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Freeze Thaw Susceptibility of Natural Stone – Characterization of the Mechanical Strength and Microstructure During Frost Cycling

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ABSTRACT

Frost resistance of natural stones is complex phenomena. Different intrinsic properties (e.g. porosity and mineral composition) as well as extrinsic properties (e.g. presence of salts, temperature variation, humidity) influence frost resistance of stone. In some countries frost is consider as being one of the most potent causes of decay, although attribution of deterioration features of in-built stone only to one factor is ambiguous.

The test method for determination of susceptibility of natural stone to frost deterioration is standardised with CEN standard EN 12371. Additional requirements for testing are given in appropriate harmonised standards for natural stone products, e.g. EN 1469 for cladding slabs. Although standard EN 12371 has been used for some years now, it has been established that a robust correlation of test results to actual condition is difficult to make.

The main objective of the research presented in this paper was to give insight into frost deterioration of two selected marbles and two limestones during 104 cycles of standardised test. Relationships between intrinsic properties of stone (porosity and mineral composition) and frost resistance, which was determined by mechanical characterization of stone (flexural strength and USV measurement) after 12, 24, 56 and 104 frost cycles, are given. The results of research can be used as input information for modelling the life span and risk assessment of natural stone façade when subjected to frequent freezing.

KEYWORDS

Frost resistance, Natural stone, Porosity, USV, Strength

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1 INTRODUCTION

During its life span natural stone product is exposed to various degradation processes. Their damage effects can be additive, antagonistic or synergetic [Wessman 1997]. Among many acting mechanism the actual cause for stone deterioration [‘Fig. 1’] is sometimes difficult to define. Nevertheless, freeze-thaw cycles are generally considered as one of the main decay factor of natural stone, especially in northern and central European countries.

Although generally assessed as important parameter, detailed mechanisms of stone frost deterioration are still not fully understood. Freeze-thaw durability depends greatly upon stone’s intrinsic and extrinsic parameters. Porosity, the moisture content and presence of dissolved salts highly influence performance of stone while exposed to frost action [Lindqvist *et al.* 2007].

Current practice of assessing the effect of freeze-thaw cycles on natural stone product’s characteristics (flexural strength, dowel hole strength, compressive strength) is based on CEN standard EN 12371. After certain number of cycles of freezing in air and thawing in water [e.g. 48 cycles for stone pavements – EN 1341 and 1342, or 12 cycles for stone cladding – EN 1469], the frost resistance is determined as the change of mean strength or as the number of cycles necessary to initiate cracks or rupture. However, such concept is difficult to apply to in-built performance of stone products, since some products show cracks and spalling after a while, although they have passed the frost test, while others not passing the test exhibit good performance during their life span in building [Ingham 2005].

In this study, susceptibility to freeze and thawing was determined for four selected natural stones, two marbles and two limestones. With flexural strength and USV measurements after 12, 24, 56 and 104 cycles, different performance for four selected stone was determined. Additionally, materials were characterised by measurements of open porosity and apparent volume.

In this study, hypothesis about deterioration rate differences between studied samples is examined. Following this hypothesis, prediction of life span of natural stone products exposed to natural cycling of freezing and thawing must be based on detailed studies, since different behaviour can be established even among same rock types.

Figure 1. Here, deterioration of calcitic marble in the form of intense cracking is visible. The actual cause for deterioration is difficult to define; probably it is due to simultaneous action of freezing and thawing and thermal degradation, or even mechanical loading.

2 MATERIALS AND METHODS

Four samples have been chosen for determination of frost resistance; two marbles (one dolomitic, one calcitic) and two limestones. In [Table 1] a list of samples is presented. Samples were tested according to CEN standards or other methods, e.g. EN 12371 – Determination of frost resistance, EN 12372 – Determination of flexural strength, EN 14579 – Determination of sound speed propagation, EN 1936 – Open porosity and apparent volume, OM – Optical microscopy, SEM – Scanning electron microscopy, Hg – Mercury porosimetry, EN 13755 – Water absorption at atmospheric pressure, EN 13364 – Determination of dowel hole strength. Only part of results (mechanical strength, apparent volume and porosity) is presented in this paper.

Table 1. List of samples tested in the frame of frost resistance study.

Sample no.	*Petrographic name*	*Number of specimens*	*Dimension of specimens [mm]*	*Method according to standard*
1	Dolomitic marble	63	30x50x180	EN 12371, EN 12372, EN 14579*
		57	30x30x30	EN 1936, OM, SEM, Hg
		12	30x30x30	EN 13755*
		10**	200x200x30	EN 13364
2	Calcitic marble	63	30x50x180	EN 12371, EN 12372, EN 14579*
		57	30x30x30	EN 1936, OM, SEM, Hg
		12	30x30x30	EN 13755*
		10**	200x200x30	EN 13364
3	Limestone	63	30x50x180	EN 12371, EN 12372, EN 14579*
		57	30x30x30	EN 1936, OM, SEM, Hg
		12	30x30x30	EN 13755*
		10**	200x200x30	EN 13364
4	Limestone	63	30x50x180	EN 12371, EN 12372, EN 14579*
		57	30x30x30	EN 1936, OM, SEM, Hg
		12	30x30x30	EN 13755*
		10**	200x200x30	EN 13364

* Deviations from standard's requirements regarding size of specimens

Freeze-thaw cycling was carried out according to test procedure described in EN 12371:2001. Five batches of specimens with denotations *A* – *E* were sawed from cladding panels of 20 and 30 mm thickness. On specimens from batch *A*, initial properties of fresh samples [flexural strength, speed of sound propagation and open porosity] were determined according to corresponding standards [EN 12372, EN 14579, EN 1936]. Specimens from batches *B*, *C*, *D* and *E* were then exposed to freeze-thaw cycling. After every 12th cycle apparent volume and visual examination were carried out. After 12, 24, 56 and 104 cycles, specimens of corresponding batches were taken out from frost chamber, dried at 70 ^{o}C in ventilated oven to constant mass, after which USV, flexural strength and open porosity, were again determined.

3 RESULTS AND DISCUSSION

3.1 Visual Examination

Four samples exhibit different characteristics during frost exposure. The most decaying material is white calcitic marble (sample no. 2), in the case of which signs of deterioration had been observed even before exposure. Poor cohesion between mineral grains in sample no. 2 is marked by degranulation or “sugaring”.

During frost exposure this material becomes progressively deteriorated. After no more than 12 cycles changes in colour can be observed and thin hair-like cracks start to form, although none of the specimen had completely disintegrated during 104 cycles. During exposure other samples didn’t change significantly, with exception of slight rounding of edges. Cohesion between stylolites in sample no. 3 is good even after the end of exposure.

3.2 Mechanical Strength

Results of initial flexural strength measurements and measurements of flexural strength after 12, 24 and 56 cycles, are given in [Table 2] and ‘Fig. 2 and 3’.

The lowest flexural strength can be observed in the case of sample no. 2, while the highest flexural strength has micritic limestone with stylolits, sample no. 3 [‘Fig. 2’].

On ‘Fig. 3’ different characters of flexural strength decrease, or in the case of #3 slight increase, can be observed.

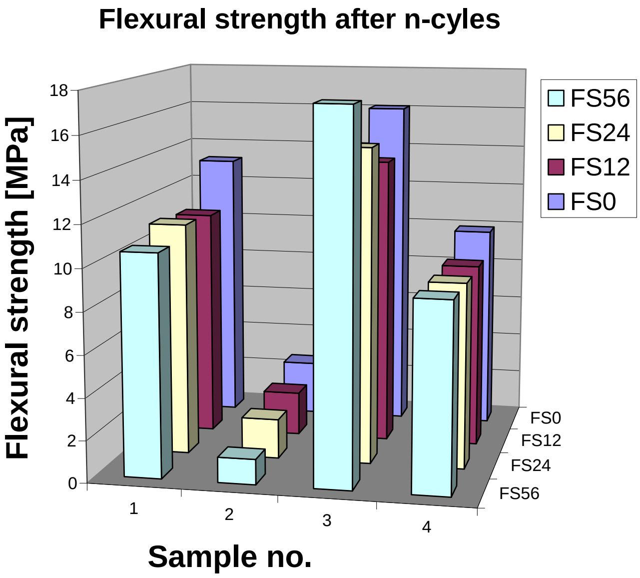

Figure 2. Flexural strength of samples before exposure (*FS0*) and after 12 (*FS12*), 24 (*FS24*) and 56 (*FS56*) cycles.

Table 2. Decrease/increase of flexural strength before exposure [Rtf_0] and during 12, 24 and 56 cycles [Rtf_{12}, Rtf_{24}, Rtf_{56}, respectively].

Sample		Rtf_{nave}	$Stdev_0$	*Δ [%]*
1	Rtf_0	13,2	1,8	0
	Rtf_{12}	11	0,5	-16,7
	Rtf_{24}	11,2	0,9	-15,2
	Rtf_{56}	10,6	0,8	-19,7
2	Rtf_0	2,6	0,6	0,0
	Rtf_{12}	2,1	0,5	-19,2
	Rtf_{24}	1,9	0,4	-26,9
	Rtf_{56}	1,2	0,3	-53,8
3	Rtf_0	16,1	2,6	0,0
	Rtf_{12}	13,9	1,5	-13,7
	Rtf_{24}	15,1	2,3	-6,2
	Rtf_{56}	17,5	2,5	8,7
4	Rtf_0	9,9	0,9	0,0
	Rtf_{12}	8,9	3,2	-10,1
	Rtf_{24}	8,9	1,2	-10,1
	Rtf_{56}	9,0	0,8	-9,1

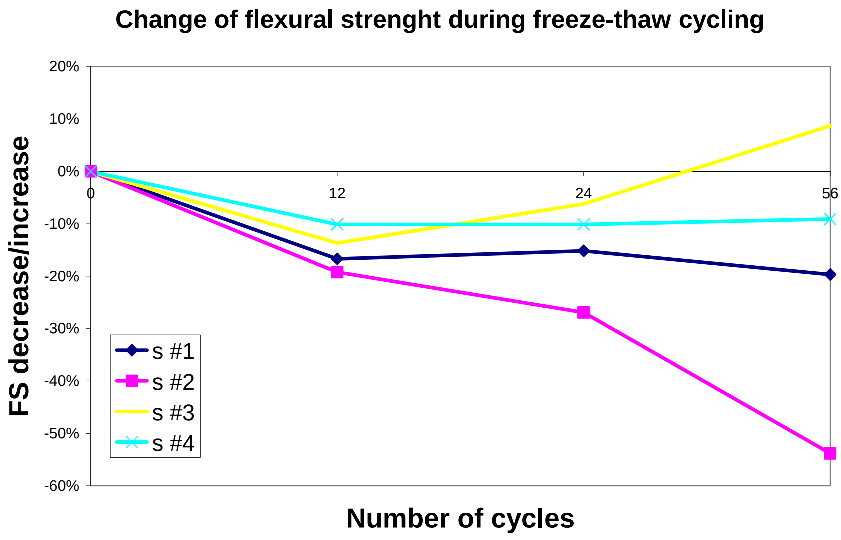

Figure 3. Change of average flexural strength (in percentage) during 56 cycles.

3.3. Ultrasonic Velocity

Average speeds of sound propagation and rates of decrease [increase] during exposure are listed in [Table 3]. In general, USV degradation curve [‘Fig. 4’] follows the flexural strength degradation curve [‘Fig. 3]. Again, velocity of sound propagation decrease with the highest rate in the case of sample 2, while sample 3 shows constant increase in speed propagation.

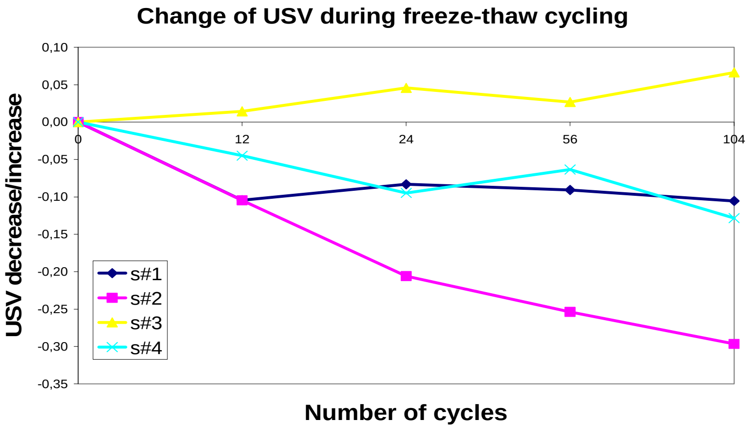

Figure 4. Change of USV during 104 cycles.

Table 3. Change of USV after 12, 24, 56 and 104 cycles.

Sample		USV_{0ave} [km/s]	$Stdev_0$ [km/s]	USV_{nave} [km/s]	$Stdev_n$ [km/s]	*Δ* [%]
1	v_{12}	5,94	0,18	5,32	0,36	-10,4
	v_{24}	6,02	0,29	5,52	0,19	-8,3
	v_{56}	5,95	0,29	5,41	0,25	-9,1
	v_{104}	6,07	0,21	5,43	0,18	-10,5
2	v_{12}	2,87	0,51	2,57	0,43	-10,5
	v_{24}	3,06	0,55	2,43	0,37	-20,6
	v_{56}	2,60	0,23	1,94	0,19	-25,4
	v_{104}	3,17	0,34	2,23	0,18	-29,7
3	v_{12}	6,97	0,65	7,07	0,69	1,4
	v_{24}	7,00	0,4	7,32	0,45	4,6
	v_{56}	7,07	0,36	7,26	0,46	2,7
	v_{104}	7,08	0,6	7,55	0,57	6,6
4	v_{12}	5,63	0,41	5,61	0,37	-0,4
	v_{24}	6,02	0,41	5,75	0,24	-4,5
	v_{56}	5,91	0,51	5,35	0,48	-9,5
	v_{104}	5,99	0,45	5,61	0,45	-6,3

3.4 Apparent Volume

No significant change in apparent volume can be seen during freezing and thawing, although with other methods deterioration trend could be observed. Following this, despite of different broad range regarding frost resistance of studied materials [material with high rate of deterioration, material with no deterioration], method of measurement apparent volume after every 12 cycles is too robust to determine susceptibility of stone to frost action.

On 'Fig. 5' apparent volume of sample no. 2 after 12, 42 and 104 cycles is presented.

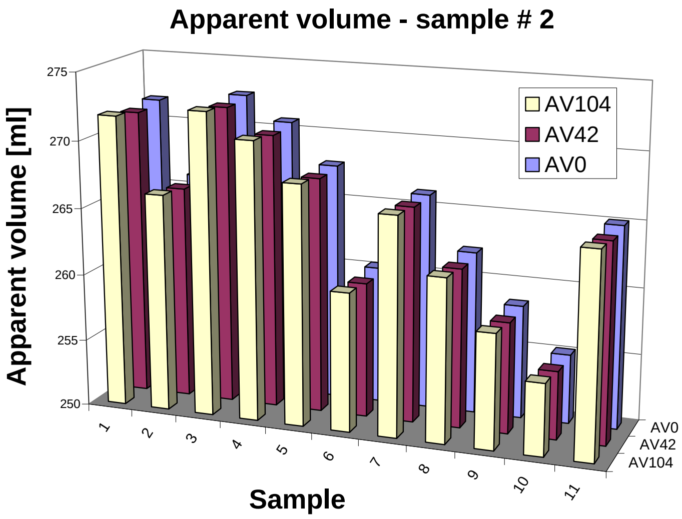

Figure 5. Apparent volume of sample no. 2 after 0, 42 and 104 cycles.

3.5 Open Porosity

In the state of art only open porosity for marbles has been determined [Table 4]. No change in porosity is observed in the case of dolomitic marble, which also shows good performance after exposure and a relatively moderate decrease of USV and flexural strength. A slight increase of open porosity was measured in the case of calcitic marble.

Table 4. Open porosity of sample no. 1 and 2 before exposure and after 104 cycles.

Sample	*Average open porosity before exposure*	*Average open porosity after 104 cycles*
Sample 1	0.5	0.5
Sample 2	0.6	0.7

5. CONCLUSIONS

Frost susceptibility of four samples of two different marbles and limestones has been studied. It has been established that there is significant difference in deterioration rate due to freeze thaw cycling even among samples of the same rock group. While three of the studied samples show general decrease in flexural strength and USV, compact micritic limestone shows distinctive increase of mechanical properties.

While in the case of flexural strength this could be explained on the first glance by heterogeneity of natural stone, steady increase of USV shows this is not so. The detailed mechanism of improvement of mechanical properties of some samples during frost exposure can not be explained in this stage. Further explanation of the mechanism could be given after detailed study of nature of porous and rock microstructure.

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