Simple chemical treatments for a successful consolidation of marble objects
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This study focuses its attention on the chemical treatment of marble samples in order to create conditions for the protection of cultural heritage objects that consist of these materials. Water penetration, or its vapor condensation in the pores of these materials leads to the formation of crystalline ice embryos, which depending on the environmental conditions create internal tensions and disrupt their micro-structure. Their consolidation was carried out by a three stages treatment, starting with 5% calcium acetate solution for 60 minutes at 200 °C. The second stage occurs after a draining step at 700 °C and for 30 min, and involves the samples treatment with 5% ammonium sulphate solution. After the application of the same draining procedure as previous, it followed with the third stage which includes the treatment with ammonium oxalate, followed by the same draining procedure. The marble samples were subjects of: 10, 20, 30, 40, and 50 treatments respectively, revealing each time weight increase. Their porosity and specific surface area, assessed by gas porosimetry measurements, continuously decrease at until the last treatment.

Keywords: Gas Porosimetry, marble, ammonium oxalate, chemical treatment, protection, porosity

1. Introduction
Protection of cultural objects of marble, travertine and other stone types is an ongoing concern in the international scale, due to the great value that they carry. Marble is a material that is found constantly in the building, whether for structural purposes (columns, floors, etc.) or decorative (friezes, reliefs, statues, etc.). Marble is a noble material with a special charm and easily processed, but is sensitive to changes in natural atmospheric agents or others resulting from urban and industrial activity. Marble is formed through a process of metamorphic sedimentary rocks such as limestone and dolomite[1]. The marble is a small porous material, which is constantly building, whether for structural purposes or decoration. The marble colors depend on the presence of impurities. If its pores are as small as nano size orders the capillary condensation process of water vapors happens. Given its abundant presence in buildings with historic and artistic value, this has led to a particular interest in understanding the processes of marble changes as its preservation and restoration. The reasons for deterioration and degradation of stone are mainly erosion and weathering. The main aggressive elements are water and rain. About 15 years ago the first experiments were carried out in the Scientific Laboratory of the OpificiodellePietreDure in Florence in order to test the possibility of a new approach to the problem of protecting marble and limestone monuments and artifacts exposed outside from acid attack [2]. 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 [3]. The materials used until now to preserve marble include polyesters, acrylics, urethanes, silicones, alkoxysilanes and other organic/inorganic polymers [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 this study we consider the penetration of solutions with concentrations of 5% [6] in them, and the precipitation of the dissolved substances from them, onto the pore surfaces. In this way, crystallization centers are formed, which grow further as a consequence of the deposition of cations and anions present. 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. This study is oriented on the restoration of buildings and monuments of art that as a result of the impact of external factors have suffered damage of their structure, being subjected to “micro erosion”. In our study we considered the chemical processing of the marble samples, and performed characterization of their porosity by gas porosimetry, to determine the effectiveness of the consolidation method. According to the acquired results in our laboratory, we draw conclusions and give recommendations for further applications of this procedure in the field of protection of heritage and cultural marble objects. The essential of our sample treatment is the obtaining of insoluble precipitates inside the pores, which is tracked by fast sampling gravimetric determination as well as by porosimetric method.

\[ V_{\text{cum}} = n_{\text{ads}} \cdot V_{\text{max}} \]  

(1)

During our experiments using the volumetric methods with cylinder scalable we collected the following data summarized in Table 1.

<table>
<thead>
<tr>
<th>Number of treatments</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>m (g)</td>
<td>3.33</td>
<td>3.74</td>
<td>3.85</td>
<td>3.76</td>
<td>3.74</td>
<td>3.65</td>
</tr>
<tr>
<td>V (cm³)</td>
<td>1.2</td>
<td>1.3</td>
<td>1.3</td>
<td>1.4</td>
<td>1.4</td>
<td>1.3</td>
</tr>
<tr>
<td>d (g/cm³)</td>
<td>2.7</td>
<td>2.8</td>
<td>2.9</td>
<td>2.6</td>
<td>2.6</td>
<td>2.8</td>
</tr>
</tbody>
</table>

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

**Figure 1:** A) Density values for the marble samples from number of treatments. B) Specific surface by the number of treatments for marble. C) Differential distribution of pore size for marble.
Table 2: The pore volume and specific surface values of the marble treatments number.

<table>
<thead>
<tr>
<th>Number of treatments</th>
<th>(V_{pore}) cm(^3)/kg</th>
<th>(S_{specific}) m(^2)/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>173.68</td>
<td>8.23</td>
</tr>
<tr>
<td>10</td>
<td>171.92</td>
<td>6.91</td>
</tr>
<tr>
<td>20</td>
<td>201.67</td>
<td>5.93</td>
</tr>
<tr>
<td>30</td>
<td>134.75</td>
<td>6.17</td>
</tr>
<tr>
<td>40</td>
<td>125.85</td>
<td>3.43</td>
</tr>
<tr>
<td>50</td>
<td>98.34</td>
<td>2.74</td>
</tr>
</tbody>
</table>

As shown by Figure 2 A, 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, 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. This fact is obvious on Figure 2B. These “new pores” are filled up with depositing material due to the latter treatments.

3. Experimental Section

For the marble treating experiments, marble slabs that to build the pyramid of the cultural center of Tirana during 1986-1988 in Albania were used. The marble samples employed in this study are cut in parallelepiped form blocs with lengths of 25 ± 1mm, widths and thicknesses of 7 mm. To remove the attached dust, the prepared samples were dipped in distilled water for 2-3 hours followed by drying to 6 hours at 70 °C, 6 hours at 100 °C and 12 hours to 125 °C. The sample consolidation was carried out by a three stages treatment, starting with 5% calcium acetate solution \(Ca\,(CH_3COO)_2\) \(\cdot\) \(H_2O\) for 60 minutes at 20°C. The second stage occurs after a draining step at 70°C and for 30 min, and involves the samples treatment with 5% ammonium sulphate solution \((NH_4)_2SO_4\). After the application of the same draining procedure as previous, it followed with the third stage which includes the treatment with ammonium oxalate \((NH_4)_2C_2O_4\) \(\cdot\) \(H_2O\), followed by the same draining procedure. The marble samples were subject of: 10, 20, 30, 40, and 50 treatments respectively, revealing each time weight increase.

The steps of this treatment can be explained by the following reactions:

1. \(Ca\,(CH_3COO)_2\) + \((NH_4)_2SO_4\) \(\rightarrow\) \(CaSO_4\) + 2\(NH_4\)C\(_3\)H\(_2\)O\(_2\)

2. \(CaSO_4\) + \((NH_4)_2C_2O_4\) \(\rightarrow\) \(CaC_2O_4\) + \((NH_4)_2SO_4\)
4. Conclusions

The marble sample from the slabs of the Tirana Cultural Centre “The Pyramid” was used. The marble samples consolidation is done in three stages treatment starting with 5% calcium acetate solution $(\text{Ca} \ (\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O})$ for 60 minutes at 20 °C. The second stage occurs after a draining step at 70 °C and for 30 min, and involves the samples treatment with 5% ammonium sulphate solution $(\text{NH}_4)_2\text{SO}_4$. After the application of the same draining procedure as previous, it is followed with the third stage which includes the treatment with ammonium oxalate $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$, followed by the same draining procedure. The marble samples were subjects of: 10, 20, 30, 40, 50 treatments respectively, revealing each time weight increase. By applying the method of marble samples accurate treatment and by following the progress of weight increase it is reached in the parameters optimization, such as: the optimization the drying time after each impregnation and the optimization of the treatment number based on the gravimetric method. Our consequent measurements revealed progressive sample weight increase within 50 treatments. These sample weight increase occur due to the deposit of the insoluble substances inside and in the samples surface.
Optimal conditions for samples drying are: $T = 70 \, ^\circ C$ 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 (Fig.1A and Fig.2A). Marble samples adsorption-desorption isotherms measurement proved capillarity condition $P_{eq} > 0.8P_0$. Based on the differential curve it clearly shows that the untreated samples pores distribution varies from 9-10 nm. Thus for samples with 10, 20, 30, 40 and 50 treatments, the pores differential distribution by size results respectively within the range 8-9 nm, 9-11 nm, 13-16 nm and 4-5 nm. Porosity displacements of the samples radius are observed after 40 treatments, showing a gradual reduction of the capillary effect reducing therefore the structural damages that may result from temperature changes. From the first 10 treatments resulted a decrease in the samples volume (as theoretically expected). While within the interval of 10 to 20 treatments, the sample volume 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.

**References**