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Original Research Article

EVALUATION OF FROST RESISTANCE OF STONE MATERIALS IN DE-ICING SALT SOLUTIONS

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Abstract

Due to the fact that no standard method for testing the frost resistance of stone materials in the presence of deicing salts has been developed so far, a new method is proposed in this article. The test method was based on the PN EN 12371 and PKN-CEN /TS 12390-9 standards and consisted of freezing to -12^{O}C and thawing samples in salt solutions. Three criteria were used to assess the impact of the cycles: visual assessment, change in mass, and change in compressive strength. Nine different stone materials were selected, samples of which were subjected to frost resistance testing in salt solutions with concentrations of 3% sodium chloride (NaCl), 25% NaCl, and 30% calcium chloride ($CaCl_2$). The impact of chlorides on the stone material was significant, causing, among other changes, a decrease in compressive strength, damage to the samples, the appearance of salt efflorescence, and a change in color. The greatest reduction in strength was noted for sandstones (from about 20% to over 40%). On the other hand, the most resistant were black gabbro samples (reduction in compressive strength from 2% to 7%). Comparing the solutions, the greatest reduction in the strength of the materials was obtained after cyclic freezing and thawing in a 25% NaCl solution, amounting to a 22% reduction on average. On the other hand, the compressive strength of samples subjected to frost resistance testing in other salt solutions decreased on average by 18%, and for frost resistance in water by 10%.

Keywords: compressive strength, deicing salts, freeze resistance, laboratory test, stone materials

1. INTRODUCTION

Damage to road surfaces made of stone or concrete blocks is a common problem in regions with negative temperatures. Additionally, chemical deicing agents, which are often used in the winter season, have a destructive effect on the condition of these surfaces. Therefore, in order to prevent rapid destruction of road surfaces or sidewalks, it is important to select a material that is appropriately resistant to frost in the presence of deicing agents.

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Currently, there are no applicable regulations or research methods that would allow such tests to be performed for natural stone paving stones, even though the PN-EN 1342 [1] standard recommends performing such an assessment. However, for concrete, the requirements and test methods have been developed and standardized in detail, as described in PKN-CEN /TS 12390-9 [2], ASTM C672/C672M-03 [3], and RILEM TC 117 FDC [4]. Methods PKN-CEN /TS 12390-9 [2] and RILEM TC 117 FDC [4] describe deicing agents that include a 3% solution of sodium chloride (NaCl), whereas ASTM C672/C672M-03 [3] applies a 4% solution of calcium chloride ($CaCl_2$). Depending on the method, the freezing temperature ranges between -15°C and -20°C. According to the guidelines [2–4], the assessment of the frost resistance of concrete in the presence of deicing salts is performed with regard to the mass of scaled material per surface unit, expressed in kg/m^3 (surface scaling method) or as loss of weight expressed as a percentage.

These methods have been used in many publications on the development of concrete mixture compositions for use in cold regions for structures exposed to deicing salts. In studies [5–7], changes in the appearance of samples, a slight decrease in mass, and changes to mechanical parameters were observed after the 15th–20th freezing cycle. A slight increase in mass was also observed during the first dozen or so cycles. Liu and Hansen [6] compared the results of tests after cyclic freezing and thawing in a salt solution of ordinary and high-performance concretes. Due to their very low capillary porosity, high-performance concretes were much more resistant to the destructive effect of freezing in a salt solution. This was due to their limited capillary suction of liquid from the surface and the growth of ice crystals. This result has been confirmed by the results of other studies: e.g., concretes in which the porosity was reduced by reducing the water-cement ratio and adding microsilica [8] or using hydrophobic coatings [9] were characterized by much higher resistance to the destructive effects of freezing and deicing salts. In the study of Zhao et al. [10], NaCl, $CaCl_2$, and potassium actinite were used as deicing salts. The surface exfoliation of concrete was most affected by cyclic freezing and thawing in the above solutions at a concentration of 5%.

For stone materials, the available methods for assessing direct frost resistance include freezing in the air to the temperature of -12°C and thawing in water according to PN-EN 12371 [11], as well as alternative test methods according to PN-EN 12370 [12], which is a test involving sample saturation with sodium sulfate solution and drying. Another testing standard to assess stone materials' resistance to salts is PN-EN 14147 [13], which simulates the impact of an aerosol containing NaCl coming from, for example, sea areas. The principal mechanisms of degradation by salts include crystallization and hydration, causing increased pressure in material pores, resulting in the material's weakening or degradation [14–15]. The greater the degree of filling of the pore space with salts, the more intensive the degradation process becomes [16].

Apart from crystallization pressure, there is another mechanism causing extremely negative effects on the internal structure of stone materials, namely hydration pressure. It occurs in pores with salt crystals present, and particularly intensive degradation takes place if the salts are hygroscopic. Salt hydration is the process most frequently initiated in conditions of temperature drop and increased moisture, when salt crystals combine with water molecules, which results in increased salt volume in the pores. Hydration pressure occurring in the pore space causes high tensions inside the stone components, leading to the emergence of a greater number of open pores and cracks, and, thus, to the stone's destruction. This mechanism has been confirmed by the results of Desarnaud et al. [17]. For a supersaturated NaCl solution, a crystallization pressure of the order of 135 MPa was obtained. Therefore, the crystal can grow and exert a crystallization pressure exceeding the tensile strength of the rocks. It was also indicated that salt damage becomes more visible in the case of NaCl after several cycles of humidity change, because during the cycles, recrystallization causes the precipitation of larger crystals in the pores. Hygroscopic salts, apart from hydration pressure, also cause moistening of the material. In such conditions, hydrated salt can permeate inside the stone component, where it crystallizes and causes further damage [18–20]. According to Kłopotowska [21], sandstones with a similar total porosity of about 25%, after exposure to salt mist, were characterized by significant differences in mechanical parameters. The author indicated the shape, size, and configuration of connecting pores as the main factors that allow the free flow of liquid in the rock, reducing the probability of salt crystallization in the pores.

The most common types of damage that occur after frost resistance tests in water include: peeling of surfaces and corners, washing out of particles, surface and internal cracks [22, 23], and loss of gloss [24]. Material degradation is also caused by changes in porosity and pore distribution [24]. Sometimes, after the frost resistance test, an increase in the mass and length of samples is noted. This is caused by the appearance of further microcracks [23]. The mechanism of damage formation inside the porous material is related to the increase in the pressure of freezing water at lower temperatures (Table 1) [25].

Table 1. Impact of temperature on the ice pressure [25]

Temperature [^oC]	0	-5	-10	-15	-20	-22
Pressure [MPa]	0,6	61,0	111,3	159,0	197,0	211,5

This is strictly related to the size of pores where the water freezes. The lower the pore radius, the lower the freezing temperature (Table 2 [26]).

Table 2. Correlation between pore radius and freezing point depressions [26]

Radius [nm]	22	14	10	8	6
Freezing point [^OC]	-6	-10	-15	-20	-30

The crystal structure of ice is 109% of the water volume. The essence of the destruction of rock material during freezing is the occurrence of hydrostatic pressure in the pores of the rock exceeding the tensile strength of the mineral substance that builds the rock skeleton [24–26]. Huang et al. [27] classified rocks based on frost deformation: frost uplift (for rocks with porosity $n > 5\%$) and frost shrinkage (for rocks with porosity $n \leq 5\%$). Sandstones with high porosity ($n > 5\%$) were characterized by high frost deformation during freezing, but significant residual deformation was also noted after thawing.

All these methods, however, do not reflect the problem of the simultaneous impact of temperatures below zero and substances that may cause additional damage to the stone material. Extensive studies on the effect of freeze-thaw cycling in the presence of salts on stone materials have been carried out at Lund University [25]. Two types of salts were applied, namely NaCl and Na_2SO_4, in concentrations from 0 to 10%. The test method was mainly based on the frost-resistance test method for thawing salts, namely the "cube test" according to PKN-CEN/TS 12390-9 [2]. Various concentrations of salt solutions were analyzed to determine which concentrations gave the most degradation. During the freeze-thaw cycles, samples were completely immersed in brines of prepared concentrations. The research involved 20 freeze cycles to a temperature of approximately -15°C and thawing at a temperature of approximately 20°C. The greatest mass loss was noted for NaCl concentrations ranging from 1% to 3%. For rocks with the highest porosity, even a 15% mass loss and the complete destruction of the samples were noted. Similar results were observed for changes in the dynamic modulus of elasticity.

Based on the guidelines of the PKN-CEN/TS 12390-9 standard [2], Kotan and Ardahanlı [28] performed tests on the frost resistance of paving stones in order to compare the resistance of concrete and stone pavements. After 60 cycles, no changes were visible on the basalt samples, and the mass loss after abrasion on the Böhme disc did not exceed 2%. However, most of the concrete samples were degraded by the 40th cycle. Cui et al. [29] performed tests on the frost resistance of sandstones in a NaCl solution with a concentration below 1%. When freezing to -20°C after 60 cycles, they obtained a reduction in mechanical parameters of over 20%.

There have been few published studies on the simultaneous impact of freeze-thaw cycles and salts used for surface deicing. This article proposes a method for testing stone materials under the simultaneous impact of freeze-thaw cycles and deicing agents. The concept of the new method is based on two applicable standards: frost resistance testing of stone materials PN-EN 12371 [11] and PKN-CEN /TS 12390-9 [2]. The number of cycles and temperature range was adopted from the PN-EN 12371 [11] standard. The tests were carried out in three solutions with the following concentrations: 3% NaCl, 25% NaCl, and 30% $CaCl_2$, and also in deionized water. The selection of deicing agents and their concentrations was developed based on the PKN-CEN /TS 12390-9 [2] and the Regulation of the Minister of Environment of 27 October 2005 (Poland) on the types and conditions of use of agents that can be used on public roads, streets, and squares [30]. The method was tested on rocks with various physical and mechanical properties.

2. MATERIALS AND METHODS

2.1. Materials

The tests were carried out on rock samples formed during mechanical processing from larger fragments of stone raw materials. Four series of 11 cubic samples with dimensions of 50x50x50 mm were prepared for each test condition (one sample for temperature control). Table 3 lists the types of rocks together with the location of the deposit and the designation of the samples. Figure 1 presents photographs of the reference samples.

Table 3. Research material

Deposit/Location	Type of rock	Sample marking
Barwałd deposit Poland	Krosno sandstone	PKB
Głębiec Brenna deposit in Poland	Godula sandstone	PGB
Żerkowice deposit, Poland	Upper Cretaceous sandstone	PKŻ
Lompnes Mine, Rhone Alpes area, France	Hauteville Jurassic Limestone	WJH
Strzelin Massif, Poland	Coarse-grained biotite granite	GGS
Strzegom Massif, Zimnik Deposit, Poland	Fine-grained light gray granite	GDZ
Strzegom Massif, Zimnik Deposit, Poland	Medium-grained gray granite	GSZ
Zhytomyr Oblast, Ukraine	Dark gray gabbro	GCZ
Black Swede Lonsboda, Sweden	Black gabbro, norite type	GCL

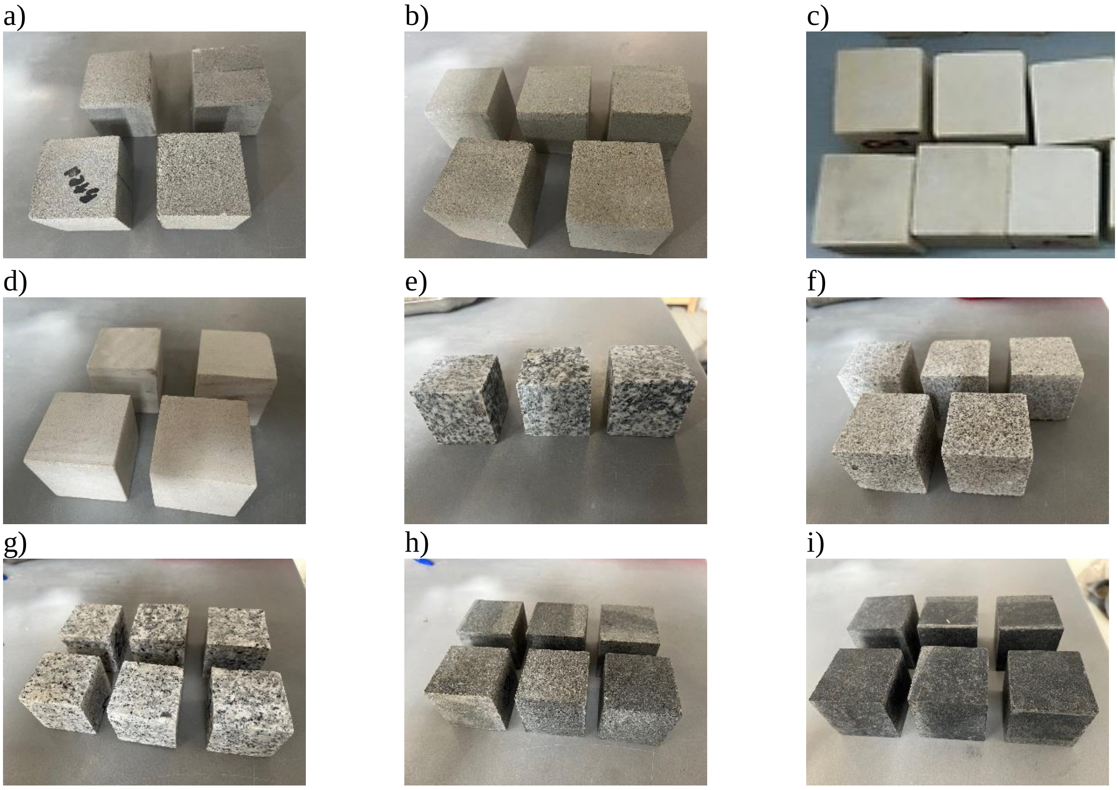

Fig. 1. Appearance of samples used in the study: a) sandstone from Barwałd (PKB), b) sandstone from Brenna (PGB), c) sandstone from Żerkowice (PKŻ), d) Hauteville limestone (WJH), e) granite from Strzegom (GSS), f) fine-grained granite from Zimnik (GDZ), g) medium-grained granite (GSZ), h) gabbro from Zhytomyr (GCZ), i) gabbro from Lansboda (GCL)

Before starting the frost resistance tests, the physical properties were determined, i.e., the bulk density and abraded porosity according to PN-EN 1936 [31], water absorption at atmospheric pressure according to PN-EN 13755 [32], and the compressive strength of reference samples in the air-dried state according to PN-EN 1926 [33]. The results of these tests are presented in Table 4.

Table 4. Physical and mechanical properties of the tested rocks: bulk density, open porosity, water absorption and compressive strength of reference samples

Sample marking	Volumetric density [kg/m^3]		Open porosity [%]		Water absorpcjon [%]		Compressive strength [MPa]	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PKB	2593	31	3,0	0,5	1,1	0,2	134	16
PGB	2472	24	6,8	0,3	2,7	0,2	113	19
PKŻ	2053	11	12,4	0,7	6,0	0,3	44	6
WJH	2687	17	0,7	0,1	0,3	0,1	142	21
GGS	2668	29	1,0	0,1	0,4	0,1	189	19
GDZ	2576	2	1,2	0,2	0,6	0,1	210	14
GSZ	2619	3	0,9	0,1	0,3	0,1	192	21
GCZ	2914	6	0,3	0,1	0,1	0,0	223	8
GCL	2941	54	0,2	0,1	0,1	0,0	134	16

SD - Standard deviation

The lowest volumetric density was observed for sandstones, particularly sandstone from the Żerkowice deposit, on average amounting to 2,053 kg/m^3. Also, the open porosity and water absorption values for this rock significantly differed from those obtained for other rocks. The volumetric density of the granites amounted to approximately 2,600 kg/m^3, similarly for limestone. For gabbro, these values almost reached 3,000 kg/m^3. The volumetric density values correlated with the open porosity and water absorption. For sandstones, the open porosity remained within a range below 20%, for granites and limestone it was about 1%, whereas gabbro recorded an extremely low value of approximately 0.2%. The result was marginal value of water absorption. The highest water absorption of several percent was recorded for sandstones, while for the other stone materials it did not exceed 1%. The compressive strength of the tested stone materials also varied. The material with the lowest compressive strength was sandstone from the Żerkowice deposit (44 MPa). For the remaining sandstones, the compressive strength was over 100 MPa, for limestone it was 142 MPa, for granites about 200 MPa, and for gabbro over 200 MPa.

2.2. Salt solutions

Three solutions were used for the tests, in which cycles of freezing and thawing of rock samples were performed, with the following concentrations:
– 3% NaCl solution,
– 25% NaCl solution,
– 30% $CaCl_2$ solution.

A 3% NaCl solution is recommended by the PKN-CEN /TS 12390-9 standard [2] for testing the frost resistance of concrete, while a 25% NaCl solution and a 30% $CaCl_2$ solution were selected based on Regulation [30] (Table 5).

Table 5. Conditions for using de-icing agents in moist form [30]

Water solution		Application temperature [ºC]	Reason for use		
Substance	Concentration [%]		Glaze	Icing	Icing prevention
NaCl	25	do-6	40-100 ml/m^2	80-100 ml/m^2	100-160 ml/m^2
$CaCl_2$	15	do -5			
$CaCl_2$	30	do -10			
$MgCl_2$	30	do -10			

NaCl is the most commonly used agent for winter road maintenance. It is widely available and relatively cheap. NaCl occurs naturally in rock salt deposits as the mineral halite and is usually extracted by mining methods. $CaCl_2$ is an inorganic compound obtained during the production of sodium carbonate using the ammonia method (Solvay process). It is a hygroscopic compound that absorbs water vapor during the exothermic process of hydration until it completely dissolves in the solvent (water). The hydration process is accompanied by the release of heat, which is an additional factor that increases the compound's effectiveness in combating winter slipperiness [34]. The most important physicochemical properties of the deicing salts selected for laboratory tests are included in Table 6.

Table 6. Physicochemical properties of sodium chloride and calcium chloride [35, 36]

Property	Sodium chloride (NaCl)	Calcium chloride ($CaCl_2$)
Density	2 g/cm^3	2,15 g/cm^3
Bulk density	1400 kg/m^3	750 – 900 kg/m^3 (cereal) 600 – 750 kg/m^3 (powder)
Solubility in water and other solvents (at 20^{O}C)	In water 358 g/l, insoluble in ethanol	In water 745 g/l, soluble in ethanol
PH value (5% aqueous solution)	8	8 - 9
Physical form, color, odor	Under normal conditions it is a colorless solid, forming crystals in a regular arrangement, odorless, with a salty taste. At -10^{O}C it forms a hydrate $NaCl{\cdot}2H_2O$	Solid – flakes, powder or solid mass, white, yellow or pink (depending on the oxidation state of iron, which is an impurity), odorless

2.3. Test method

The following equipment was used to carry out frost resistance tests in the presence of deicing salts:
– a chamber with an automatic control system allowing appropriate freezing and thawing cycles to be set with an accuracy of 1.0^{O}C (Fig. 2a),
– tight containers allowing a series of samples to be placed in an appropriate salt solution (Fig. 2b),
– a scale with an accuracy of at least 0.01% of mass (Fig. 2c),
– a dryer (Fig. 2d),
– a magnifying glass (Fig. 2e),
– a testing machine according to PN-EN 1926 [33] (Fig. 2f).

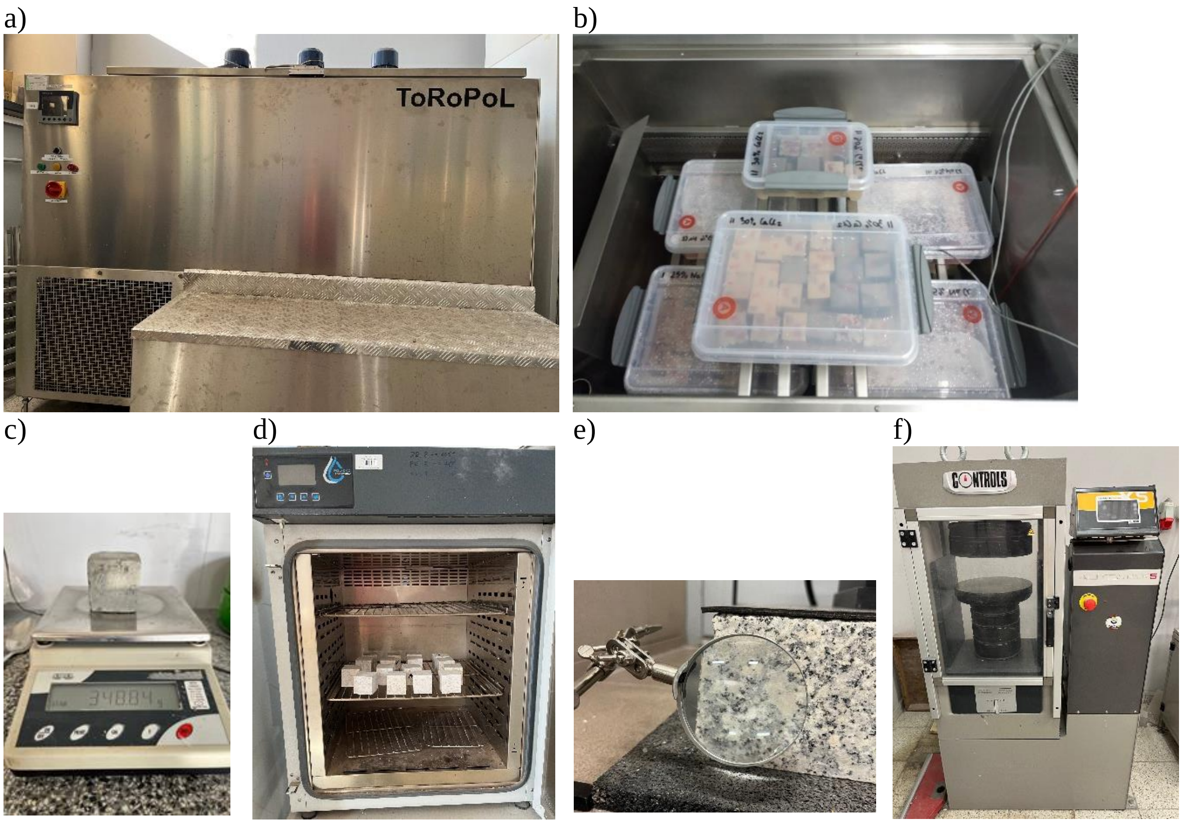

Fig. 2. Equipment for testing frost resistance in de-icing salts: a) freezing chamber, b) containers with salt solution, c) scale, d) dryer, e) magnifying glass, f) compressive strength testing machine

Each cycle was completed within 12 hours and was carried out in accordance with the requirements of the PN EN 12371 [11] standard. The freezing time was 6 hours at a temperature of up to -12^{O}C (Fig. 3), while during defrosting, the containers were partially immersed in water with no possibility of mixing the water from the chamber with the solution from the containers. In accordance with PN EN 12371 [11] and the PKN-CEN /TS 12390-9 “cube test” [2], 56 cycles were performed. The course of the study is presented in Table 7.

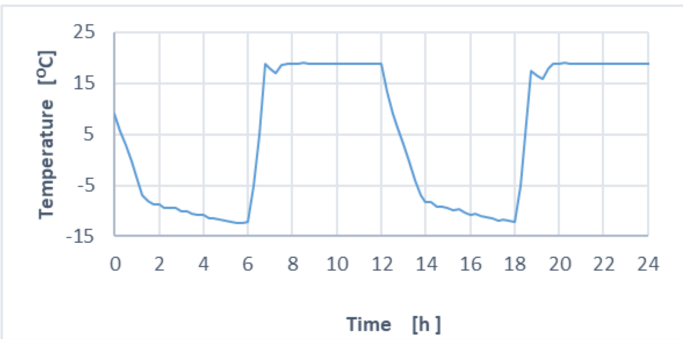

Fig. 3. Temperature range during freeze-thaw cycle (2 cycles)

Table 7. Scheme of laboratory frost resistance testing in salt solutions

Phase	Description of the procedure
I	Drying to a constant mass at a temperature of 70^{O}C
II	Placing in tight containers with water and salt solutions. Saturation of samples for 48 h at a temperature of (20±2)^{O}C
III	Weighing samples (M_1)
IV	Placing containers in a freezer, performing 56 freezing and thawing cycles of samples immersed in water and salt solutions.
V	Weighing saturated samples after the test (M_2), performing a preliminary visual assessment
VI	Drying samples to a constant mass at a temperature of 70^{O}C
VII	Performing a visual assessment
VIII	Performing a compressive strength test
IX	Assessment of the impact of freezing and thawing cycles on the tested samples according to the criteria included in point 2.4. (visual assessment, calculation of the change in mass (formula 2.1), calculation of the change in compressive strength (formula 2.2)

2.4. Frost resistance in deicing salts assessment criteria

The assessment of the impact of freeze-thaw cycles in the presence of deicing salts was performed using three criteria:
– visual assessment,
– weight change,
– compressive strength measurement.

Visual assessment was performed with the use of a magnifying glass. All the sample surfaces were carefully checked, and their condition was evaluated according to the following scale:
0 – sample intact,
1 – very low damage (rounded corners and edges), not causing sample disintegration, appearance of salt efflorescence and discoloration on the surfaces,
2 – one or just a few small cracks (up to 0.1 mm width) or separation of small fragments (up to 30 mm² per fragment),
3 – one or a few cracks, holes, or separation of fragments bigger than in point 2, or material deformation in veins, or the sample shows significant symptoms of crumbling or disintegration,
4 – sample in pieces, broken into two or more parts, or disintegrated.
A sample was considered damaged when, in visual assessment, it was evaluated as 3.

Weight change measurement was performed on the basis of the determined sample weight before and after a specific number of freeze-thaw cycles. Weight loss was calculated as a percentage according to (2.1)

$$\Delta M = \frac{M_1 - M_2}{M_1} \cdot 100 \text{ [\%]} \tag{2.1}$$

where:
M_1 – weight of saturated sample before the test [g],
M_2 – weight of saturated sample after a specific number of freeze-thaw cycles [g].
A sample was considered damaged when the recorded weight loss was greater than 1%.

The compressive strength tests must be performed on samples thawed and dried to a solid mass according to the requirements of PN-EN 1926 [33]. Change to the mean compressive strength with respect to the reference samples was calculated according to formula (2.2):

$$\Delta R_c = \frac{R_{c2} - R_{c1}}{R_{c1}} \cdot 100\ [\%] \quad (2.2)$$

where:
R_{c1} – average compressive strength of reference samples in the air-dried state [MPa],
R_{c2} – average compressive strength of samples following a specific number of freeze-thaw cycles in the salt solution, in the air-dried state [MPa].

According to the standard PN-EN 1342:2013-05 [1], a stone material is considered frost resistant in the presence of deicing agents if its compressive strength is not reduced by more than 20%.

3. RESEARCH RESULTS AND DISCUSSION

3.1. Visual assessment of samples

According to the visual assessment scale presented in section 2.4., all the samples were visually assessed after 56 freeze-thaw cycles in the salt solutions. Following the five-grade scale, particular stone materials were graded depending on their condition. The results are presented in Table 8.

Table 8. Visual assessment of samples following frost resistance test in salt solutions

Sample marking	Points awarded according to the scale of changes after frost resistance testing in solution			
	In the water	3% NaCl	25% NaCl	30% $CaCl_2$
PKB	0	1	2	1
PGB	0	1	1	1
PKŻ	0	3	3	1
WJH	0	3	3	2
GGS	0	0	0	0
GDZ	0	0	0	1
GSZ	0	0	0	1
GCZ	0	0	0	0
GCL	0	0	0	0

Analyzing the appearance of the samples after testing for frost resistance in water, it can be stated that none of the samples showed visible damage after testing in water. However, after testing in salt solutions, the greatest damage to the surface was noted with the samples of sandstone from Żerkowice (Fig. 3) and Hauteville limestone (Fig. 4 and 5). The probable cause of the detachment of fragments of some samples was the stylolite seams present in the near-surface layer, filled with minerals that were not resistant to salt solutions. Minor damage in the form of chipped corners was observed in samples of sandstone from Barwałd and Brenna. On all the sandstones, after testing in solutions with a concentration of 25% NaCl or 30% $CaCl_2$, significant salt efflorescence appeared, especially in the sandstone from Żerkowice (Fig. 3). Such surface salinization did not occur on the limestone, granites, and gabbro. Only in 30% $CaCl_2$ solution, for the granites from the Zimnik deposit (samples 15–24 GDZ and samples 15–21 GSZ), a darkening of the color of whole samples was observed (Fig. 6a and 6b), and in some limestone samples dark brown spots appeared (Fig. 5b). For granites and gabbro, no changes in the form of detachment or cracks were observed (Fig. 6).

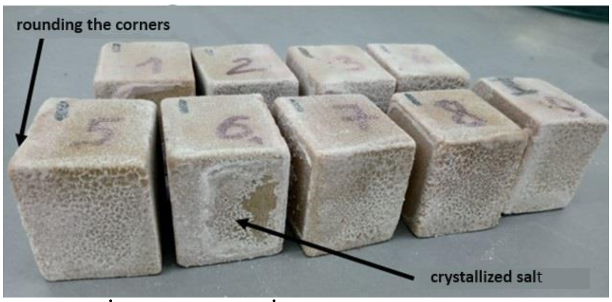

Fig. 3. Samples of sandstone Żerkowice (PKŻ) after 56 freeze-thaw cycles at 25% NaCl solution (Foto K. Burzec)

a) b) c) d)

Fig. 4. Samples of Hauteville (WJH) limestone after 56 freeze-thaw cycles at 3% NaCl solution

a) b)

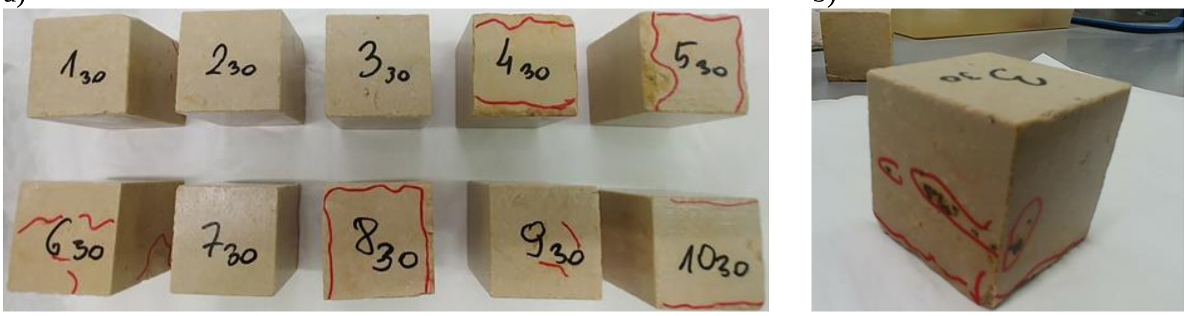

Fig. 5. Samples of Hauteville (WJH) limestone after 56 freeze-thaw cycles at 30% $CaCl_2$ solution: a) chipping of the corners (sample 4) and the top surface (sample 5), b) color change

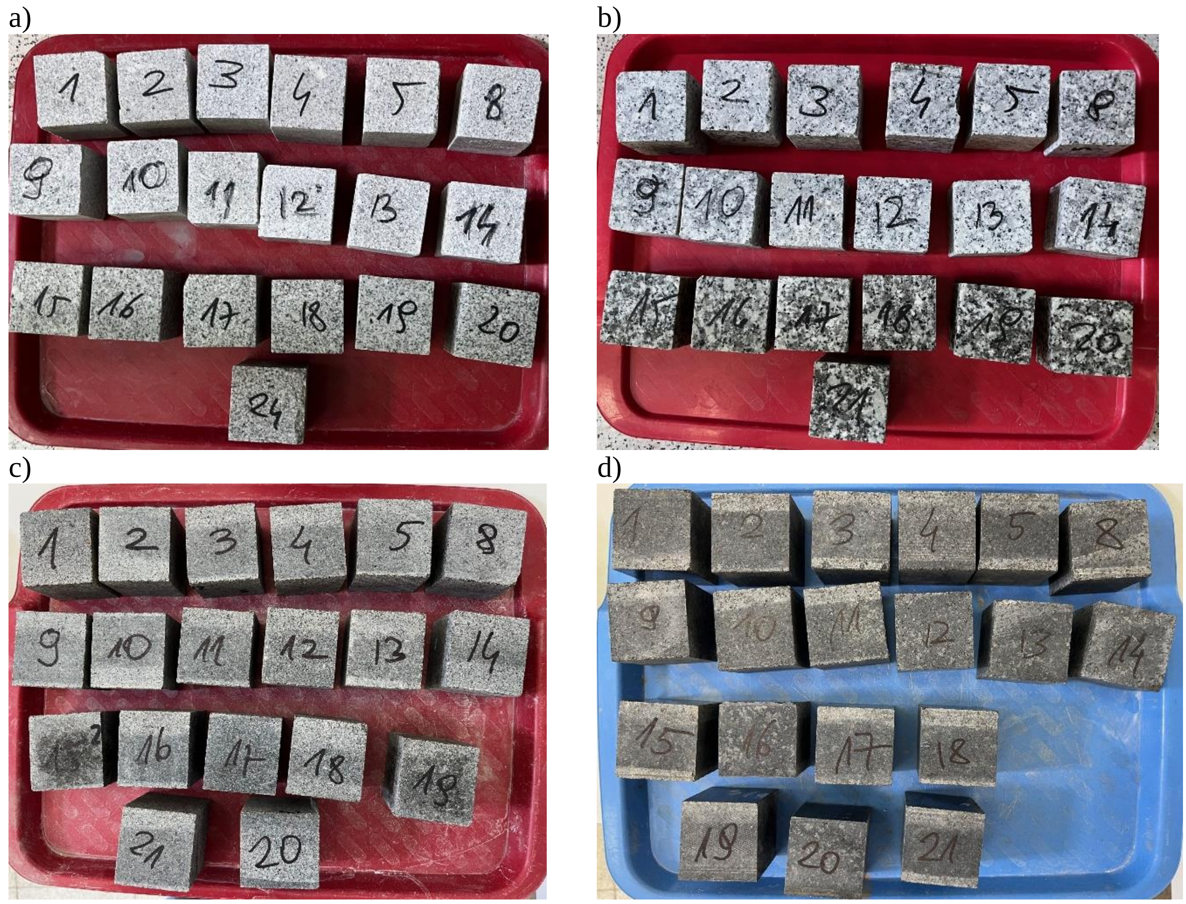

Fig. 6. Samples after testing for frost resistance in salt solutions and after drying to constant mass: a) Zimnik fine-grained granite (GDZ), b) medium-grained granite (GSZ), c) Zhytomyr gabbro (GCZ), d) Lansboda gabbro (GCL)

3.2. Weight change

The most significant weight loss was recorded for samples of limestone tested in 3% and 25% NaCl solution, as well as sandstone from Żerkowice frozen in 25% NaCl and 30% $CaCl_2$ solution. In turn, the samples of granites and gabbro revealed marginal weight losses or slight increases in weight. Detailed results for weight loss in accordance with formula (2.1) are illustrated in Table 9. The weight loss values for particular samples correlated with their visual assessment.

Table 9. Weight change in stone samples subject to frost resistance testing in salt solutions

Sample marking	Weight loss after frost resistance testing in solutions [%]							
	In the water		3% NaCl		25% NaCl		30% $CaCl_2$	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PKB	0,05	0,02	0,11	0,07	0,74	0,24	1,02	0,24
PGB	0,04	0,02	0,54	0,08	0,98	0,15	1,26	0,40
PKŻ	0,43	0,30	0,27	0,06	3,87	1,20	3,06	0,35
WJH	0,00	0,00	2,63	1,23	2,65	0,98	1,64	0,56
GGS	0,02	0,01	0,02	0,01	0,13	0,03	0,19	0,01
GDZ	0,02	0,01	0,00	0,00	-0,11	0,01	-0,19	0,02
GSZ	0,02	0,01	0,02	0,01	-0,03	0,01	-0,08	0,01
GCZ	0,03	0,01	0,05	0,01	0,03	0,01	0,01	0,01
GCL	0,01	0,00	0,05	0,01	0,09	0,02	0,01	0,00

3.3. Change in compressive strength

Rock samples after 56 freeze-thaw cycles in the analyzed salt solutions and in water were subjected to a compressive strength test in accordance with the PN-EN 1926 standard [33]. A summary of the average results for individual rocks is presented in Table 10. Table 11 presents the percentage change in the compressive strength value after the frost resistance test in a given solution with respect to the compressive strength value of the reference samples (in the air-dried state, included in Table 3), in accordance with formula (2.2).

Table 10. Compressive strength of samples subjected to frost resistance after 56 freeze-thaw cycles in water and salt solutions

Sample marking	Compressive strength [MPa]							
	In the water		3% NaCl		25% NaCl		30% $CaCl_2$	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD
PKB	131	31	99	28	101	26	80	23
PGB	109	5	77	33	72	27	81	25
PKŻ	27	9	32	8	25	7	35	7
WJH	149	35	137	42	126	49	141	28
GGS	176	20	161	50	156	41	131	49
GDZ	198	38	169	47	169	29	180	45
GSZ	170	20	154	47	141	58	170	24
GCZ	188	13	178	24	180	55	187	12
GCL	257	20	271	24	265	17	257	69

Table 11. Change to compressive strength vs. air-dried state and condition after frost resistance test in water

Sample marking	Change to compressive strength after frost resistance testing [%]			
	In the water	3% NaCl	25% NaCl	30% $CaCl_2$
PKB	-2,2	-26,1	-24,6	-40,3
PGB	-3,5	-31,9	-36,3	-28,3
PKŻ	-38,6	-27,3	-43,2	-20,5
WJH	4,9	-3,5	-11,3	-0,7
GGS	-6,9	-14,8	-17,5	-30,7
GDZ	-5,7	-19,5	-19,5	-14,3
GSZ	-11,5	-19,8	-26,6	-11,5
GCZ	-15,7	-20,2	-19,3	-16,1
GCL	-6,9	-1,8	-4,0	-6,9

The most significant decrease in compressive strength following the frost resistance test was recorded for samples of Żerkowice sandstone, regardless of whether the test was conducted in water or in salt solutions. Compressive strength decreased over a range from 20% to over 40%. This was the material with the lowest compressive strength in the air-dried state (44 MPa) and with the highest open porosity (12%). Furthermore, visual assessment revealed both damage in the form of cracking and crumbling grains, as well as significant salination of the surface. Similar results were observed for the sandstones from Barwałd and Brenna, although after the frost resistance test in water, the samples showed minimal reduction to compressive strength, of up to 3.5%. In salt solutions, however, regardless of the concentration or type of salt, the reduced compressive strength values ranged from approximately 25% up to as much as 40%. Granites and gabbro, characterized by a remarkably high compressive strength in the air-dried state, amounting to approximately 200 MPa, and very low open porosity, following the frost resistance test in water, showed compressive strength reduction at a level from 1.8% for black gabbro from Lonsboda up to 20.2% for dark-grey gabbro from Zhytomyr. The frost resistance test in 3% NaCl solution caused a further reduction in compressive strength by a further several percent. In the case of granites, for the coarse-grained granite from Strzelin with 30% $CaCl_2$ solution, for the medium-grained granite from Zimnik with 3% NaCl solution, and for the gabbro from Zhytomyr with a 3% NaCl solution, the observed reduction in compressive strength exceeded 20%. For these rocks, visual assessment did not point to any changes and, despite reduced compressive strength, the parameter ranged from 130 to almost 180 MPa. The black gabbro samples from Lonsboda were the most resistant to salt freezing cycles. Regardless of the concentration and type of solution, the reduction in compressive strength did not exceed 7%. Interesting results were found for the Jurassic Hauteville limestone: despite the samples showing significant damage on visual assessment after the test in salt solution, the changes to compressive strength were slight, up to a maximum of 11% for 25% NaCl solution.

The obtained research results are consistent with the observations presented in other publications, e.g., Wessman [26] and Cui et al. [29], and indicated that the greatest influence on the occurrence of material destruction as a result of the simultaneous action of freezing and salt solutions was the porosity of the rocks. This was particularly noticeable in the case of sandstones. The most resistant were the igneous rocks, i.e., granite and gabbro, which is in line with the results obtained by Kotan and Ardahanlı [28].

4. CONCLUSION

The results of tests on stone materials according to the proposed method for testing frost resistance in deicing salt solutions indicated the need to perform such tests before using a particular material for paving stones.

The analysis of the impact of deicing salt on the durability of stone materials confirmed that freeze-thaw cycles with chlorides present bring negative effects. The impact of chlorides on the stone material was significant, causing a reduction in compressive strength, sample damage, salt efflorescence on the surface, and discoloration. The decrease in compressive strength of the samples following the frost resistance test in salt solutions vs. reference samples was noticeable in each of the analyzed cases. Their impact, however, varied. The average drop in compressive strength of all the samples analyzed for one salt gave the following results:

– frost resistance in water – compressive strength dropped on average by 10%,
– frost resistance in 3% NaCl – compressive strength dropped on average by 18%,
– frost resistance in 25% NaCl – compressive strength dropped on average by 22%,
– frost resistance in 30% $CaCl_2$ – compressive strength dropped on average by 18%.

The above results showed that the greatest impact on the reduction of rock durability was exerted by testing frost resistance in a 25% NaCl solution.

The proposed test method requires further testing and validation, particularly in the selection of salt solution concentration and freezing temperature. Although performing freezing and thawing cycles according to PN-EN 12371 [11] also allowed the durability of the stone materials as a result of the impact of freezing water and salt solutions to be compared.

The proposed method of testing frost resistance in deicing salts requires the use of five series of samples for each of the test conditions. This is dictated by the requirements of the standard for testing compressive strength according to PN-EN 1926 [33] and the standard for paving stones PN-EN 1342:2013-05 [1]. Samples from each series are tested separately. Rocks are non-homogeneous materials, and the material for testing should be selected very carefully. However, in the case when the selection of samples for testing is random, it would be a better solution to use non-destructive tests, e.g., the dynamic modulus of elasticity test, to assess the freezing and thawing cycles.

To better understand the mechanisms of the destruction of stone materials by the combined impact of freezing and thawing cycles, it would also be necessary to carry out microscopic analyses, e.g., using scanning electron microscopy (SEM) or X-ray computed tomography (CT).

ADDITIONAL INFORMATION

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