Portuguese marble response to SO2 and thermal ageing

Summary of dissertation for the degree of Master in Mining and Geological Engineering

Ana Sofia Angélico[1]
[1]Instituto Superior Técnico, Universidade Técnica de Lisboa, Portugal
ana.angelico@tecnico.ulisboa.pt

ABSTRACT

The effects of fires on natural stone have been studied in recent years, but many do not take into account the previous effects of decay agents such as sulfur dioxide (SO_2). In this study, a comparison of the effects of high temperatures was carried out on two varieties of Portuguese marble with and without exposure to an atmosphere rich in SO_2 (25ppm). The samples were heated to 600ºC for 2h, and submitted to rapid (immersion in water at room temperature) and slow cooling (inside the muffle). The evaluation of their behavior involved quantification of color, gloss, capillarity water absorption, open porosity, apparent density, velocity of elastic waves and elastic parameters. Exposure to a rich atmosphere in SO_2 induced changes in the surface characteristics of both marble varieties, with a reduction in gloss and luminosity, as well as a slight reduction in open porosity and in the capillary water absorption coefficient. The behavior of these physical properties was accompanied by a slight increase in apparent density and maintenance of the elastic waves velocity and elastic parameters. The thermal aging (with the two types of cooling) of the two groups of samples (with and without exposure to SO_2) did not cause notable differences in the parameters analyzed in the two marble varieties. However, in all simulations, heating at 600ºC caused a significant increase in open porosity, in capillary water absorption coefficient, accompanied by a reduction in P and S waves velocity and elastic constants. These changes were accompanied by a change in the color of the surfaces (greater luminosity and increased chromatic coordinates a* and b *). The type of cooling also influenced the physical properties evaluated, with greater changes in samples subjected to rapid cooling.

Keywords

Portuguese marbles; Accelerated ageing tests; SO_2, Temperature (600ºC), Rapid and slow cooling, Physical properties.

1. INTRODUCTION

Historic buildings are severely damaged by fires, which represents great losses both culturally and economically. In the European Union, it is estimated that on average one historic building is damaged by fire per week [1]. [1]. Fire can cause irreversible and long-lasting effects [2][3], partially due to high temperature. Although before a fire, stone is subjected to the effects of different decay agents like water, salts and atmospheric pollution [4], that can cause extensive damage. Air pollution is also a major threat to natural stone, especially in urban environments because accelerates the deterioration process that already exists [5][6]. Over the years, monuments such as Taj Mahal (India) and Acropolis of Athens (Greece) have been the subject of study with the aim of understanding the extent of the damage caused by air pollution [7].

Among the variety of stone materials, marble is one of the most applied stones in sculptures and buildings due, above all, to its aesthetic characteristics. Although it's vulnerable to weather agents [8] such as SO_2. The effects of heat and SO_2 in marbles has been extensively studied separately, however there is not much research about the effects of fire on stones previously degraded due to SO_2.

2. Related Work

2.1. Effects of atmospheric contaminants on stone materials: the action SO_2

2.1.1. Stone performance

The increase of fossil fuels consumption has caused a considerable increase in the concentration of pollutants in the atmosphere (e.g. SO_2, NO_x) mainly in urban areas [9]. These gases are capable of dissolving in water, which produces acidic solutions [9]. Sulphur dioxide (SO_2) from all the pollutants produced by fossil fuels, is the most important in stone decay processes [10] due to its high acidity and also because it accelerates stone degradation process [7].

In marble, the development of black gypsum crusts is one of the main forms of degradation occurring in an urban environment [10]. It is produced through the sulfation of calcite, where SO_2 reacts with marble producing gypsum crusts. This crust can acquire a dark colour, known as black crust, or white colour, depending on it's exposure for example to rain [11].

2.1.2.1. Mineralogical and physical changes

The calcite sulfation is the process where SO_2 reacts with calcite ($CaCO_3$) and produces gypsum. This process is influenced by the near surface conditions like temperature and relative humidity [9]. The marble sulfation can occur through dry deposition or wet deposition. Wet deposition is characterized by the dissolution of SO_2 in water, forming sulphuric acid that reacts with the calcite to form gypsum [9]. Dry deposition is characterized by the reaction between the marble surface and SO_2, to form calcium sulphite and afterwards gypsum [10].

The SO_2 deposition on marble is greatly influenced by the relative humidity, temperature and concentration of SO_2 and nitrogen dioxide (NO_2). In dry or low humidity environments, the deposition of SO_2 is very low [12]. High humidity accelerates the deposition process of sulphur dioxide on the marble surface due to the decrease in surface resistance [12]. The exposed area of the rock also influences the action of SO_2. Even though the sulfation process is a chemical process, the gypsum crusts can damage the stone physical and mechanical properties. Gypsum crystals undergo an increase of 30% in volume [13] during calcite sulfation, which causes an increase in tensions, because microcrystals and crypto gypsum crystals growth usually occurs between the grains and in the microcracks [14]. This usually leads to grains detachment[11].

2.2. Effect of high temperatures on stone

2.2.1. Stone performance

The forms of degradation (e.g.[3]) observed in real case studies and laboratory simulations, can be grouped into 4 families according to the terminology proposed by ICOMOS-ISC (2018) [2]: Cracks and Deformation; Forms due to material loss; Detachment in area; Chromatic alteration and Deposit, which are independent of the type of lithology. Additionally, the effects induced by fires on the stones do not follow any pattern even the same lithology [2], because the damage is highly conditioned not only by the fire characteristics but also by the stone characteristics and conditions at the time of the fire [6].

2.1.2.1. Mineralogic Changes

Marble performance up to 600ºC is mainly influenced by the anisotropic expansion of calcite and dolomite [15]. As the temperature increases, the mineral experiences an elongation in the c-crystallographic axis, and contraction in the remaining directions [1], that increases with temperature increase [16]. Thermal anisotropy develops microcracks [17] and microfractures due to the weakening of intergranular and intragranular cohesion [1], which in some cases leads to total deterioration of the rock [15].

In general, calcination occurs at temperatures above 700ºC and is characterized by the thermal decomposition of calcite ($CaCO_3$) and dolomite ($CaMg(CO_3)_2$)[15]. Due to the increase in temperature occurs a chemical reaction, where calcite transforms into calcium oxide [8] and dolomite into magnesium oxide[18]. After this reaction the stone becomes more susceptible to water and begins to react with atmospheric moisture. The result is the formation of portlandite that increases in volume and leads to the stone disintegration [15].

2.1.2.2. Surface characteristics

Mineralogic characteristics like mineralogy, size, shape and arrangement of the grains influence the colour of the stone [2], so it's colour changes are controlled by mineralogic alterations [15]. In marbles, these variations can generally be separated into three phases: i) up to 200ºC the colour variations are minimal; ii) between 200ºC and 700ºC there is an increase in yellow and red pigmentation; iii) after 800ºC marble acquires a white colour [2], due to stone calcination. In general is observed a reduction in the stone gloss, due to the effect of high temperatures. It's usually noticeable to the naked eye [19]. Sarici [20] studied the gloss changes in carbonate rocks after thermal ageing and thermal shock ageing and verified that deterioration in thermal shock specimens was higher due to rapid thermal expansion and contraction because of the heat and water (during cooling), which had a disrupting effect on surface quality.

2.1.2.3. Petrophysical properties

Porosity is key parameter in the evaluation of natural stone, subject to high temperatures, because it influences directly or indirectly, most of the physical and mechanical properties [4]. It's highly dependent on the stone mineralogy and internal characteristics [2]. In marble, the anisotropic growth of the calcite and dolomite grains and the low porosity, cause an increase in tensions in the grains, which results in the formation of microcracks primarily along mineral boundaries [19]. The development of microcracks leads to an increase in stone's capillary network of the rock and subsequently in porosity. Many of the variations observed in density, are also associated with porosity. However, the evolution of these properties is not similar. Up to 600ºC, the variations observed in the bulk density in carbonate rocks are usually negligible [2]. For higher temperatures, between 700ºC and 800ºC, a significant reduction in density occurs due to the increase in the porous space, but mainly due to the marble decomposition (calcination) [21]. The increase of open porosity and water absorption coefficient of capillarity also influences the elastic waves velocity. The elastic

waves velocity is used to study the physical and mechanical properties of rocks, and also to assess the stone degradation degree [19], because it depends on the density and elastic parameters of the medium [22]. Several authors [19][23] observed in carbonated rocks, a reduction in the P (Vp) and S (Vs) waves velocity, and their elastic parameters, related with the increase in temperature. For example, Murru *et al.*[23] and Vagnon *et al.*[24], observed from 300ºC-400ºC a significant reduction in elastic wave velocity and elastic parameters. For temperatures above 400ºC the reduction observed is very high (between 40% and 90%) due to the increase in porosity and the development of fractures parallel to the direction of anisotropy [24]. In general, the Young's modulus (E) is the parameter that presents the greatest reduction in marble. This parameter is dependent on the chemical composition and microstructure of the stone, therefore, its variation is associated with the acceleration of degradation induced by the creation of micro-cracks [23], and by the alteration of some mineral components. The Poisson's ratio (v) is strongly dependent on the ratio between the P and S waves velocity, which means, that if the ratio Vp/Vs is low, the Poisson's ratio will also have a low value [23]. Anisotropy indices vary according to the ratio of the three velocities determined in the stone three orthogonal directions [25]. In the laboratory work carried out by Murru *et al.* [23], the marble anisotropy rate (SMM) increased significantly after the first thermal cycle compared to the limestone (SCL), whose variation was less than 3%. In this case, the increase in anisotropy was justified by the authors by the increase in microfissures in a preferential direction, due to the anisotropic expansion of the calcite grains.

3. Materials and Methods

3.1. Materials

Two Portuguese marbles were selected for this study: Rosa Venado da Maroteira (M) and Rosa Venado do Olival da Encostinha (E). The specimens are calcitic marble with fine to medium grain. According to Carvalho *et al.*[26], Portuguese marbles usually present very low porosity (0,2-0,5%), water absorption (0-0,2%) and high bulk density (2710-2790kg/m^3).

Blocks of Maroteira (Vila Viçosa) and Encostinha (Borba) marble were collected, in quarries located in Estremoz anticlinal, provide by CECHAP (Centro de Estudos de Cultura, História, Arte e Património) then cut in GeoLab.(Laboratório de Geociências e Geotecnologias do Instituto Superior Técnico) Thirty two cubic samples (5x5x5 cm) for each marble type were obtained, and identified with the respective code (M and E) and number. The parallel faces were also identified with different numbers and colours (Figure 1).

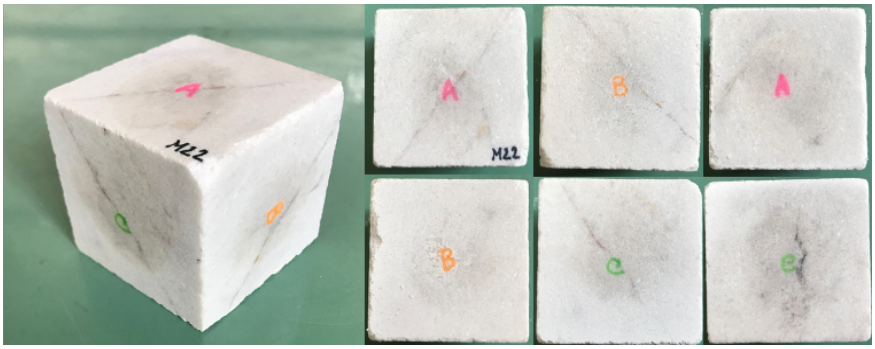

Figure 1 Example of one of Maroteira's samples, with the designation of the variety and the identified faces: Faces A with pink color; B faces with orange color; and Faces C with green color.

3.2. Laboratory SO_2 ageing procedure

Half of the samples (numbered 1 to 16) from each marble were placed in a climatic chamber (FITOCLIMA 3000EDTU Arala) and exposed to a synthetic atmosphere rich in SO_2 during 50 days. Each cycle lasted 12.5 hours, and was divided into four segments, two simulating the summer (40ºC and 30%RH) and winter (15ºC and 85%RH) conditions for 6 hours each, and two for the transition of conditions lasting 15 minutes (segments 1 and 3) . During the entire procedure, the SO_2 concentration was kept constant: the SO_2 container was diluted to 3% in 3000ppm, of nitrogen and then dosed to a concentration of 25 ± 1ppm, a value much higher than the current levels of SO_2 in the largest part of Europe (average value 0.00076 ppm, according to http://www.eea.europa.eu/themes/air/interactive/so2). Segment 2 simulated winter conditions with a temperature of 15ºC and 85% relative humidity, and segment 4 simulated summer conditions with a temperature of 40ºC and 30% RH. Water from the public supply network was used in the climate chamber to ensure the desired environmental humidity conditions.

3.3. Thermal ageing procedure

To simulate the effects of fire related temperatures, a thermal ageing test was carried out. SO_2 aged and reference (sound) samples from the two marble varieties, were heated at 600ºC for 2 hours in an electric oven, with an oxidizing environment (Ehret Mufla Furnance), and with a heating rate of 11 ± 4ºC/min. Then half of the samples (samples 1-8 and 17-24) were maintained inside of the oven until they reached room temperature, which took about 6 hours (referred to as slow cooling), and the rest (samples 9 - 16 and 25-32) were removed from the oven, completely immersed in water (at room temperature) for 10 seconds and then allowed to cool in the air (referred to as rapid cooling).

3.4. Testing Methods

3.4.1. Scanning electron microscopy

For this analysis fragments of samples (M15 and E15) after SO_2 exposure. A Hitachi S-400 SEM scanning electron microscope (available at Microlab IST-UL) with a Nano GmBH Bruker Quantax energy dispersed X-ray spectrometer and elementary light detectors (XFlash 5010) was used. The measurements were performed with an acceleration voltage of 10kV, resolution from 1 to 10 µm and magnifications from 170 to 6000x. Samples were previously coated with an ultra-thin conductive film of gold and palladium alloy (Au-Pd) and dried in a vacuum, at room temperature, for further analysis.

3.4.2. Gloss

The glossimeter used in this study was the NOVO-GLOSS Lite which measures the brightness at 20º and 60º. The measurements on the samples were made with a 60º angle (suggested for samples with reduced brightness [11]). In this study, brightness measurements were performed on all samples before and after each ageing test. In each specimen, 4 readings were taken, in different places on the same face. The value considered corresponds to the average of the four measurements.

3.4.3. Color

The colour changes were quantified with a Chroma Meter CR-400 Konica Minolta colorimeter, which has a diffuse lighting system, an observation angle of 8º over the normal to the sample under study (geometry d/8), and measurement area of 8mm^2. In the measurements made, the standardized CIE 2º observer and the illumination D65 (representing the average daylight including ultraviolet radiation with correlated colour temperature 6504) were used. In order to quantify the colour, the chromatic coordinates were used in the CIE 1931 colorimetric reference system in the CIE 1976 uniform chromatic space (CIELAB). In this study, 6 measurements were made in each sample, each value being an average of 3 readings. To calculate the total colour variation (ΔE^*_{ab}), the expression proposed by Mokrzycki and Tatol [27] presented in equation 3.1 was used.

$$\Delta E^*_{ab} = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad \textbf{(1)}$$

3.4.4. Coefficient of water absorption by capillarity

This test was carried out according to standard NP EN 1925 [28]. The water absorption by capillarity was measured after 15, 30, 60, 90, 120, 180, 240 and 300 min for samples before the thermal ageing test, and 0.5, 1, 1.5, 2, 3, 4, 5, 6, 7 min for samples after the thermal ageing test. These measurements correspond to the absorption phase of the rock until the beginning of saturation (C1 in the standard). With the results were plotted in graph (g/m^2 vs s$^{0.5}$) and a line was adjusted to the first experimental points (at least 5 and a correlation coefficient equal to or greater than 0.50). The capillarity coefficient (C) in g/m^2/s$^{0.5}$ corresponds to the slope of the line.

3.4.5. Open Porosity

The tests were performed according to the standard NP EN 1936 [29]. Samples water absorption, under vacuum, until saturation was measured, in order to determine open porosity.

3.4.6. Bulk Density

The bulk density (ρ) is characterized by the relation between mass of the stone and it's total volume (including voids). It can be determined by the Archimedes method, which consists of measuring the volume of the stone through water displacement when the sample is submerged [2]. The bulk density is the ratio between the stone weight and it volume.

3.4.7. P and S wave velocity

The P and S waves travel times were measured using an oscilloscope and a signal generator measured in 3 directions (A, B, C) in each of the samples, then the respective velocities were calculated. Measurements were performed readings on all samples at the various stages of laboratory work,.

The equipment used consists of: a generator (BK Precision 4011 5MHz function generator), amplifier, oscilloscope (Rohde & Schwarz HM01002 Series 1GSa/s/1MB), and two piezometric sensors (an emitter and a receiver). In the tests, given the differences in propagation to P and S waves, different sensors were used. For the P waves, the PXRw model

piezoelectric sensors manufactured by Peng Xiang Technology Co., Ldt, which have a contact surface of 2 mm in diameter, were used, and for the S waves, the SW37 model sensors manufactured by the company Ultran, whose contact area is 9.5mm in diameter.

The waves velocity is the ratio between the length of the sample and the arrival time obtained. Through the the P waves velocity (Vp) and the S waves velocity (Vs), the elastic constants were calculated.

The equations that establish the relationships between the velocity of the elastic waves and the elastic parameters are [24], and anisotropy are:

$$\mu = \rho V_s^2 \quad (2)$$

$$\lambda = \rho(V_p^2 - 2V_s^2) \quad (3)$$

$$K = \rho(V_p^2 - \frac{4}{3}V_s^2) \quad (4)$$

$$E = \rho V_s^2 \frac{3V_p^2 - 4V_s^2}{V_p^2 - V_s^2} \quad (5)$$

$$v = \frac{V_p^2 - 2V_s^2}{2(V_p^2 - V_s^2)} \quad (6)$$

The determination samples anisotropy was performed using the method proposed by J. Guyader and A. Denis [30]:

$$dm\% = \left[2\frac{(Vp_{max} - Vp_{mean})}{(Vp_{mean} + Vp_{max})}\right]100 \quad (7)$$

$$dM\% = \left[1 - \left(\frac{2Vp_{min}}{(Vp_{mean} + Vp_{max})}\right)\right]100 \quad (8)$$

4. Results

4.1. Surface Properties

In both varieties of marble, the values of luminosity (L*) are high, while the values of the other chromatic coordinates a* and b* are practically null (Table 1 and 2). These results are in agreement with the macroscopic observation carried out, that is, a whitish colour, with a slight variation of hue in the hollow areas, which justifies values slightly below and above 0 in the component a* and b*, respectively (slight green and yellow pigmentation). After continuous exposure to SO_2, some changes in gloss and colour were observed macroscopically, confirmed with the measurements made. In terms of specular gloss, there was an average reduction of around 25% for both marble varieties. The average total colour difference (ΔE_{ab}) recorded was close to 5 units (Table 1), which was influenced especially by the coordinate L*. These same samples were subsequently subjected to the thermal ageing test. In general, there was a very slight reduction in the specular gloss values (max 13.8%). In terms of colour, a positive variation was registered in all coordinates. Was observed an increase in the red and yellow pigmentation, and increase of L*. When analysing the variations in gloss and colour of the samples only subjected to the thermal ageing and slow cooling test, it appears that the brightness of these samples has been reduced by about 25% (Table 2), compared to the values recorded initially, which corresponds to a decrease of 0.7GU in samples from Maroteira and 0.8GU in samples from Encostinha. In samples subjected to rapid cooling, the reduction was not so marked (17,7% in Maroteira samples and 21,9% in Encostinha samples).

4.2. Petrophysical properties

4.2.1. Bulk density, open porosity and capillarity

Both varieties of marble have similar values in terms of apparent density, although the marble of Encostinha has slightly higher values (Table 1 and 2). The open porosity and the capillarity water absorption coefficient of the two marble varieties are very low, below 0.40% and 0.90g/m^2.s^{0,5}), respectively.

After continuous exposure to an SO_2-rich environment, there is a slight reduction (about 18%) in the open porosity values for both marble varieties, accompanied by a slight increase in the apparent density values (Table 1). However, in the values of the water absorption coefficient by capillarity, a slight increase was observed, about 18% in Maroteira and 13% in Encostinha. Figure 2 obtained in SEM, after the samples exposer of SO_2 sub-products. It was possible to observe that Maroteira and Encostinha specimens, do not present formations or traces of SO_2 sub-products.

After the thermal ageing (Table 2) in SO_2 samples, a slight reduction in bulk density was observed in the two marble varieties, more pronounced in the samples submitted to rapid cooling. In fact, there was an average reduction of 0.71% and 1.76% in the samples of Maroteira submitted to slow and fast cooling, respectively, while in the samples of Encostinha the reduction was 1.84% in samples of the one submitted to slow cooling, and 3.31% in samples subjected to rapid cooling.

In terms of open porosity and capillarity water absorption coefficient (Table 1), a very noticeable increase was observed after the thermal aging test of samples previously subjected to continuous exposure to SO_2. The results of open porosity recorded are: 13 times higher in samples from Maroteira AL; 21 times higher in samples from Maroteira AR; 17 times higher in the samples from Encostinha AL; and 12 times higher in Encostinha AR samples, compared to samples contaminated with SO_2. In the capillarity water absorption coefficient, the increase was higher. The registered capillarity water absorption coefficient, compared to samples contaminated with SO2, is: i) about 235 times higher in samples from

Maroteira AL; ii) about 165 times higher in the samples of Encostinha AL; iii) about 296 times higher in samples from Maroteira AR; and iv) about 310 times higher in the AR samples.

With regard to the reference samples (Table 2) of both marble varieties and after performing the thermal aging test, there is a marked increase in the open porosity (about 10 times) and the absorption coefficient of water by capillarity. In the two marble varieties, a reduction in apparent density was observed, corresponding to 2.25%, except in the samples of Maroteira submitted to slow cooling, which was 1.36%. Compared to the variation observed in open porosity, the increase observed in the water absorption coefficient by capillarity was much higher: in Maroteira samples the results obtained in slow cooling are 171 times and in rapid cooling 229 times higher, however in samples from The results were close to 1.5 times higher, compared to Maroteira..

4.3. Elastic waves velocity

It is possible to verify that the P and S velocity, Vp /Vs and the elasticity parameters do not differ much in the two marble varieties (Table 1 and 2).

Table 1– Average value of surface and petrophysical properties, elastic waves, elastic parameters and anisotropy, of specimens 1-16.

	Maroteira				Encostinah			
	Reference	SO^2	Thermal (SC)	Thermal (RC)	Reference	SO^2	Thermal (SC)	Thermal (RC)
60° (GU)	2,7	1,9	2,0	1,9	2,7	2,0	1,9	1,7
*ΔE*ab*	-	5,40	16,81	12,35	-	4,86	12,70	89,54
L*	88,14	79,68	94,71	93,61	91,03	81,96	94,43	0,87
*a**	-0,82	-0,96	0,13	0,56	-0,74	-0,84	0,36	6,19
*b**	2,16	3,26	4,22	5,02	1,82	2,86	4,84	9,16
Vp (m/s)	4577,45	4489,46	965,98	887,16	4452,04	4502,67	1269,92	1134,61
Vs (m/s)	2695,34	2703,47	636,52	558,99	2680,15	2723,92	825,54	733,45
Vp/Vs	1,70	1,66	1,52	1,61	1,66	1,65	1,54	1,55
v	0,23	0,21	0,10	0,14	0,21	0,21	0,13	0,13
μ 10^{10} (Pa)	1,98	1,99	0,12	0,09	1,96	2,01	0,20	0,16
K 10^{10} (Pa)	3,07	2,85	0,11	0,11	2,80	2,83	0,20	0,17
E 10^{10} (Pa)	4,86	4,81	0,26	0,21	4,75	4,86	0,45	0,35
dm (%)	3,32	3,11	6,52	9,14	3,50	2,88	23,54	18,93
dM (%)	7,70	7,46	32,98	23,73	4,10	3,46	23,28	21,51
ρ (kg/m^3)	2685,12	2763,94	2667,87	2635,68	2728,37	2732,55	2732,55	2732,55
po (%)	0,24	0,15	2,66	3,20	0,24	0,15	0,15	0,15
C (g/m².s^{0,5})	0,46	0,38	81,66	117,05	0,49	0,32	0,32	0,32

Table 2 – Average value of surface and petrophysical properties, elastic waves, elastic parameters and anisotropy, of specimens 17-32.

	Maroteira			Encostinha		
	Reference	Thermal (SC)	Thermal (RC)	Reference	Thermal (SC)	Thermal (RC)
60° (GU)	2,7	2,1	2,1	2,7	2,2	2,0
*ΔE*ab*	-	84,79	86,00	-	82,84	84,36
L*	88,14	1,12	1,07	91,03	1,09	1,04
*a**	-0,82	3,75	3,80	-0,74	4,75	3,80
*b**	2,16	6,49	7,83	1,82	13,18	11,33
Vp (m/s)	4577,45	1008,08	908,47	4452,04	1189,98	1104,12
Vs (m/s)	2695,34	639,25	560,24	2680,15	791,00	723,31
Vp/Vs	1,70	1,58	1,42	1,66	1,50	1,53
v	0,23	0,15	0,13	0,21	0,10	0,12
μ 10^{10} (Pa)	1,98	0,12	0,10	1,96	0,17	0,14
K 10^{10} (Pa)	3,07	0,13	0,10	2,80	0,16	0,14
E 10^{10} (Pa)	4,86	0,27	0,22	4,75	0,37	0,32
dm (%)	3,32	9,01	15,35	3,50	19,45	21,58
dM (%)	7,70	32,29	33,34	4,10	19,88	22,29
ρ (kg/m^3)	2685,12	2637,35	2707,07	2728,37	2643,35	2653,97
po (%)	0,24	2,60	3,10	0,24	2,49	2,93
C (g/m².s^{0,5})	0,46	93,79	123,13	0,49	66,16	89,97

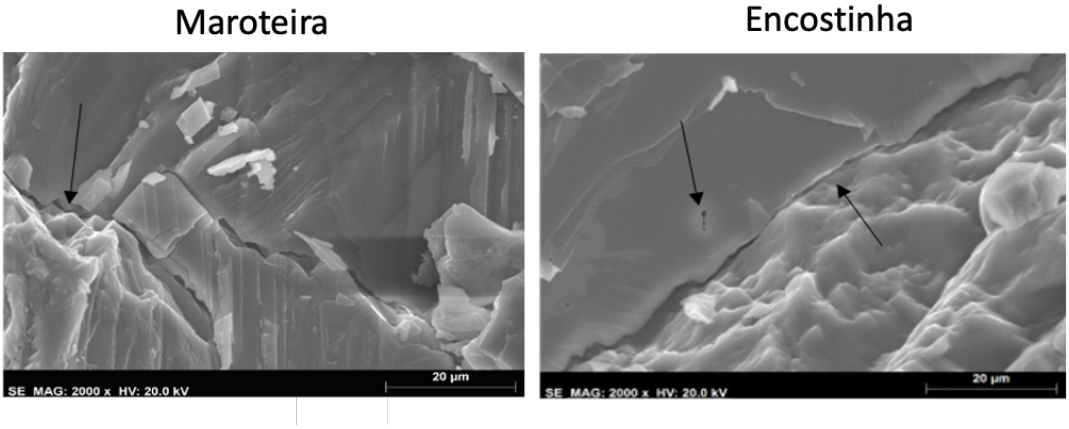

Figure 2– SEM images of M15 and E15 specimens after SO_2 ageing showing small voids and microcracks.

The dispersion observed in the values of velocities and elasticity parameters is related to the fact that some samples present a direction with slightly anomalous velocity, that is, these marble varieties have some anisotropy. The results obtained in the reference samples, referring to the anisotropy indices, are relatively low. It should also be noted that both varieties have a very high standard deviation, greater than 50% in samples from Maroteira and above 70% in samples from Encostinha.

The exposure to SO_2 (Table 1) did not cause significant changes in Vp, Vs, Vp/Vs and elasticity parameters, in the two marble varieties, since the observed changes were lower at 5% (with the exception of K and v, which showed a reduction of less than 10%). In the results regarding the anisotropy of the samples from Maroteira and Encostinha, no significant changes were observed in the anisotropy indexes (less than 25%).

After carrying out the thermal aging test on samples previously exposed to SO_2, there was a marked reduction in the velocity of propagation of elastic waves (over 70%). The velocity of the P waves was slightly reduced, compared to the velocity of the S waves (about 2.5%), in the two marble varieties. The elastic parameters were the variables that suffered the greatest reduction (greater than 90%), with the exception of the poisson's ratio. In the values referring to the poisson's ratio, of the samples of Maroteira, a reduction of 51% was observed in the samples submitted to slow cooling and 38% submitted to rapid cooling. In the Encostinha samples, the reduction observed in the values referring to the poisson's ratio was 30% and 43%, in the slow and fast cooling, respectively.

Both marble's varieties have negative values in the poisson's ratio and lamé's ratio (Table 1). In the remaining parameters, it is possible to observe a clear distinction between the average values in the samples of Maroteira and Encostinha, mainly in the slow cooling, since the parameters of Encostinha are almost double, compared to the values of Maroteira.

Anisotropy index results also showed an exponential increase after the thermal aging test. In the samples of Maroteira, the anisotropy rates increased about four to six times, compared to the values of the samples after SO_2 exposure. In the samples from Encostinha, the variation, in relation to the values of the samples after SO_2 exposure, was even greater. In samples submitted to slow cooling it was about 10 times in dM and 18.5 times in dm while in samples submitted to RC, the increase was approximately 13 times in dM and 37 times in dm.

In what concerns to the reference samples submitted to the thermal aging test (Table 2), it can be seen that the P and S waves velocity of the samples of Maroteira and Encostinha suffered a reduction greater than 70%. The reduction observed in P waves was about 2.5% higher than the reduction in S waves, which influenced Vp/Vs (reduction between 7% and 14%). The elastic parameters showed an average reduction of more than 90%, with the exception of v, in the two marble varieties. The values referring to v show a reduction between 41% and 43%. Due to the reduction observed in the poisson's ratio and Lamé's coefficient, some samples of Maroteira and Encostinha show negative values. The rapid cooling, caused a greater reduction in all variables, except in the poisson's ratio, both in the samples of Maroteira and Encostinha.

The thermal ageing test in the reference samples, also caused a sharp increase in the anisotropy rates. In the samples of Maroteira (SC and RC), the increase was approximately four times for the dM and eight times for the dm. In the samples from Encostinha the increase was higher compared to the samples from Maroteira. Anisotropy rates in Encostinha samples compared to reference samples are about 8 times higher in samples submitted to SC and 9 and 30 times higher in dM and dm, respectively, in samples submitted to SC.

5. Discussion

The two marble varieties have a low specular gloss (less than 3.5GU) associated with the fact that the samples did not have any type of additional finish,

only that associated with the preparation of the specimens. Similar results were obtained by Sarici [20], on carbonated rocks.

After the exposure test to an atmosphere rich in SO_2, no traces or formations of SO_2 subproducts were observed. However, there were changes in the gloss of the sample, visible to the naked eye and confirmed by the measurements (25%, equivalent to 0,7GU). In colour, there was a slight variation influenced by the variation in the L* coordinate.

In the thermal ageing test there was a reduction in the gloss of the reference samples (25%), however in the samples previously exposed to an atmosphere rich in SO_2 the variation was lower (max. 13,8%). In the reference samples, the anisotropic growth of calcite was the deterioration mechanism of the marble that led to the loss of gloss [20]. In terms of colour, an increase in yellow and red pigmentation in all sample was observed. This behaviour was also studied by Ozguven and Ozcelik [8] when heating carbonated rocks to 600ºC. The colour change in the samples were essentially due to the presence of other mineral components in the marbles. The changes observed in the L* coordinate in the previously contaminated samples and in the reference samples were distinct. In the reference samples there was a reduction, while in the samples contaminated with SO_2 there was a positive variation. In the tests performed by Ozguven and Ozcelik [8] and Sarici [20], the thermal test caused different types of changes in the L* chromatic coordinate. In the first work mentioned, the marble test pieces showed a small positive variation ($\Delta L^* < 5$) up to 400ºC, and a negative one up to 600ºC, while in Sarici's work [20] a slight increase was observed in the aging and thermal shock test .

The values corresponding to the apparent density of the reference samples, are in accordance with the values stipulated for Portuguese marbles [31]. The open porosity and water absorption coefficient by capillarity of the reference samples and after exposure to an atmosphere rich in SO_2 are very low, which is in agreement with the results obtained in the of the elastic waves velocity. In the case of open porosity, the values observed in the reference samples are similar to the values reported by several authors [31] but the capillarity coefficient values are slightly higher [24]. Regarding the results of the P and S waves velocity of the reference samples, there was some heterogeneity between the three orthogonal directions of the samples. This behaviour is reflected in the result of the anisotropy indices. Published works in which marbles were studied, several obtained values between 4000m/s and 5500m/s [22,25], which are similar to the values observed in this study. The elastic parameters observed in the reference samples are within the ranges of values proposed by: i) Sharma [19] for the poisson's ratio (ν) and Vp/Vs in crystalline rocks; ii) Telford et. al. [32] for the μ, K and E. Anisotropy rates are slightly higher than the results observed by Murru *et al.*[19] for marble (SMM marble dM = 1.77% and dm = 1.36%), which can be explained by the heterogeneity observed in the Vp.

After the SO_2 exposure test, there was a slight reduction in open porosity and a slight increase in the water absorption coefficient by capillarity. However, no significant changes were observed in the P and S waves velocity, elastic parameters and anisotropy indices. These changes indicate that the variations observed in open porosity and capillary water absorption coefficient were not significant.

Anisotropic expansion of calcite minerals is one of the main mechanisms of deterioration of carbonated rocks subject to thermal aging [15]. This behaviour can be observed at reduced temperatures, but with increasing temperature the growth rate of the mineral increases [15]. In low porous rocks, an increase in stresses is generated, [24] as a consequence, the rock tends to develop microcracks and voids to accommodate the changes caused in minerals [15]. This behaviour causes a slight decrease in density, as was observed in the reference samples and in the samples exposed to SO_2, which probably correspond to small losses of material in the corners of the samples [1] and detachment of minerals.

Published works, such as Martinho and Dionísio [1] (limestone), Ozguven and Ozcelik [24] (marble), Sippel *et al.*[15](marble) report a high level of degradation in carbonated rocks subjected to 600ºC. The observed changes are generally due to an exponential increase in voids accompanied by a drastic reduction in elastic parameters and, consequently, elastic waves velocity.

In the work carried out by Vagnon *et al.*[24]and Yavuz *et al.* [23] similar results were observed in relation to open porosity (po ~ 2.5% and po ~ 3%). The changes observed in porosity are greatly influenced by the formation of voids with capillary diameters like in Murru et al. [19]. The increase in porosity and capillarity of the rocks is accompanied by a reduction in the elastic waves velocity, due to the decrease or loss of cohesion between the grains [24], which causes a delay in the propagation of the elastic waves [33].. For example: i) Yavuz *et al.*[23] observed a reduction in Vp (about 70%) in marbles heated to 500ºC; and ii) Murru *et al.*[19] also observed an average 70% reduction in Vp, and an increase in heterogeneity in the samples; iii) Vagnon et al.[24] observed a slightly more pronounced reduction in Vp in relation to Vs. In the study by Murru *et al.*[19] a heterogeneity in the variation of Vp was also observed, which caused an increase in the anisotropy indices, as was observed in this study. This behavior is justified by the formation of micro-cracks with a preferential direction, which causes different levels of degradation in the rock [24]. The dm was the index that suffered the greatest variation

because the difference between the lower velocity and the average velocity is bigger. The degradation of the rock is also reflected in the reduction of elastic parameters. Several authors have observed similar changes, such as: i) reduction of E greater than 90% [19]; ii) reduction of Vp/Vs and poisson's ratio (v) [24]; iii) negative v [24]. The negative values obtained in the poisson's ratio (v <0) correspond to auxetic materials (material expands, in the direction perpendicular to which the force is applied) [1]. This behavior was influenced by the reduction of Vp/Vs, which consequently caused a reduction in the v. Even though these values are not accepted for isotropic materials, the same behaviour was observed in limestones [1] and marbles [24] in published works. The hypotheses that seems to fit this study was proposed by Vagnon *et al.* [24]: the weak connection between the minerals, caused by the microcracks, eventually produces unconsolidated material that under tension has a plastic behaviour [24]. This hypothesis is the one that best applies to the studied samples, because some Vp values were lower than 1000m/s, which correspond to unconsolidated material such as soil and sand [33].

Regarding the type of cooling, slightly lower values were observed in rapid cooling, due to the thermal shock (600ºC -> 20ºC), caused by the immersion of the rock in water [5], which causes a more pronounced deterioration of the rock.

6. Conclusion

The development of this dissertation aimed to contribute to the knowledge of the performance of marble when subjected to two types of accelerated aging. In this study, two varieties of marble (Maroteira and Encostinha) were subjected to continuous exposure to SO_2 and thermal ageing (temperature of 600ºC). The influence of the type of cooling (slow or fast) after exposure to a temperature of 600ºC was also analysed.

The continuous exposure of SO_2 caused changes only on the surface of the samples due to the fact that both marble varieties have low porosity and capillarity, which protected both stones against the action of SO_2. The conditions of humidity, temperature and the lack of other polluting gases, may also have acted as a preventive factor in relation to the formation of gypsum, since this was not found in the samples. Regarding the studied surface properties, a great reduction in brightness was observed, visible to the naked eye. In the colour data, the observed changes were controlled by variations in the luminosity of the samples. The changes observed in petrophysical properties, elastic waves velocity, elastic parameters and anisotropy rates are negligible.

The results obtained in the thermal aging test of the samples contaminated with SO_2, were similar to the results obtained in the reference samples, except for the results related to gloss. The two varieties of marble showed that the high temperatures induced noticeable changes in all the properties studied. In the surface properties, there was an increase in red pigmentation and intensification of yellow, which are not visible to the naked eye. The changes observed in the gloss of the samples previously contaminated with SO_2, are very small. However, in the reference samples there was a significant reduction in brightness, mainly in samples subjected to slow cooling.

Heating at 600ºC also caused a sharp increase in open porosity and in the capillarity coefficient. This behaviour is due to the development of microcracks caused by the anisotropic thermal expansion of calcite. The elastic waves velocity (Vp and Vs) and the elasticity parameters were highly influenced by this behaviour, with a marked decrease in the values of these parameters. The dispersion of the values of Vp, Vs and the elasticity parameters show that the heating accentuated the anisotropy of the two marble varieties. In the samples of Maroteira the changes were slightly more accentuated.

Regarding the type of cooling, the changes observed in the surface properties were not significant. However, there were differences in open porosity, capillarity coefficient, P and S waves velocity and, consequently, in elastic parameters and anisotropy. Rapid cooling caused an increase in open porosity, a coefficient of water absorption by capillarity and anisotropy indices, and a decrease in the propagation velocity of elastic waves and elastic parameters.

After completing this dissertation, some suggestions for future developments are highlighted to complement the work developed:

1. Study of the performance of a marble subject to saline contamination and thermal aging;

2. Study of the performance of a calcite marble and a dolomitic marble, exposed to an atmosphere rich in SO_2 and high temperatures;

3. Study of the performance of a marble and a limestone, exposed to an atmosphere rich in SO_2 and high temperatures;

4. Study of the effect of atmospheric contaminants (SO_2, NOx, CO_2) after a fire on a marble and a limestone.

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