 - Natural stone test methods. Determination of frost resistance) recommend performing 56 freeze-thaw cycles. Martinez-Martinez et al. [2] noted that increasing the number of cycles to above the standard recommendation allows more effective classification of the material in terms of frost resistance. This is related to time necessary for the pores to be filled with water to a critical degree. Capillary pores and capillary pressure generated inside them have a special role to play. The phenomenon occurs in a wide range of pore sizes, from several millimetres to several nanometres. In theory - Setzer [3], the value of pressure is inversely proportional to the pore radius, but hydraulic resistance to flows increases with the fourth power of the inverse of the radius, hence the rate of filling the materials with smaller pores may be significantly lower. At the onset of the testing, the degree of filling the pores with water may vary considerably from rock to rock and change further during subsequent freeze-thaw cycles. The degradation process will start when the saturation degree in the sample locally exceeds the critical level (ice volume exceeds the volume of available pores). In special cases, this will take place in the initial freezing cycles. In some rock materials, the specificity of pores delays the occurrence of critical conditions and the degradation starts much later or does not occur at all. The classification of rocks in terms of frost durability is preceded by petrographic analyses. It is generally assumed that, compared with silicate rocks, carbonate rocks are more susceptible to physical weathering, freeze-thaw cycles included. The size and arrangement of the crystal grains also affect the potential resistance of the rock. Fine-grained rocks give more optimistic predictions than coarse-grained rocks. After Lindqvist et al. [4] the varied size and better complexity of the mineral grains in terms of the spatial distribution contribute to their higher resistance to cyclic temperature changes. The resistance of rock material to frost damage is primarily dependent on the pore structure. The shape and size of pores, their interconnections and total volume are influenced by the rock genesis. Pore characteristics define the amount of water and the temperature at which this water changes into ice. Part of the water located (mainly adsorbed) inside the smallest pores do not freeze, as described by the Gibbs-Thomson formula. The relationship between the properties of the pores and the genesis and mineral structure of rock has not been clearly explained yet.

This paper compares frost durability of rock samples of varied genesis and subjected to freeze-thaw cycles with their microstructure characteristics. The tests were performed on rocks with similar capillary absorption by volume, about 1%.

2. Study of microstructure and physical features of rocks

2.1. Subject and methods

Selected material was taken directly from the stone pit in the form of rock blocks with an average volume of 20 dm^3. The rocks were marked as follows: A (gneiss), B (sandstone), C (dolomite), D (dolomite). The specimens for frost durability, bulk density and water capillary absorption tests were the drilled cores 50 mm in diameter and 150 mm high (160 mm for frost resistance tests). The specimens tested in the mercury porosimeter and those for specific density tests were irregular in shape. X-ray and derivatographic examinations were conducted on powdered specimens. All the specimens were dried at a temperature of 105°C.

A helium pycnometer was used to study the specific density of the rocks. The bulk density was determined using the hydrostatic method on specimens coated with a paraffin wax layer. The water absorption was measured on vacuum saturated specimens. Dry specimens were stored under reduced pressure (1 bar) for an hour and then soaked in water of 80°C. The immersed specimens were stored in closed containers until constant mass was reached. Capillary action of water was tested on cylindrical specimens with insulated lateral surface. The specimens were immersed in water to the depth of 1 cm. The mass increase measurements were made at 1, 3, 5,10,15, 30, 60,180, 420 minutes and then every 24 h. The testing ended when the difference between two consecutive measurements was not greater than 1% of the mass of water absorbed by the specimen.

A polarised light microscope with an attached camera was used for microscopic observations of the rocks. The tests were conducted on thin sections in polarised passing light. The standard method used for the analysis and description of the specimens consisted of the identification of the mineral composition, the measurements of grain size and roundness, and the analysis of the binder character. X-ray diffraction was used to identify crystalline phases including fine-grain minerals with grain sizes from 0.01 to 0.1 μm, and polymorphic variations of the minerals. To study phase composition of the rocks, the differential thermal analysis was used. Solid specimens were observed in ESEM microscope, owing to which tedious preparation of thin foils was not necessary. Rock fractures were studied at magnification from 100x to 24000x.

The AutoPore IV 9500 mercury porosimeter was used to determine pore size distribution. The chippings studied were up to 16 mm in dimension. To calculate the pore size, the constant wetting angle of 130° was taken and the mercury surface tension of 485 dyn/cm.

The direct frost resistance tests were conducted on cylindrical specimens with benchmarks fitted to allow measurements of the specimen length in a Graf-Kaufman apparatus. A hundred freeze-thaw cycles were performed. The specimens were frozen in air and thawed in water. Changes in mass, linear strain and visible signs of damage were recorded every 10 cycles.

2.2. Results

Table 1 summarizes basic physical properties of rocks. Table 2 shows the results from the tests for capillary absorption by volume. Figures 1 to 4 illustrate the microstructure characteristics of the rocks. Figure 5 shows a differential pore size distribution determined semi logarithmically using the MIP method. Figure 6 summarises the observation results for changes in mass and length of the rock specimens subjected to cyclic freezing.

Table 1. Basic physical properties of the rocks.

Physical features	A	B	C	D
Specific density, g/cm^3	2.66	2.67	2.72	2.81
Bulk density, g/cm^3	2.62	2.60	2.68	2.75
Porosity, %	1.44	2.56	1.45	2.17
Absorption by weight, %	0.45	0.47	0.42	0.52
Absorption by volume, %	1.18	1.24	1.13	1.43

Table 2. Results for water capillary action.

Capillary saturation by volume, %	A	B	C	D
after 1 h	0.15	0.15	0.10	0.12
after 3 h	0.28	0.26	0.28	0.19
after 10 h	0.55	0.46	0.48	0.29
after 100 h	1.08	1.12	0.89	0.75
final	1.16	1.20	1.04	1.04
Degree of capillary saturation of rock specimens[1),]%	98	97	92	72
Degree of pore filling[2)], %	81	47	72	48

[1)] – capillary to total absorption ratio; total absorption determined by vacuum method

[2)] – capillary absorption by volume to pore volume ratio

ROCK A

General characteristics: finely and medium crystalline gneiss, quartz-feldspar-biotite metamorphic rock, silver-grey.

Mineral composition:

- planimetric analysis: quartz 58%, potassium feldspar 13%, plagioclase 20%, other 9%
- X-ray: quartz and feldspar – albite, microlith and illite

Size of crystallites:

- 15 do 60 μm – 22%
- 60 do 100 μm - 38%
- 100 do 200 μm -35%

Polarizing microscope 120x ESEM 6000x

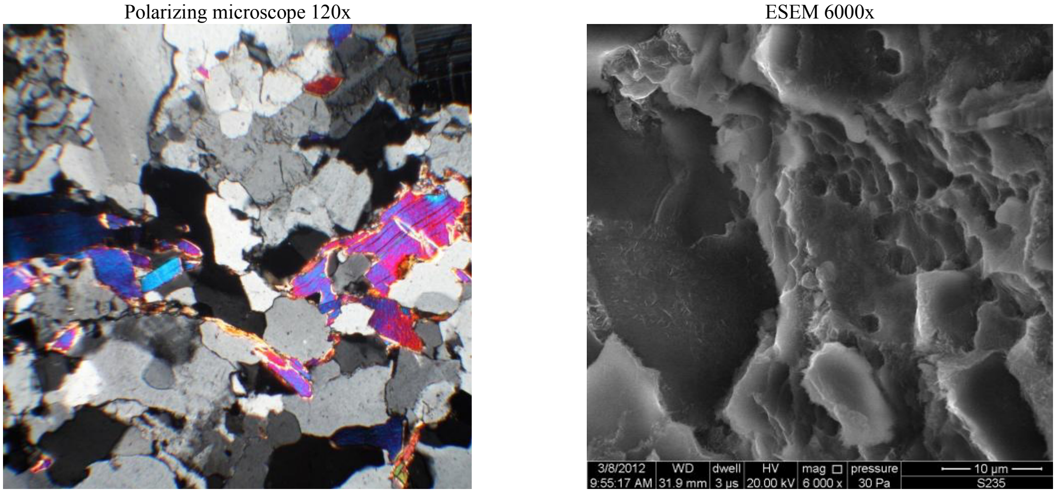

Fig. 1. Microscopic characteristics of rock A.

ROCK B

General characteristics: quartzitic sandstone, fine-grained crystalline structure, massive texture, cross-bedded, grey and yellow-grey.

Mineral composition:

- planimetric analysis: quartz grains 91%, quartz cement 3% and clay cement 1.5%, feldspar grains, and other
- X-ray and DSC-TGA: quartz and small amounts of clay minerals

Size of crystallites:

- 100 do250 μm – 92%
- 250 do 500 μm - 5%

Polarizing microscope 100x ESEM 6000x

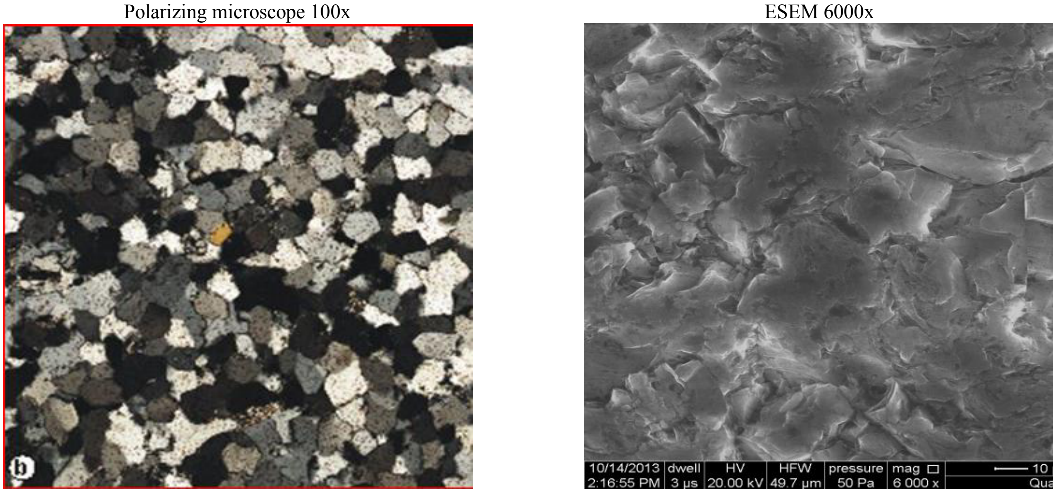

Fig. 2. Microscopic characteristics of rock B.

ROCK C

General characteristics: fine-crystalline dolomite, Devonian rock, dark grey to black in colour.

Mineral composition:

- planimetric analysis: dolomite 100%
- X-ray: dolomite 95%, small amounts of quartz and calcite
- DSC-TGA: 95-98% dolomite, small amounts of clay minerals

Size of crystallites:

- 15 do 60 µm – 97%
- 60 do 100 µm - 3%

Polarizing microscope 120x ESEM 6000x

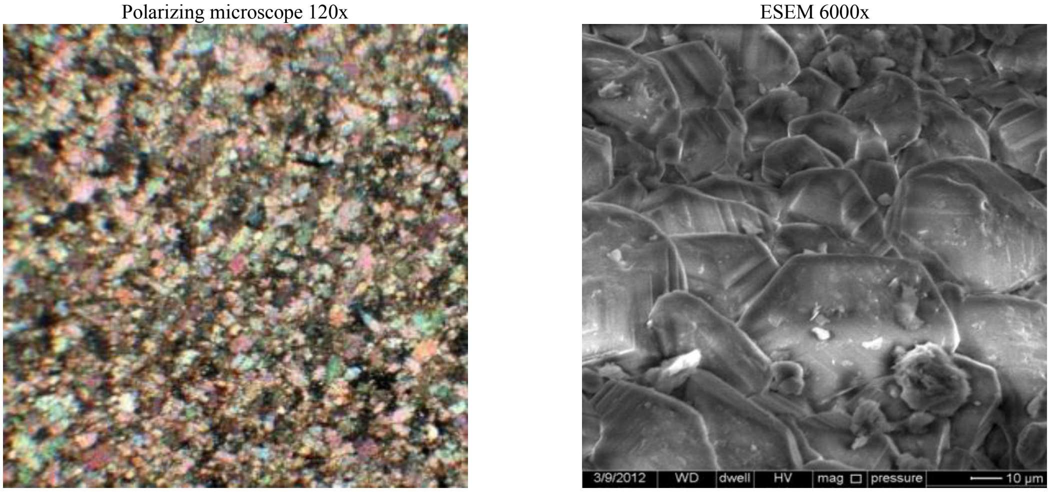

Fig. 3. Microscopic characteristics of rock C.

ROCK D

General characteristics: fine-crystalline dolomite, Devonian rock, gray to black in colour.

Mineral composition:

- planimetric analysis: dolomite 95%, calcite 5%

- X-ray and DSC-TGA: dolomite 95%, small amounts of calcite and quartz (clay minerals)

Size of crystallites:

- 10 do 50 μm – 12%
- 50 do180 μm - 71%
- 180 do 270 μm – 17%

Polarizing microscope 100x ESEM 6000x

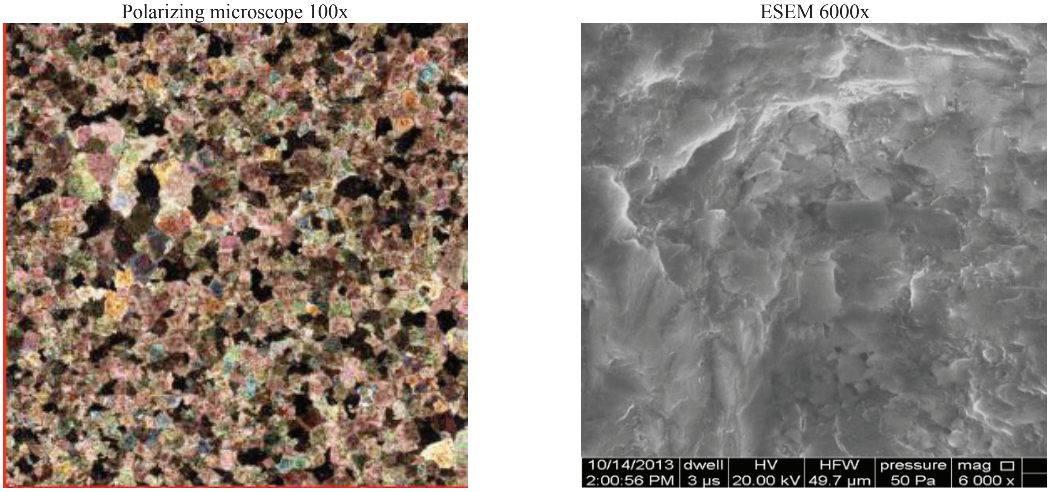

Fig. 4. Microscopic characteristics of rock D.

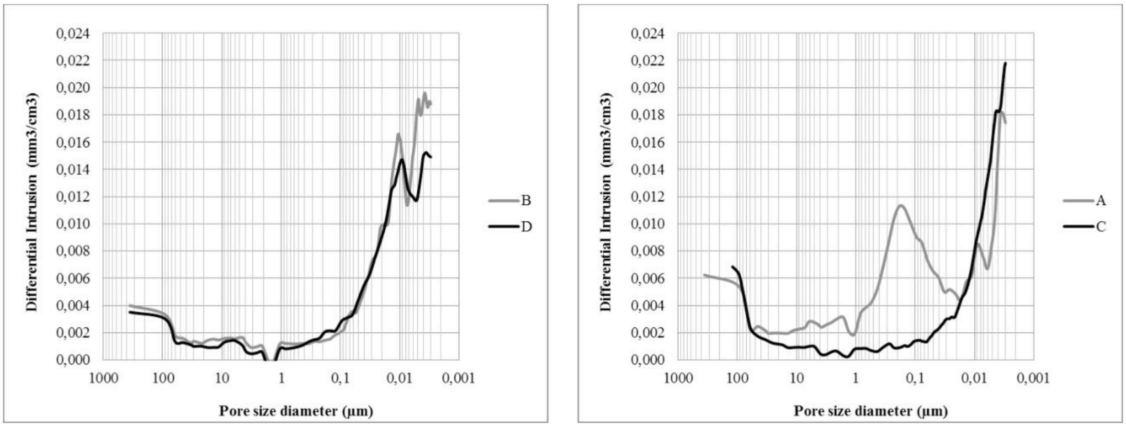

Fig. 5. Logarithmic differential distribution of pore sizes (MIP),
left – frost resistant rocks, right- non frost resistant rocks.

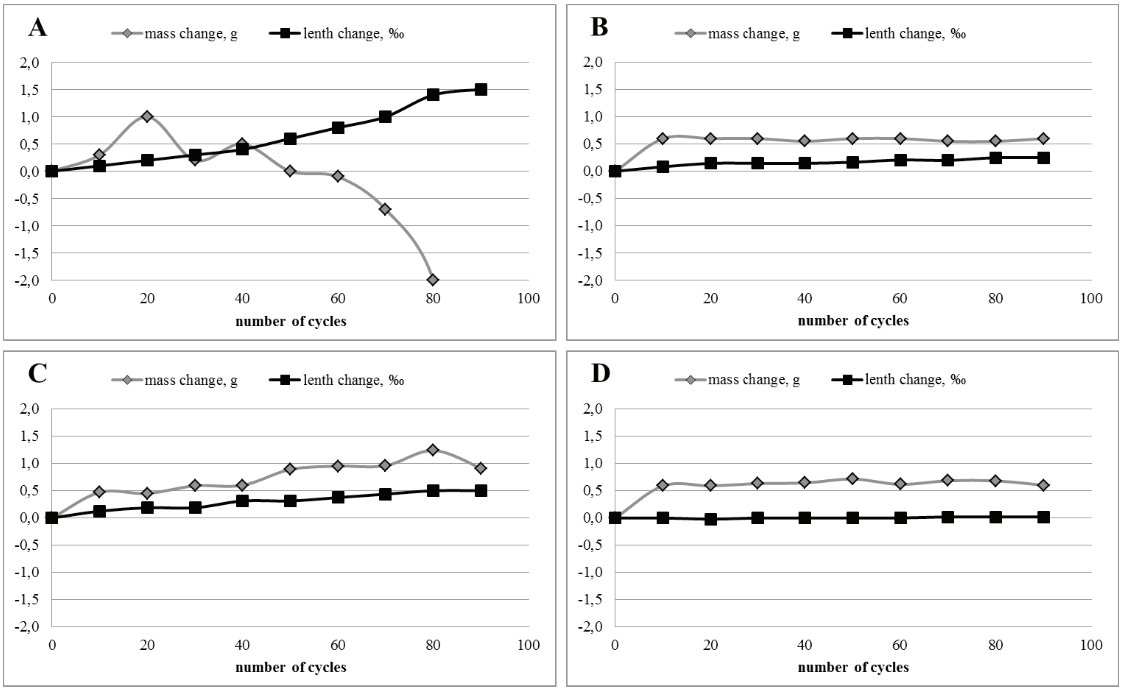

Fig. 6. Changes in length and mass of the specimens during freezing cycles.

2.3 Analysis of the results

The frost durability tests indicate variations in the resistance of the rock materials (Fig.6). Gneiss A appeared to be the least resistant to cyclic freezing, whereas dolomite D and sandstone B survived 100 freeze-thaw cycles with no signs of damage. After several dozen cycles, clear indications of early deterioration were found in dolomite C – steady rate of permanent deformation and the gain followed by loss in mass. After the initial phase consisting of 10-20 cycles, rocks D and B had stabilised values of both mass and length. No macroscopic changes were found on the surface of the specimens. The change in mass observed after first cycles was probably associated with the pores being filled up with water as a result of a "pumping effect" – Setzer [5]. It has to be noted that the reliability of observations improved radically as a result of a larger number of freezing cycles relative to that recommended in the standards.

Absorption by weight of the rock with lower durability, A (gneiss) and C (dolomite), was 0.45% and 0.42%, respectively. The frost resistant rocks, B (sandstone) and D (dolomite) absorbed more water: 0.47% and 0.52% – Table 1. Despite lower water absorption by weight, during the cyclic freezing test, rocks A and C appeared to be less resistant than rocks B and D. General absorption values of all the rocks are similar and do not exceed those given in the standards for road pavement elements.

Microscopic observations and the instrumental analysis of the rocks (Figs.1-4) did not confirm the claim about general relationships occurring between genesis and mineral structure of the rock and its susceptibility to frost action - Lindqvist [4]. The least resistant gneiss A was the most varied of all in terms of the composition and pore size. From the two dolomites, dolomite D turned out to be more durable, with the grain (50-180 μm) coarser than that of dolomite C (15-60 μm). The analysis of a few cases is insufficient to draw general conclusions, but it is clear that carbonate rocks with physical parameters similar to those of silicate rocks may be more frost resistant.

Frost durability, as widely assumed, is associated with the characteristics of pores in the material. Pore size distribution showed in Fig. 5 indicates the presence of a significant group of pores about 200 nm in diameter in gneiss A. The water in such pores builds up readily and freezes at temperatures between -1°C and 0°C. In the remaining rock types, the pores with similar sizes did not form the predominant group. Unlike the rocks with low durability, frost resistant B and D rocks showed local low accumulation of pores about 10 nm in diameter. Despite these differences, the results from the MIP method tests must be treated with caution due to its imperfections.

Two coefficients deserve attention: the degree of saturation and the degree of filling the pores with water due to capillary saturation – Table 2. As a result of capillary saturation, rocks A, B and C reached more than 90% of the maximum absorption level. Frost resistant sandstone B attained 97%, very close to the level of the least resistant gneiss A. The frost resistance level correlates better with the pore filling coefficient. Non resistant rocks A and C reached 81% and 72%, while resistant rocks reached 47% and 48%. Here a question arises about the character, structure and ration of void pores, inaccessible to water during the rock saturation process and their contribution to alleviating freezing effects. It follows from the analysis that these are not, at least in a significant part, pores corresponding to air pores in concrete.

3. Conclusions

- Frost durability of rock is not determined by its mineral structure, crystal size or genesis.
- Absorption by weight parameter is insufficient as a diagnostic tool.
- Increasing the number of freeze-thaw cycles up to 100 is a justifiable call in terms of rock frost durability prediction.
- The extent to which the pores are filled with water is an interesting coefficient supporting the rock classification process for the production of building elements exposed to moisture and frost. This observation requires confirmation by further research.

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