

Step-by-step reduction of travertine porosity using low soluble inorganic salts

Rihana Terziu^{*1,3}, Mihane Dauti², Kledi Xhaxhiu², and Edlira Baraj³

¹ Department of Chemistry, Faculty of Natural Sciences, Albania, E-mails: mihane.dauti@fshnstudent.info (M.D.); kledi.xhaxhiu@unitir.edu.al (K.X.)

² Department of Chemistry, Faculty of Mathematical Engineering and Physics Engineering, Albania, E-Mail: edlirabaraj@yahoo.co.uk (E.B.)

³ Department of Pharmacy ALDENT University, Albania, E-mail: rihana.terziu@gmail.com (R.T.)

*Author to whom correspondence should be addressed; E-Mail: rihana.terziu@gmail.com

Tel.: 00355692744571

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In the present study the treatment by three chemical solutions (5%) of travertine is considered. The overall process assumes the structural pore reduction due to the continuous controlled crystallization of low soluble inorganic salts such as calcium sulfate and calcium oxalate. Travertine samples of monolithic blocks of Turkish origin previously cut in form of parallelepiped blocs with length of 25 ± 1 mm, width and thickness of 7 mm are employed in this study. The prepared samples were dipped in distilled water for 2-3 hours followed by drying up to 6 hours at 70 °C, 6 hours at 100 °C and 12 hours to 125 °C. Consolidation of travertine samples is carried out by treatment in three stages: the first stage involves treatment with calcium acetate ($\text{Ca}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$), the second stage involves the treatment with ammonium sulphate ($\text{NH}_4)_2\text{SO}_4$ followed by the third stage includes the treatment with ammonium oxalate ($\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The decreasing of porosity and surface area is monitored by continuous gravimetric measurements followed by gas- and mercury porosimetry measurements. After each treatment, the sample weight increases and its porosity decreases. All samples were subject of: 10, 20, 30, 40, 50 treatments respectively.

Keywords: Gas porosimetry, travertine, gravimetric measurements, ammonium oxalate, chemical treatment.

1. Introduction

Travertine is a sedimentary rock, limestone widely used for building purposes [1]. For this reason protection of travertine cultural objects and other stone types is an ongoing concern in the international scale, due to the great value that they carry. Limestone is one of the most present in nature formed because of the interaction of calcium carbonates with water. Travertine consists mostly of aragonite and calcite and is formed as a result of supersaturated water and geothermal alkaline with a partial pressure of carbon dioxide [2]. The color of travertine depends on oxides, which has

built-in (which happens quite easily, being by nature a fairly porous stone). The natural color of travertine varies from milky white to hazelnut because of the nuances from yellow to red. When pure, travertine is white, but often is brown to yellow due to impurities. In general travertine is a solid and flexible stone. Travertine could be used in both interior and exterior of buildings and in some cases used in sculpture. As a porous material, it suffers from the same problem as marble and is often subject of micro- and macro-structure disruption due to water penetration/condensation in its pores. If its pores are as small as nano-size orders the capillary condensation process of water vapors

happens. The reasons for deterioration and degradation of stone are mainly erosion and weathering. The main aggressive elements are water and rain [3]. Water that penetrates the pores of the stone interior due to the capillary forces has adverse effects both physical and chemical. It assumes that in the pores of the stone biological effects occur as well [4]. It is very important that the applied materials should have a good penetrating ability, good use on the construction site and also to be matched with biological requirements [5]. In the present study we consider the pore volume minimization due to the continuous treatment by three chemical solutions of 5% [6]. The overall process assumes the structural pore reduction due to the continuous controlled crystallization of low soluble inorganic salts such as calcium sulfate and calcium oxalate. Theoretically, the overall process is completed when the pore volume approaches zero. Very important in this process is the fact that the material which will be deposited is similar to the pore material, leading therefore to a better adhesion. The decreasing of porosity and surface area is monitored by continuous gravimetric measurements followed by gas- and mercury porosimetry measurements. After each treatment, the sample weight increases and its porosity decreases. In our study all samples were subject of: 10, 20, 30, 40, 50 treatments respectively.

2. Results and Discussion

Travertine samples of monolithic blocks of Turkish origin previously cut in form of parallelepipedic blocs with length of 25 ± 1 mm, width and thickness of 7 mm are employed in this study. A total of 36 samples are prepared in 5 sets and 1 white test. Each set contains 3 samples of travertine shown by Figure 1.

This work aims to determine the structural changes that have occurred in samples processed realized through: measuring the samples density and porosity before and after processing. Density is a direct reflection of the material porosity. The higher the density, the lower is the porosity; it means that they are in inverse proportion to one another. The density values



Figure 1: The samples of travertine.

for the marble samples are shown in Table 1 (Figure 1A). The results presented in graphical show that porosity of travertine (Figure 2B) is higher than the marble samples because of lower density, matching well with theory. Besides determining the density the samples porosity measurement before and after treatments were performed. The obtained isotherms reveal the presence of meso and macro-pores, which is confirmed by the respective hysteresis. Gas-porosimetry is used to define the micro-pores with radiuses: $r < 2$ nm [7]. According to the adsorption isotherms, the number of moles adsorbed at a certain pressure is determined. In the micro pores a significant adsorption growth occurs due to the surface forces overlap. The continuous increasing of the gas pressure leads to a considerable activity of capillary forces in the transitional pores. Compared to the flat surfaces, the micro and macro pores show a considerable adsorption. The later increases with the decrease of the pore sizes and occurs at lower pressures. Based on nitrogen adsorption measurements of this study, the adsorbent parameters are defined, such as: the pore volume, specific surface, pore radius and integral and differential pore distribution. The pore volume and specific surface values of the travertine treatments number, based on nitrogen adsorption measurements are shown in Table 2. In our study, various curves are depicted, in order to have a clear view of the material's porosity. The increase of the height and the sharpness of the differential pore dis-

tribution curve (Figure 1C) correspond to a narrow pore size interval. Therefore, a change of the shape of differential pore distribution curve is directly related to the changes of the material's porosity. This fact is obvious based on the curves of Figure 1C. Based on the number of treatments and the respective pore volume plots, his amount of material adsorbed can be calculated according to the following equation:

$$V_{\text{cum}} = n_{\text{ads}} * V_{\text{max}} \quad (1)$$

As shown by Figure 2A, with the increasing of the number of chemical treatments, the overall pore volume decreases. During this trend, some anomalies are observed, especially after 20 treatments (Figure 2B), where the sample porosity slightly increases due to the temporary increase of the porosity as a consequence of the formation of big crystals within the existing pores. These "new pores" are filled up with depositing material due to the latter treatments. Using the volumetric methods with cylinder scalable for the travertine samples we collected the following data summarized in Table 1:

Number of treatments	0	10	20	30	40	50
m (g)	2.9	3.6	2.3	2.2	3.2	1.1
V (cm ³)	1.1	1.5	0.98	0.9	1.4	0.5
d (g/cm ³)	2.68	2.42	2.37	2.46	2.30	2.28

Table 1: Density values for the travertine samples from 0 to 50 treatments.

3. Experimental Section

The prepared samples were dipped in distilled water for 2-3 hours followed by drying up to 6 hours at 70 °C, 6 hours at 100 °C and 12 hours to 125 °C. In the present study the treatment by three chemical solutions (5%) of travertine is considered. Consolidation of travertine samples is carried out by treatment in three stages: the first stage involves treatment with 5% calcium acetate solution (Ca(CH₃COO)₂ • H₂O), the second stage

involves the treatment with 5% ammonium sulphate solution (NH₄)₂SO₄, followed by the third stage includes the treatment with 5% ammonium oxalate solution (NH₄)₂C₂O₄ • H₂O. After each treatment, the samples drying for 30 minutes to 70 °C. The formed calcium oxalate formed inside the pores highly insoluble; its solubility in water at a temperature of 13 °C is 0.00067g for 100 g water [8]. All samples were subject of: 10, 20, 30, 40, 50 treatments respectively. Before starting the gas adsorbed amount measurement, the device evacuation through the pump for about 45-50 min it is done. It is closed the sample vessel through the tap (R1) and is weighed in an analytical scales with a precisely of 0.0001 mg. The samples are inserted in the vessels, and connected with the device and last are inserted into a heating stove with a temperature of 150 °C. It is held there for 60 min, meanwhile continuing the device evacuation, also it is complete the sample degassing. After degassing the sample is accurately weighted. After this the sample is reconnected with the device and it is drowned in Dewar vessel, filled with liquid nitrogen. As last procedure, the entire device evacuation is done, until the Piran-pressure gauges shows a constant value. At these conditions the gas

adsorption starts. Nitrogen (at 77K) is the more suitable absorbent for determining the specific surface standard. The container tap is closed and the gas nitrogen is inserted in the reservoir under a specific pressure. After the gas pressure measurement in the reservoir is done, it is opened the sample vessel tap as consequence the gas is inserted inside and we wait until the balance is established. The needed time to achieve balance is 5-10 minutes. The pressure indicator at Pirani pressure gauge is recorded, which represents the first point in the adsorption isotherm. The procedure is repeated by raising the pressure, until the day atmospheric pressure is reached. After this moment the pressure does not change, and any gas amount added

in the sample vessel it returns in the liquid state. After completing the adsorption process, the desorption process begins by reducing the nitrogen pressure within the reservoir. The gas absorbed amount is measured by glass devices. In similar way the desorption isotherm is recorded while setting the sample under vacuum. The obtained data, by this process lead to the adsorption and desorption isotherms and to the calculations of the parameters of the adsorbent, the pores volume, specific surface, and pores integral and differential distribution.

4. Conclusions

In this study travertine samples of monolithic blocks of Turkish origin was investigated. While treating them by three chemical solutions (5%) in order to form insoluble precipitates inside them. All samples were subject of: 10, 20, 30, 40, 50 treatments respectively. After each treatment, the sample weight increases and its porosity decreases. Our consequent measurements revealed progressive sample weight increase within 50 treatments. These sample weight increase occur due to the depo-

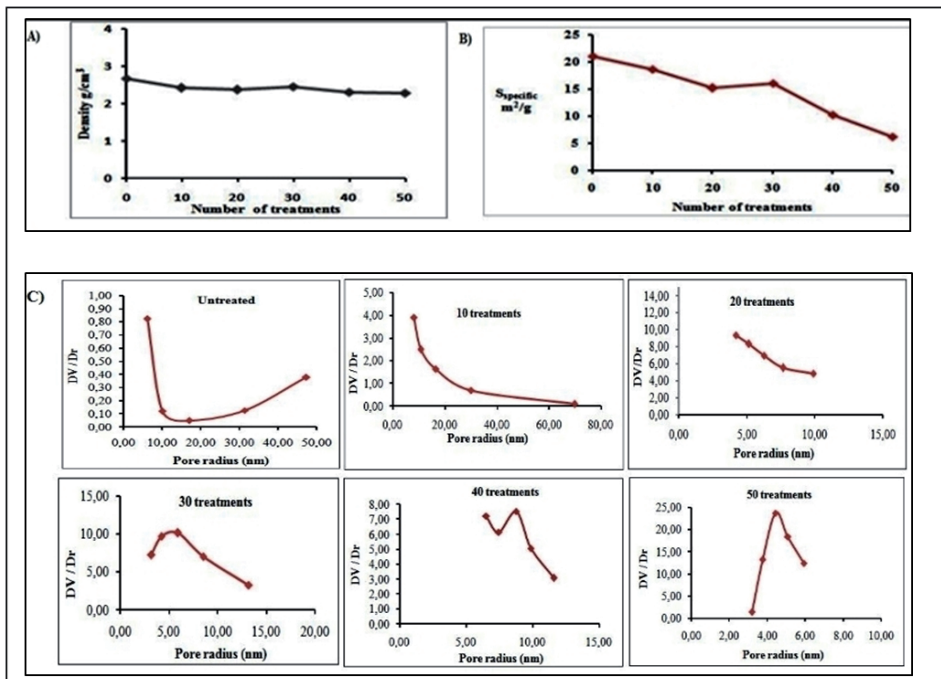


Figure 1: A) Density values for the travertine samples from number of treatments. B) Specific surface by the number of treatments for travertine C) Differential distribution of pore size for travertine.

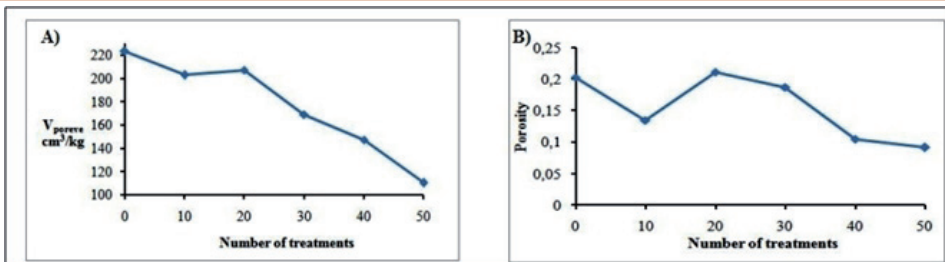


Figure 2: A) The increasing of the number of chemical treatments, the overall pore volume decreases. B) The porosity of the travertine treatments number.

sition of the insoluble substances inside and in the samples surface. Optimal conditions for samples drying are: $T = 70\text{ }^{\circ}\text{C}$ and time 30 min. During this work we determined the structural changes as a consequence of the treatments by: measuring the samples density and porosity before and after processing. The increasing of the sample density is directly related to the decrease of their porosity showing thus an inverse proportional relation to each other. Travertine samples adsorption-desorption isotherms measurement proved capillarity condition $P_{eq} > 0.8P_0$. Based on the differential curve it clearly shows that the untreated travertine samples pores distribution varies from 9-10 nm. Mean while for the samples with 10, 20, 30, 40 and 50 treatments, the pores differential distribution by size resulted respectively, 9-11 nm, 4-5 nm, 5-6 nm, 8-9 nm and 4-5 nm (Figure 1C). The displacement of the samples radius up to 40 treatments gradually avoids the capillarity effect, reducing therefore the chance of structural damages that may result from temperature changes. From the first 10 treatments resulted a decrease in the samples volume (Figure 2A). While within the interval of 10 to 20 treatments, the sample volumes increase unlike from the expectations. This is probably of the large crystals and their cavities resulting at this stage of treatment. The increase of the number of treatments reduces the cavities, filling them by smaller crystals and changing thus their geometry. After 50 treatments, the samples pores volume resulted the lowest compared to the previous treated samples. With this method we confirmed that by increasing of the number of chemical treatments an overall reduction of the travertine sample porosity can be achieved.

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Conflicts of Interest

The authors declare no conflict of interest.

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