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Simulation of temperature and chemical weathering effect on marble rocks

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Abstract. Physical and mechanical properties of building stones can vary due to different degradation mechanisms caused by temperature and chemical agents. The problem of chemical and thermal weathering on marble rocks is an important issue to consider for designing building façades since it may cause sugaring, bowing, cracking and spalling. Moreover, an accurate comprehension of induced damages is required for restoration and conservation of heritage monument purposes. While thermal weathering has been widely studied in the last years, the combined effect of thermal and chemical weathering (that here is intended as the combined action of rainwater and atmospheric pollutants) is still poorly understood. In this study, no-destructive (ultrasonic pulse velocities) and destructive tests (bending tests) were performed on Carrara marble slabs in natural and after thermal (with target temperatures respectively of 50 and 90°C) and thermo-chemical treatment. Thermo-chemical treatments were performed by soaking the specimens in a 5×10^{-6} mol/l solution of sulphuric acid at pH=5 to simulate the acid rain behavior, at constant target temperatures, for one week. In general, for each weathering mechanism, progressive degradation of the physical and mechanical properties of marble specimens was observed. In particular, a marked drop in flexural strength, mirrored by a wide variation in P- and S-wave velocity, was found in specimens chemically treated at target temperature equal to 90 °C.

1. Introduction

The physico-mechanical degradation of rock properties due to exposition to natural weathering factors (as rain, snow, ice and wind), temperature and chemical agents (air pollution) is fundamental for designing many mining and civil constructions and for planning restoration in cultural heritage. Usually, two or more weathering factors contemporary occur [1], increasing the effect of deterioration on rocks and the strength reduction.

Since ancient time, marbles were used as building material as a facing stone for temples, mosques, churches, palaces and other monuments. Marble is a metamorphic rock mainly made of calcite ($CaCO_3$), with a massive crystalline structure and very low porosity (0.1-0.5%). It is highly sensitive to acid attack that compromises its durability and its mechanical properties. Acid rain causes dissolution of the marble, increasing porosity and allowing a higher circulation of salt within microstructures [2] (and references therein). Moreover, if the effects of acid rain are coupled with thermal gradients, a more severe degradation of the physico-mechanical properties is expected. In fact, due to the anisotropic thermal expansion of grains, thermal stresses arise within the marble structure, leading deflection, bowing and spalling phenomena [3].

Acid rain are rich in sulphur dioxide and nitrate [4] that cause chemical deterioration on carbonate stones [5], formation of soluble Ca_2^+, HCO_3^-, SO_2^-, salt enrichment and discolor stone surface [6]. The dissolution is a three stages mechanism [7]: 1) attack by SO_2; (2) dissolution during “clean” rain events; (3) acceleration of dissolution due to rain acidity.

Acid rain effects were studied in laboratory by many researchers by following two different methodologies: 1) by immersion of the samples in an acid solution [8-10], 2) in complex chambers that simulated acid rain by spraying the samples or by applying a constant water current on the stone [11-13].

The induced thermal stresses were also extensively studied in recent years [3, 14-16]: however, the combined effect of temperature and atmospheric chemical agents is still poorly understood.

In this study, seismic measurements and three-point bending tests were performed on natural, thermally and thermo-chemically treated Carrara marble samples. The thermo-chemical treatment was performed by immersing the marble slabs into a $5x10^{-6}$ mol/l solution of sulphuric acid at pH=5, at constant target temperatures, for one week. In general, for each weathering mechanism, a progressive degradation of physico-mechanical properties of marble specimens was observed. In particular, a marked drop in flexural strength, mirrored by a wide variation in P- wave velocity (respectively VP and VS), was found in specimens chemically treated at target temperature equal to 90 °C. Scanning Electron Microsopy (SEM) analyses were performed on sections coming from the natural and treated specimens for the identification of dissolution processes inside the marble slabs and the definition of possible sulfate weatering thickness. Microanalysis and mechanical results were also compared and deeply discussed.

2. Methodology

2.1. Rock sample characteristics

Twenty 195x60x30 mm slabs were cut from a unique block of “Bianco Venato” Carrara marble collected in the Gioia quarry in the Apuan Alps (Carrara municipality, Italy). The Bianco Venato is made up of a medium-grained white to pearl-white colour, with a few dark short veins, millimeter to sub-millimeter in thickness. It is mainly composed of calcite grains, with dimensions ranging from 60 to 600 μm, with the presence of pyrite microcrystals, quartz and muscovite.

This type of marble is extensively used as a building material, especially in building façade due to its strength characteristics, its color and its low porosity.

The main physical and mechanical characteristics of the material are listed in table 1.

Table 1. Main physico-mechanical characteristics of the Bianco Venato marble.

Parameters	Mean value	Standard deviation
Unit weight [kg/m^3]	2710	5.2
Porosity [%]	0.4	0.02
UCS [MPa]	101.4	10.8
Flexural strenght [MPa]	11.6	2.5

2.2. Weathering test

In order to study the effect of temperature and chemical agents separately, the specimens were group into 5 sets (4 specimens for each set, in order to verify the repeatability of the measurements). The first set represents marble in natural conditions (named “natural” in the following). Two sets were composed of specimens subjected to a comparable thermal treatment but reaching different target temperatures. Target temperatures of 50 °C (TT50) and 90 °C (TT90) were applied [17] to the different sets.

The thermal cycle consists of a first stage where the samples were heated in a furnace at a heating rate of 0.06 °C/s. Once the target temperature was reached, the specimens were held in the furnace for five days and cooled down to room temperature in the furnace.

The other two sets were subjected to the same chemical treatment [18] at variable target temperature, respectively of 50 °C and 90°C (TTC50 and TTC90). The specimens were immersed in a Plexiglas box (figure 1a) in a 5×10^{-6} mol/l solution of sulphuric acid at pH 5. The box was then placed into a thermostatic bath (figure 1b) that reproduced the same thermal cycle previously described. Ph measurements were performed once a day and acid solution was added in case of significant pH variations. The texts were performed at the Department of Earth Sciences – University of Torino in the Geotechnical and Geophysical Lab.

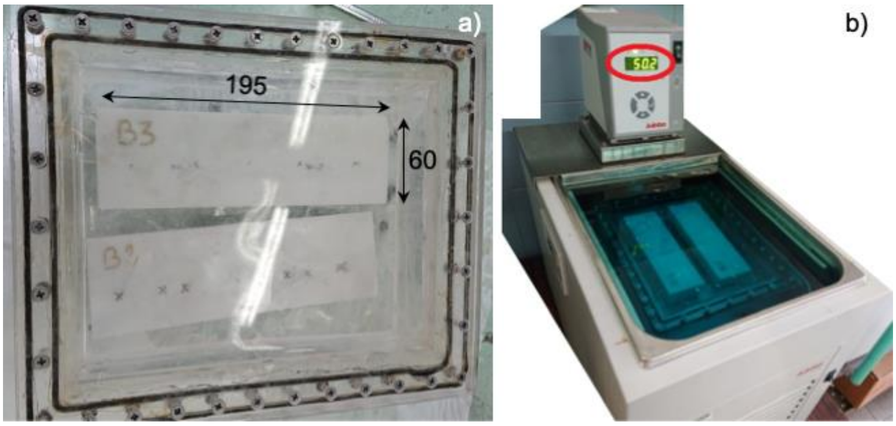

Figure 1. a) Plexiglas box and b) thermostatic bath for the thermo-chemical treatment of marble slabs.

2.3. *Physical and mechanical measurements*

V_P and V_S measurements were performed using a pulse generator and acquisition system (Pundit Lab, Proceq) with two cylindrical 250 kHz tx-rx probes, in natural conditions and after thermal and thermo-chemical treatments. Two different measurement schemes were followed ([19] standard), depending on the position of the probes (figure 2a): the direct and the surface methods. Results of the two methods were then averaged.

Three-point bending tests ([20] standard) were conducted using an MTS apparatus (MTS System Corporation) equipped with a load cell of 100 kN (figure 2b) and an LVTD transducer for measuring the deflection during tests. Mechanical tests were performed at the Politecnico di Torino Geotechnical Lab.

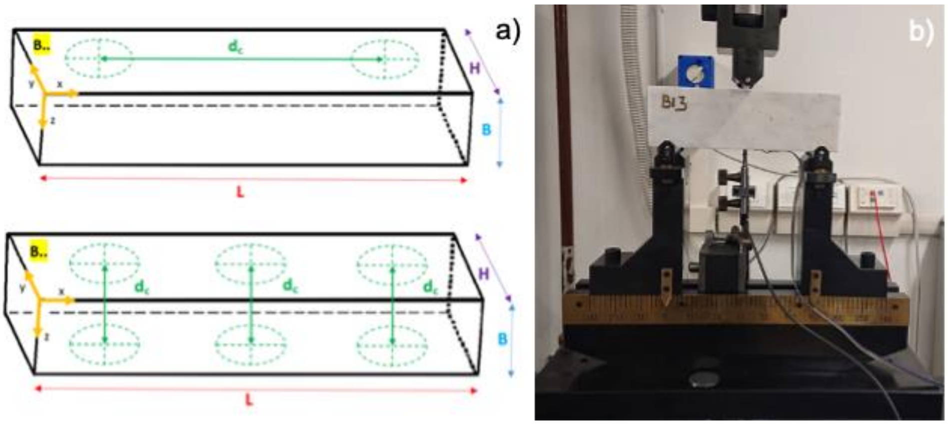

Figure 2. a) Seismic measurement schemes and b) bending test apparatus used.

2.4. SEM-EDS analysis

Scanning Electron Microscopy (SEM) imaging coupled with Electron Dispersion Analysis (EDS) was performed on 60x30mm sections of the failure surface generated after bending test. The samples were coated with graphite to make them electrically conductive. SEM-EDS analyses were performed using a JSM IT300LV High Vacuum – Low Vacuum 10/650 Pa - 0.3–30 kV (JEOL USA Inc.) equipped with secondary electron (SE) and backscattered electron (BSE) detectors and W electron gun. For the morphological analysis, the typical experimental conditions were EHT 20 kV, working distance 5 mm, while EDS analysis was performed using EHT 15 kV, high current probe and working distance 10 mm.

3. Results

3.1. Physical and mechanical measurements

Observation to the naked eye showed an evident change in colour between natural and thermochemical treatment, that shifted from pearl-white to beige colour. Moreover, especially the samples thermo-chemically treated at 90 °C, were covered by a white powder.

Both physical and mechanical tests were evaluated firstly for each sample and then as an average over samples subjected to the same thermal (same target temperature) and thermochemical treatment.

Figure 3 shows the results of the physical and mechanical tests performed on the marble slabs after thermal (TT) and thermochemical treatment (TTC).

An evident decrease in P- and S-wave velocities (figure 3a and 3b) and flexural strength, σ_T, (figure 3c) and a slight increase in maximum deflection, f_{max}, (figure 3d) were found with increasing target temperature. The drop in V_P and σ_T is more marked after thermochemical treatment. On the contrary, V_S (figure 3b) and f_{max} are not sensitive to thermochemical treatment.

For each parameter, an exponential relationship was fitted to the average values of each treatment (TT an TTC); high R^2 values, ranging from 0.51 to 0.99, were obtained.

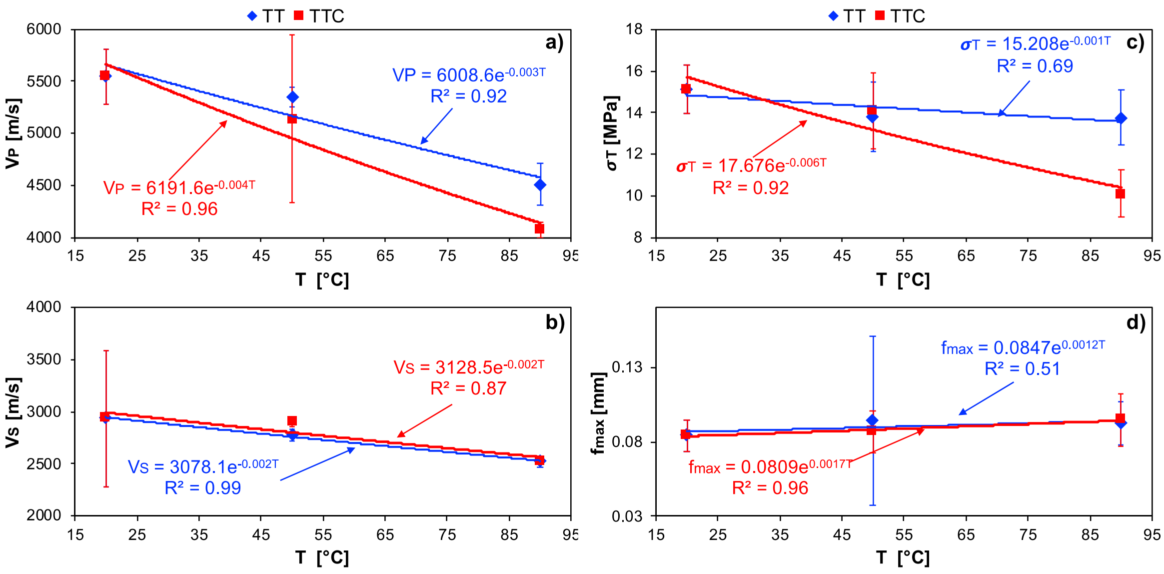

Figure 3. Relationship between a) P-wave velocity, b) S-wave velocity, c) flexural strength σ_T and maximum deflection at the mid-section of the slab and temperature for thermal (TT) and thermochemical (TTC) treatment.

3.2. SEM-EDS analysis

Morphological analysis was performed in order to evaluate the effect of the thermochemical treatments at the microscopic scale to emphasize potential correlations between the microscopic behavior of the sample and its mechanical properties.

Although we expected visible widening of pores and cracks related to the dissolution of the carbonate in acidic conditions from the samples' external weathered shell toward the core, no such features were recognized.

Unexpectedly, at the interfaces between calcite crystals building the rock and their joints, they are undoubtedly recognizable some surface dissolution features. In particular, the typical rhombohedric etch pits with two edges parallel to the direction $[\bar{4}41]$ and rounded closure related to the dissolution of the $\{10\bar{1}4\}$ rhombohedron of calcite is frequently recognized, as shown in figure 4b. The etch pits are distributed in rows on the calcite surfaces, indicating the existence of dislocations (hints of deformation) whose presence is usual in metamorphic rocks.

The etch pits' presence is discernible until a depth of about 3 mm from the sample surface toward the core, indicating the deepening of chemical weathering.

The microprobe analysis of the sample did not highlight a calcium sulfate passivating coating. The lack of such a layer is related to the low concentration of calcium sulfate in the solution, lower than the saturation value for gypsum. It must be pointed out that gypsum's solubility is much higher than calcite at the same temperature even if the two phases have both reverse dependency of the solubility from the temperature at the operating range (T=50°C s_{Cc}=0.005g/L, s_{Gyp}=2.07g/L; T=90°C s_{Cc}=0.003g/L, s_{Gyp}=1.73g/L).

4. Discussions

The thermal treatment induces a decrease in physical and mechanical properties at each applied target temperature and a slight increase in deformation. Exponential relationships between all parameters and temperatures are found, in good agreement with recent studies [14-15]. In particular, fitting parameters for the seismic parameters fall in the range proposed by [15].

Exponential laws are also fitted for parameters of the thermochemically treated samples. Whereas a significant drop is detected in V_P and flexural strength after TTC, especially at 90 °C, V_S and deflection are not significantly sensitive to TTC. Thermal and thermo-chmical effects may be neglected at temperatures below 50 °C.

Since during the weathering tests the pH is kept constant and equal to 5, the calcite dissolves to Ca^{2+} as described by the following reaction:

$$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3 \tag{1}$$

The interaction between marble and solutions with high SO_4^{2-} concentrations lead to gypsum precipitation on the surface of the dissolving calcite [10, 21-23]:

$$Ca^{2+} + SO_4^{2+} + 2H_2O = CaSO_4 \cdot 2H_2O \tag{2}$$

This process has two main consequences: one negative and one partially positive. The negative one is related to the lower physico-mechanical characteristics of the deposited gypsum compared to the marble ones. However, the gypsum coating has a positive effect since it drastically reduces the surface porosity and progressively reduces the dissolution rate of calcite. Despite this, the gypsum has a higher solubility in water and consequently, the gypsum coating can be easily removed by clean water (i.e. during rainfalls). This mutual process is the main cause of marble degradation related to thermo-chemical weathering. Consequently, the evaluation of the possible damage depth is a fundamental aspect in the forecasting of the marble performances, especially when it is used as a building stone. In fact, sulfate weatering thickness reduces the resisting marble surface, mirroring a decrease in flexural strength (see figure 3c): greater is the thickness of gypsum coating, greater is the reduction in flexural strength.

The chemical weathering does not directly influence the deformation, which is completely related to thermal stress (figure 3d). In fact, if thermal stresses are generated within marble due to temperature variation, irreversible deformation (bowing phenomena) can be detected [3]. Undoubtedly, the marble deformation due to bowing can be magnified by the chemical effects of acid rain. However, due to the moderate target temperature reached, the deformation increase is limited (figure 3d).

Even if the damage depth is not constant, since it depends on the heterogeneity in porosity distribution and the presence of natural cracks, it can be roughly estimated by using the measured V_P variation (figure 3a) and by assuming an average V_P for the sulfate surface. Figure 4a shows the scheme used for the evaluation of sulfate weatering thickness. The thickness d, can be estimated by solving the system of equations:

$$\begin{cases} V_{P_{Marble}}(T) = \frac{B-2d(T)}{t_{TTC}-\Delta t_{TTC}} \\ \frac{2d(T)}{\Delta t_{TTC}} = V_{P_{Sulphate\,surf}}(T) \\ V_{P_{Marble}}(T) = \frac{B}{t_{TT}} \end{cases} \tag{3}$$

where $V_{PMarble}(T)$ is the measured P-wave velocity at the fixed target temperature, d(T) is the sulphate weatering thickness, $V_{PSulphate\ surf}(T)$ is the P-wave sulphate surface velocity assumed equals to 2000 m/s. t_{TTC} and t_{TT} are the first arrival times of the P-wave measured after thermochemical and thermal treatment respectively. Δt_{TTC} is the unknown P-wave travel time inside the sulphate weatering thickness. The estimated values of sulphate weatering thickness for the two considered target temperatures are listed in table 2. These findings are confirmed by the morphological analysis at the SEM scale previously discussed that pointed out the presence of etch pits until a depth of about 3 mm from the sample surface. Even if the gypsum passivating coating is not cleary observed in the microprobe analyses, the presence of the white powder on the slabs surface after thermal treatment can be related to this process triggering. Further experiments should be performed by checking also the concentration of calcium sulfate in the solution, in order to reach the saturation value for gypsum and its precipitation.

Table 2. Input parameter used for the evaluation of sulphate weatering thickness at the different target temperatures.

Parameter	Value	
B [mm]	30	
T [°C]	50	90
$V_{PMarble}$ (TT) [m/s]	5350	4509
$V_{PMarble}$ (TTC) [m/s]	5136	4075
$V_{PSulphate\ surf}$ [m/s]	2000	
tTT [s]	5.61E-06	6.65E-06
tTTC [s]	5.84E-06	7.36E-06
d [mm]	0.37	1.27

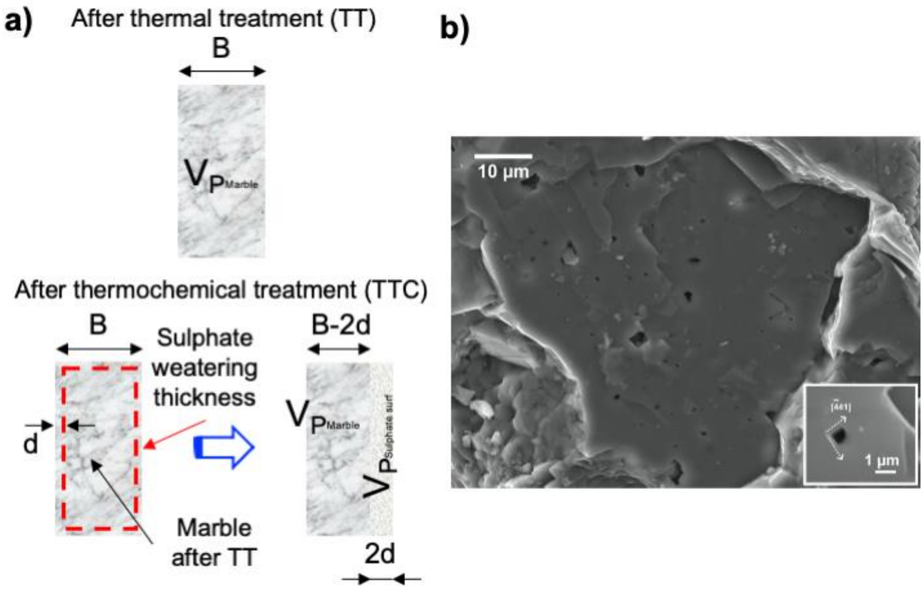

Figure 4. a) Scheme used for the estimation of the thickness of suphate surface from ultrasonic measurements and b) etch pit on a calcite crystal surface (interface) with the typical geometry referred to the dissolution of the cleavage rhombohedron.

5. Conclusions

In this paper, a series of laboratory tests were performed on the “Bianco Venato” Carrara marble for investigating the effect of the sulfuric acid solution on the physical and mechanical properties of marble. The testing procedure allows for the simulation of acid rain and temperature effects on marble slabs.

The temperature has a significant influence on the physical and mechanical properties of marble. Exponential trends were found to best fit the considered parameters with increasing thermal treatment. This degradation mechanics is even more marked when it is associated with sulfuric acid solutions. Calcite dissolution and sulphate weathering processes, as a consequence of thermo-chemical acid rain effect, induce both aesthetic flaws and mechanical alteration in marble (and generally in carbonate rocks). For the analyzed marble, the thickness of sulfate weathering ranges between 0.4 and 1.3 mm, depending on the considered target temperature. It is mainly responsible for V_P and flexural strength reduction. These values are also confirmed by analyzing SEM images: effects of calcite dissolution by low concentration sulfuric acid solutions are detected up to 3 mm from the external slab surface. Further developments should be focused on testing other acid solutions and considering different temperature ranges.

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