COMPARISON BETWEEN DIFFERENT METHODOLOGIES FOR ARTIFICIAL DETERIORATION OF STONE AIMED AT CONSOLIDANTS TESTING

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Abstract

In this paper three methodologies for artificially deteriorating natural stones and producing samples suitable for consolidants testing were investigated and compared. Three very different lithotypes were used: *Giallo Siena* (a calcareous sandstone with high porosity), *Globigerina* limestone (a limestone with very high porosity) and *Pietra Serena* (a quartzitic sandstone with low porosity). In addition, to investigate the role of porosity in determining the effectiveness of artificial deterioration by heating, additional lithotypes with basically the same mineralogical composition but significantly different porosity were also used: three limestones (*Pietra di Trani*, *Crema Luna* and *Pietra di Vicenza*) and one marble (Carrara marble). The stones were subjected to three artificial deterioration methods, meant to reproduce and accelerate weathering processes occurring in the field: heating at 400 °C for 1 hour, immersion in HNO_3 0.025 M for 24 hours, mechanical pre-stress by applying a compression load of about 70% of the failure load (parallel to bedding planes). The effects of the artificial deterioration were evaluated in terms of alterations in mechanical properties, pore size distribution and water absorption. The results show that the most effective method for artificial deterioration depends on the microstructural properties of the lithotypes. Indeed, the effectiveness of heating varies with carbonate content and porosity of the heated stone; the acidic attack is most effective on stones with high sorptivity; pre-stress seems potentially effective but has the limitation of being hardly controllable and reproducible.

Keywords: stone, artificial deterioration, heating, microstructure, consolidants

1. Introduction

The on-site application of new stone consolidating materials sometimes leads to unexpected outcome or even defects, threatening the integrity and preservation of cultural heritage. For this reason, a preliminary testing campaign at a laboratory scale is basic for the assessment of the effectiveness, compatibility and reliability of new consolidants, which however raises some key questions about the nature of the stone samples to be tested (Amoroso and Fassina 1983). On the one hand, it is almost impossible to have decayed samples (withdrawn from real buildings) in sufficient size and quantity for an extensive investigation of the effects of a new consolidating treatment. On the other hand, quarry samples, even if porous, are usually not representative of decayed stone, characterized by cracks, grains detachment, cement fraction loss, etc.

Two different approaches have been proposed to overcome these problems: i) the use of "simulated" stones, i.e. stone powder compacted to create coherent samples

(Yang et al. 2011), and artificial stones, i.e. mortars, where binder, aggregates and water to binder ratio are tailored to resemble the desired natural stone (Drdàcký et al. 2012); (ii) the use of artificially weathered quarry samples (Misfud and Cassar 2006). The first approach gave interesting results, but the actual capability of artificial stone to reproduce the naturally weathered one is still matter of investigation. The second approach was proposed long ago (Amoroso and Fassina 1983) and suggested in the Italian recommendation NORMAL 20/85. However, the methodologies proposed so far exhibit some drawbacks, such as the differential decay between external and internal parts of the artificially weathered samples (for freeze-thaw cycles and salt crystallization cycles), the excessive contamination of the altered samples (for salt crystallization cycles), the risk of complete rupture of a significant number of samples due to too severe weathering conditions (especially when standard procedures for assessing materials resistance to frost, salts crystallization, etc. are used), the scarce controllability of the final results in terms of decay level, etc. For this reason, the present paper deals with the investigation of three methodologies for artificial weathering of stone, aimed to produce effective and controllable results, for new consolidants testing. The investigated methodologies are:

- *heating*, expected to produce anisotropic deformation in the calcite fraction of the stone and, hence, cracking;
- *acid attack*, aimed to somehow reproduce the effects of acid rain attack and, hence, a partial cement fraction loss and a porosity increase;
- *mechanical pre-stress*, directed to producing microcracks in the stone.

2. Materials and methods
2.1 Materials

With the aim of testing the effectiveness of the deterioration techniques on a range of different substrates, three types of stone with very dissimilar characteristics were selected: *Giallo Terra di Siena* (GS), a calcareous sandstone with medium-high porosity (provided by Il Casone S.p.A., Italy); Globigerina limestone (GL), an organogenic limestone with very high porosity (provided by Xelini Skip Hire and High-Up Service, Malta) and *Pietra Serena* (PS), a quartzitic sandstone with low porosity (provided by Il Casone S.p.A., Italy).

Moreover, for specifically investigating how porosity influences the effects of heating, four additional lithotypes having basically the same carbonate content but increasing porosity were used: *Pietra di Trani* (PT), a limestone with very low porosity; Carrara marble (CM), a calcitic marble with very low porosity; *Crema Luna* (CL), a limestone with medium porosity, and *Pietra di Vicenza* (PV), a limestone with very high porosity. All of them were provided by Roncato s.r.l., Italy.

2.2 Characterization techniques

For assessing the mineralogical composition of the stones, powder X-ray diffraction (XRD, Philips Diffractometer PW 1840, 40kV/20mA, Cu Kα radiation) and carbonate content determination by the Dietrich-Frühling method were performed. The pore size distribution and the total open porosity (*OP*) were determined by mercury intrusion porosimetry (MIP, Fisons Macropore Unit 120 and Porosimeter 2000 Carlo Erba) on samples withdrawn from a depth of 0-10 mm from the surface of cubic specimens, after

compression test. The specific surface area (SSA) was measured by BET method (Flowsorb II 2300 Micromeritics, USA).

The sorptivity (i.e. the rate of water sorption) was measured according to EN 15801 on cubic samples (5 cm side), the water flux being in the direction parallel to the bedding planes. The water absorption by capillary after 24 hours (WA_{24}) was determined in the same conditions as the sorptivity test.

The mechanical properties of the stones, i.e. the dynamic elastic modulus (E_d), the static elastic modulus (E), the compressive strength (σ_c) and the tensile strength (σ_t), were determined on cubes (5 cm side) and cylinders (5 cm height, 2 cm diameter) according to the methodologies described elsewhere (Franzoni et al. 2012).

To assess the possible presence of salts inside stones subjected to artificial deterioration by acid attack, a comparison of nitrate content between undeteriorated and acid-deteriorated samples was performed by ion chromatography (IC, Dionex ICS 1000) after samples grinding, salts extraction with distilled boiling water and filtration.

2.3 Artificial deterioration techniques

The following artificial deterioration methods, selected with the aim of reproducing and amplifying deterioration processes that naturally occur in the field, were set up.

2.3.1 Heating

Based on the results of previous studies on the effects of different heating conditions on the modification of stone microstructural parameters (Sassoni et al. 2011; Franzoni et al. 2012), GS, GL and PS samples were artificially deteriorated by heating in an oven at 400 °C for 1 hour.

In addition, PT, CM, CL and PV samples were heated at 100 °C and 400 °C for 1 hour, to investigate the effects of heating on stones having basically the same mineralogical composition but different porosity.

2.3.2 Acid attack

After preliminary tests aimed at identifying a suitable and not too aggressive acid concentration (at least not giving rise to visible bubbles emission once in contact with the acidic solution), GS, GL and PS samples were immersed in a 25 mM HNO_3 aqueous solution (pH = 1.6) for 24 hours. De-ionized water and HNO_3 (purchased from Carlo Erba, 69.5% grade) were used. After acid attack, samples were washed by immerging them in de-ionized water for 3 days to remove nitrate salts (the water being renewed every day) and then dried at room temperature. This cycle of immersion in acidic solutions, washing and drying was repeated twice.

HNO_3 was preferred over other acids (such as sulphuric or formic acid, suggested by Amoroso and Fassina, 1983) because of the higher solubility of calcium nitrate salts. In fact, the contamination of the artificially weathered samples with salts was considered, at this stage of the investigation, not suitable, as it would considerably complicate the evaluation of a consolidant performance.

2.3.3 Mechanical pre-stress

Artificial deterioration by mechanical pre-stress was performed on GS, GL and PS cubic samples by applying, subsequently in the two directions parallel to the bedding

planes, a compression load approximately corresponding to 70% of the failure load. This condition was chosen with the aim of amplifying the microcracks and discontinuities that usually exist between the foliation planes of the stone. The presence of such microcracks and discontinuities in sedimentary stones is evidenced by the fact that ultrasonic pulse velocity (*UPV*) and E_d are generally lower in the direction perpendicular to the bedding planes. A loading value corresponding to 70% of the failure load was chosen considering that, for stone samples subjected to stress levels higher than about 50% of the compressive strength, significant decreases in *UPV* were found (Vasconcelos et al. 2008). The loading values for GS, GL and PS hence amounted to 80, 50 and 190 kN, respectively. The mechanical pre-stress was applied by an Amsler machine (maximum load 600 kN, loading rate of 2.5 kN/s).

3. Results and discussion
3.1 Materials

GS is a calcareous sandstone mainly composed of calcite, quartz and Na-feldspar (Table 1). It has a porous microstructure with quite coarse pores (Table 1, Figure 1), resulting in a water absorption of 4.0%. The mechanical properties of GS are reported in Table 2. They are characterized by some anisotropy (Table 3), the dynamic modulus perpendicular to the bedding planes ($E_{d,3(\perp)}$) being lower than in the parallel directions, as it is usually found in sedimentary stones (Vasconcelos et al. 2008).

GL is a limestone mainly composed of calcium carbonate and small amounts of quartz (Table 1). It is characterized by high porosity and coarse pores, which lead to high water absorption (Figure 1) and scarce mechanical properties (Table 1). The anisotropy between the three directions is not so evident as in the other stones (Table 3) and, notably, $E_{d,3(\perp)}$ is slightly higher than $E_{d,1(\parallel)}$ and $E_{d,2(\parallel)}$ in the parallel directions.

PS is a quartzitic sandstone mainly composed of quartz and feldspars, alongside calcite and dolomite (the equivalent calcium carbonate content, accounting for both carbonate minerals, is $CaCO_3 = 12.8\%$) and small amounts of micas and pyroxenes. Its microstructure is characterized by low porosity and very small pores (Table 1, Figure 1), with a consequent very low water absorption (Figure 1). The mechanical properties of the stone are high (Table 2) and characterized by a marked anisotropy, $E_{d,3(\perp)}$ being sensibly lower than in the parallel directions (Table 3).

PT, CM, CL and PV are all composed almost exclusively of calcite, the $CaCO_3$ content ranging 91.7 to 99.3% (Table 1). At the same time, their microstructure differs greatly, as their porosity ranges 0.4 to 24.3% (Table 1) and their pore size distribution is significantly different (Figure 2).

3.2 Artificial deterioration techniques
3.2.1 Heating

After heating at 400 °C for 1 hour, GS, GL and PS underwent significant variations in microstructural, physical and mechanical properties, with some notable differences between the three lithotypes.

GS and GL exhibited a decrease in mechanical properties, more pronounced for the former lithotype (Table 2). Such decrease can be attributed to micro- and nano-cracks that are expected to open at grain boundaries as a consequence of the anisotropic thermal expansion of calcite crystals, when exposed to thermal variations (Sassoni et al.

2011; Franzoni et al. 2012). A confirmation of the opening of new cracks can be found in the variations in pore size distribution and water absorption after heating (Figure 1). In the case of GS, increases in porosity and WA_{24} were actually found, while in the case of GL this is not so evident (Figure 1), which seems due to the different values of open porosity of the two stones: since GL is significantly more porous than GS (approximately twice, Table 1), some calcite crystal deformation is allowed to occur without causing stress and cracks opening in the stone. To verify this hypothesis, the effect of heating on stone samples with basically the same mineralogical composition but highly different porosity was investigated and the lithotypes CT, CM, CL and PV

	Mineralogical composition	CaCO$_3$ [% wt.]	OP [%]	AC [kg/m^2·s$^{1/2}$]	WA$_{24}$ [% wt.]
GS	Calcite, Quartz, Albite	84.3 (±0.6)	20.9 (±1.8)	0.168 (±0.009)	4.0 (±0.1)
GL	Calcite, Quartz	91.4 (±1.6)	40.6 (±1.8)	0.031 (±0.001)	14.0 (±0.0)
PS	Quartz, Albite, Calcite, Dolomite, Sanidine, Phlogopite	12.8 (±1.0)	6.1 (±0.3)	0.005 (±0.000)	1.3 (±0.0)
PT	Calcite	98.5 (±0.5)	0.4 (±0.2)	0.000 (±0.000)	0.2 (±0.0)
CM	Calcite	99.3 (±0.6)	0.6 (±0.2)	0.000 (±0.000)	0.1 (±0.0)
CL	Calcite	97.9 (±0.8)	7.7 (±0.8)	0.004 (±0.000)	2.1 (±0.0)
PV	Calcite	91.7 (±0.8)	24.3 (±4.6)	0.036 (±0.000)	8.9 (±0.4)

Table 1. Mineralogical composition, *CaCO$_3$*, *OP*, *AC* and *WA$_{24}$* of GS, GL, PS, PT, CM, CL and PV undeteriorated samples. *CaCO$_3$* values are averages of 2 samples, *OP*, *CA* and *WA$_{24}$* values are averages of 3 samples (standard deviations in brackets)

		E$_d$ [GPa]	E [GPa]	σ$_c$ [MPa]	σ$_t$ [MPa]
GS	**Undeteriorated**	35.3 (±1.0)	11.8 (±1.0)	43.6 (±1.0)	6.2 (±0.5)
	Heating	24.9 (±0.7)	9.4 (±0.1)	37.5 (±0.0)	5.3 (±0.8)
	Acid attack	33.9 (±1.5)	6.0 (±1.1)	39.9 (±3.7)	6.1 (±0.4)
	Mechanical pre-stress	29.8 (±0.2)	11.1 (±0.0)	40.6 (±3.0)	6.2 (±0.5)
GL	**Undeteriorated**	15.2 (±0.1)	6.5 (±0.2)	27.5 (±0.3)	3.1 (±0.2)
	Heating	11.3 (±0.5)	5.7 (±0.1)	26.6 (±1.2)	2.7 (±0.2)
	Acid attack	14.9 (±0.1)	5.6 (±0.2)	21.3 (±1.3)	2.6 (±0.2)
	Mechanical pre-stress	14.3 (±0.1)	6.1 (±0.1)	24.9 (±0.8)	3.2 (±0.3)
PS	**Undeteriorated**	32.2 (±0.3)	11.8 (±0.0)	109.4 (±0.0)	8.0 (±0.4)
	Heating	27.2 (±0.4)	12.0 (±0.0)	122.6 (±2.3)	8.8 (±0.9)
	Acid attack	28.5 (±1.3)	11.4 (±0.0)	105.6 (±0.1)	8.0 (±0.5)
	Mechanical pre-stress	23.3 (±0.7)	11.3 (±0.4)	98.0 (±13.0)	8.1 (±0.5)

Table 2. E_d, E, σ_c and σ_t of GS, GL and PS samples, undeteriorated and artificially deteriorated by heating, acid attack and mechanical pre-stress. E_d, E and σ_c values are averages of 2 samples, σ_t values are averages of 6 samples (standard deviations in brackets)

hence introduced. As shown in Figure 2, heating at 100 °C and, to a higher extent, at 400 °C leads to dramatic increases in porosity in lithotypes with very low porosity (CT and CM), while limestones with medium porosity (CL) and high porosity (PV) exhibit decreasing variations in porosity. The role of porosity in determining the effects of heating seems hence to be confirmed.
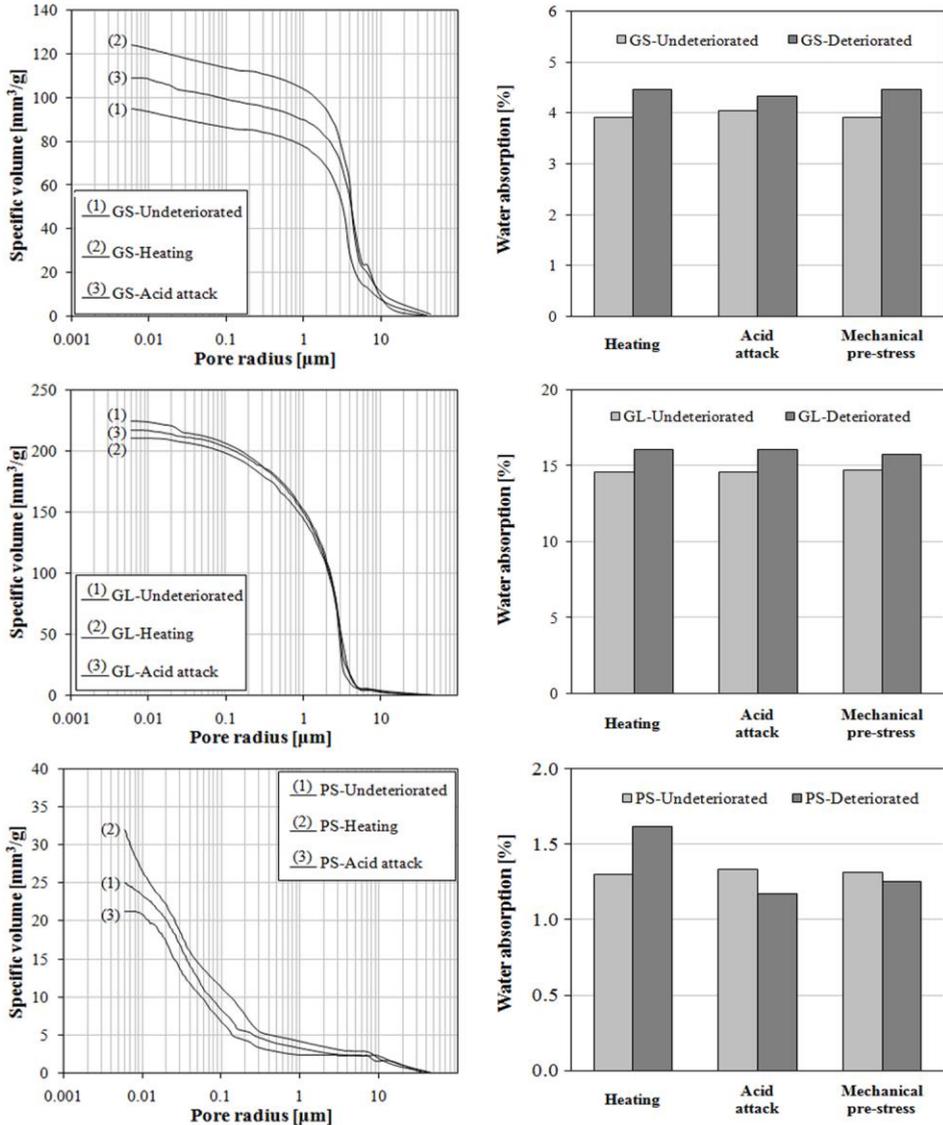
Figure 1. Pore size distribution (left) and water absorption (right) of GS, GL and PS samples, undeteriorated and artificially deteriorated by heating, acid attack and mechanical pre-stress (y-axis has a different scale for different lithotypes to allow a better readability)
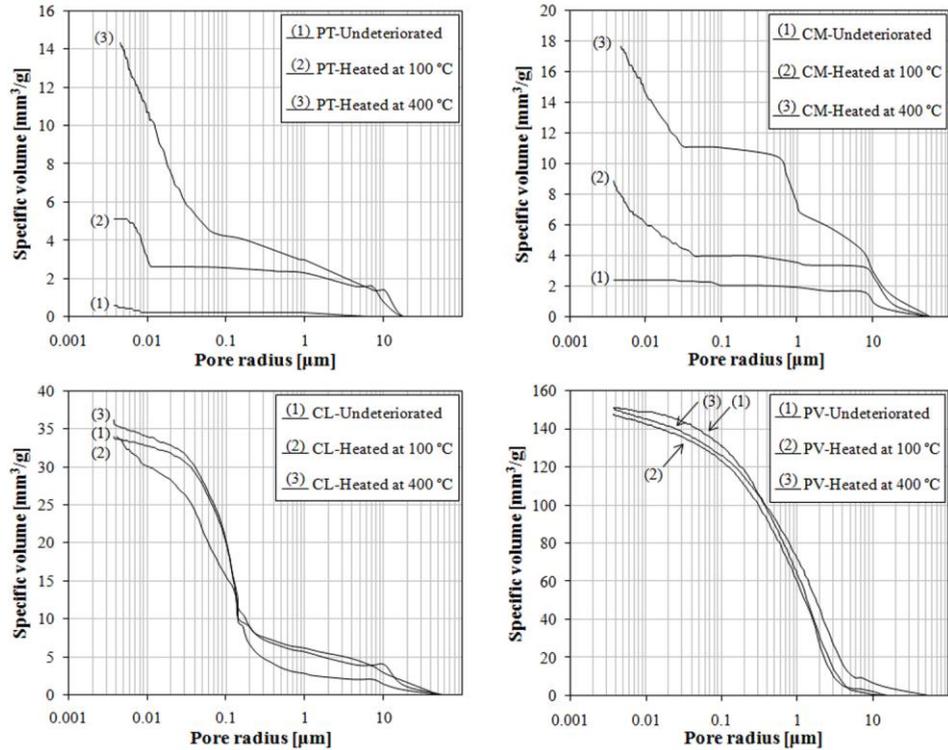

Figure 2. Pore size distribution of PT, CM, CL and PV samples, undeteriorated and artificially deteriorated by heating at 100 °C and 400 °C (y-axis has a different scale for different lithotypes to allow a better readability)

In the case of GL, even if no noticeable variation in pore size distribution was detected by MIP, the opening of cracks at the nano-scale (not detectable by MIP) is confirmed by the variation in *SSA* measured by BET method. In fact, *SSA* increases from 2.8 ± 0.2 m^2/g before heating to 3.8 ± 0.1 m^2/g after heating (average of 2 samples). The opening of nano-cracks seems hence responsible for the decrease in mechanical properties and increase in water absorption after heating.

In the case of PS, porosity and water absorption were found to increase as well (Figure 1), but heated samples exhibited an increase in strength (Table 2). The increase in porosity can be ascribed to the fact that the low porosity of the stone makes it sensitive to any calcite crystal deformation occurring during heating. Yet, the increase in mechanical properties is presumably due to the "hot-melt effect" (Zhang et al. 2009) produced by some secondary clay minerals undergoing chemical-physical transformation upon heating. The presence of clay minerals in PS was confirmed by the

fact that the static elastic modulus of this stone in water-saturated conditions is considerably lower than the one in dry conditions (Franzoni et al. 2012).

3.2.2 Acid attack

The immersion of samples into HNO_3 solutions at pH = 1.6 caused the variations in physical-microstructural properties reported in Figure 1 and the variation in mechanical properties summarized in Table 2.

GL is the lithotype that exhibits the highest decrease in mechanical properties ($\Delta\sigma_c$ = -22.5%, $\Delta\sigma_t$ = -16.1%), which is consistent with GL having the highest absorption coefficient and the highest porosity, as well as the highest carbonate content (Table 1). Such characteristics allow a large amount of acidic solution to be deeply absorbed into the stone, where the acid reacts with the calcitic substrate. Hence the calcite dissolution leads to a decrease in mechanical properties in GL, while the effects of the acidic solutions on GS, having a smaller absorption coefficient and lower porosity, are less pronounced ($\Delta\sigma_c$ = -14.0%, $\Delta\sigma_t$ = -1.6%). Finally, in the case of PS, the effect of acidic attack is very limited, as a consequence of the compact stone microstructure (slow and very scarce water absorption), limiting the stone degradation to the most external layer of the samples. In the case of acid attack, the mechanical strength results are not fully consistent with the MIP data: this can be ascribed to the fact that degradation is concentrated in the external part of the samples, where nitric acid is neutralized by the reaction with calcite and where the fragments for MIP were withdrawn. Hence, especially for the most compact stones (GS and PS), the degradation of the external stone layer is not enough to produce a significant decrease in mechanical strength.

With regard to the important issue of soluble salts removal from inside the stone, the adopted washing method proved to be fairly effective, as no increase in nitrates was found by ion chromatography in acid-deteriorated samples, compared to undeteriorated ones.

3.2.3 Mechanical pre-stress

The effects of mechanical pre-stress are reported in Table 2 and Table 3, where the variations in E_d along the three directions (parallel and perpendicular to the bedding planes) are analyzed in detail.

As expected, by applying a compression load parallel to stone bedding planes, the biggest E_d decrease was found in the direction perpendicular to the planes, as a consequence of the opening of microcracks between the bedding planes (Table 3). This is particularly evident for those lithotypes with a marked anisotropy (PS and GS, for

		$E_{d,1(\parallel)}$ [GPa]	$E_{d,2(\parallel)}$ [GPa]	$E_{d,3(\perp)}$ [GPa]	$\Delta E_{d,1(\parallel)}$ [%]	$\Delta E_{d,2(\parallel)}$ [%]	$\Delta E_{d,3(\perp)}$ [%]
GS	**Undeteriorated**	36.2	36.7	32.9	-	-	-
	Mechanical pre-stress	32.4	31.0	25.9	-10.7	-15.5	-21.3
GL	**Undeteriorated**	14.9	14.9	15.8	-	-	-
	Mechanical pre-stress	14.0	13.8	15.2	-5.6	-7.2	-3.7

PS	Undeteriorated	36.7	35.7	24.0	-	-	-
	Mechanical pre-stress	29.0	25.3	15.4	-21.0	-29.1	-35.7

Table 3. Dynamic elastic moduli parallel ($E_{d,1(\parallel)}$, $E_{d,2(\parallel)}$) and perpendicular ($E_{d,3(\perp)}$) to the bedding planes and their respective variations for GS, GL and PS samples, undeteriorated and artificially deteriorated by mechanical pre-stress. Values are averages of 2 samples

which the E_d variations are $\Delta E_{d,3(\perp)}$ = -35.7% and -21.7%, respectively), while the E_d variation is substantially similar in the three directions for GL, where only a slight anisotropy is present. However, the stone that experiences the highest decrease in σ_c after mechanical pre-stress (PS) also exhibits a high dispersion of the results (Table 2). This suggests that, owing to stone brittleness, mechanical pre-stress is a hardly-controllable and reproducible method. Remarkably, tensile strength is substantially unaltered by mechanical pre-stress (Table 2). An explanation for this behavior can be found considering that mechanical pre-stress was performed parallel to the bedding planes, so as to amplify cracks and discontinuities *between* the planes. Since the cylindrical samples used to measure stone tensile strength were core-drilled perpendicular to the bedding planes, during tensile strength determination by Brazilian test new cracks formed after pre-stress do not play a very significant role in determining stone resistance to splitting *perpendicular* to the bedding planes. As for modifications in physical-microstructural properties, MIP was not performed on samples obtained from pre-stressed specimens. In fact, in the case of the other deterioration techniques, the samples used for the MIP measurement were obtained from cubes that had been subjected to compression test. Therefore, in the case of mechanical pre-stress, the microstructural modifications induced by pre-stressing (opening and widening of microcracks) would be no longer appreciable after compression strength test.

4. Conclusions

The results of this study show that the most effective method for stone artificial deterioration depends on the specific microstructural features of the lithotypes. Indeed, the effectiveness of heating proved to vary significantly with the carbonate content and porosity of heated stones: highly calcareous stones with very low porosity are the most sensitive lithotypes, while clay-bearing stones (such as PS) may even undergo mechanical improvement upon heating. The acid attack caused the most significant variations in stones with high sorptivity and high carbonate content, while its effectiveness is limited when the acidic solution cannot penetrate deeply into the stone. Finally, mechanical pre-stress seems potentially effective, but has the limitation of being hardly controllable. Therefore, the most suitable method for artificially deteriorating stones to be used for consolidants testing should be selected by performing preliminary tests aimed at assessing the actual sensitivity of the specific stone type to the various deteriorating treatments.

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