Increase of Durability of Carbonate Stones Consolidated with Nanoparticles of Ca(OH)$_2$

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ABSTRACT

Nanotechnology offers the use of innovative products to consolidate porous stones prone to decay due to the exposure to weathering agents. Calcium hydroxide (Ca(OH)$_2$) nanoparticles are considered a good compatible consolidation materials to increase the durability of carbonate stones, where the relative humidity (RH) of the environment during the consolidation process plays an important role in the modification of the physical properties of these stones in a short and in a long term.

The durability assessment of carbonate stones (dolostone), typically used in historical buildings from Madrid (Spain) has been determined just after their consolidation with these nanoparticles at 20ºC under a dry (33%RH) and a humid environment (75%RH), and after 18 months later under room temperature and humidity conditions (20ºC±5 and 50±10% RH). The increase of durability of this dolostone is shown through the combination of non-destructive techniques (Environmental Scanning Electron Microscopy, spectrophotometry, water absorption under vacuum and capillarity, ultrasounds velocity and Optical Surface Roughness analyses) together with destructive techniques (mercury intrusion porosimetry and microdrilling resistance measurement) also necessary for a better accuracy determination of pore structure and resistance modifications. Consolidation process under both humid and dry environment gives rise to an increase in the durability of dolostone specimens. However, the humid environment favors the consolidation in a short and in a long term, being this condition necessary to take into account when Ca(OH)$_2$ nanoparticles are used to consolidate carbonate stones.

KEYWORDS

Consolidation, Calcium hydroxide nanoparticles, Carbonate stone, Durability.

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1 INTRODUCTION

Carbonate rocks have been extensively used along history as building stones, due to their abundance, availability, easy workability and beauty. However, most of this type of rocks are prone to decay due to intrinsic and extrinsic factors that determine their durability, such as porosity or composition, which makes them susceptible to physical and chemical attack, together with the environment in which they are placed which contribute in a different way to the degradation of monuments. The durability of building stone is a measure of its ability to resist weathering and so retain its original size, shape, strength, and appearance over an extensive period of time [Bell 1993].

Stone preservation involves the use of chemical treatments that prolong the life of a stone, either by preventing or retarding the progress of stone decay or by restoring the physical integrity of the decayed stone. Calcium hydroxide (Ca(OH)$_2$) is broadly known from the past for being one of the most compatible products to perform consolidation of calcareous materials such as stone sculptures, monuments or wall paintings [Ashurst & Dimes 1990].

In the search of compatible materials to increase durability of carbonates stones, nanotechnology has become an opportunity to be applied in stone preservation. The nanotechnology and nanomaterials boom have given rise to the development of Ca(OH)$_2$ nanoparticles to be used as a consolidating product for carbonate stones, solving some of the drawbacks of conventional Ca(OH)$_2$, such as the incomplete conversion of calcium hydroxide into calcium carbonate, post treatment chromatic alterations and the little penetration depth [Daniele et al. 2008]. The use of Ca(OH)$_2$ nanoparticles is funded by the fact that the specific surface area of a solid increases exponentially with the decrease of its volume, having the nanoparticles a much superior surface area available to react, and a better ability to penetrate in the stone pores net [Sequeira et al. 2006]. The use of alcohols as a substitute for water solvent in Ca(OH)$_2$ treatments also improves the consolidation process [Giorgi et al. 2000], since colloidal dispersions of these nanoparticles show a slower rate of agglomeration reducing the tendency of a white film to form on surfaces to be consolidated [Hansen et al. 2003].

In terms of durability, the selection of stone for building purposes has conventionally been based on its performance in the past and the results of standard tests [Bell 1993]. Previous research works carried out by Dei & Salvadori [2006], Daniele et al. [2008] or López-Arce et al [2010] have shown the use of different analytical techniques to characterize these nanoparticles and to evaluate the effect on the consolidation of carbonate stones.

The aim of this research was to show the durability assessment of carbonate stones (dolostone), typically used in historical buildings from Madrid (Spain) through characterization analyses using a combination of non-destructive techniques (NDT) together with destructive techniques, also necessary for a better accuracy determination of pore structure and resistance modifications. The increase in durability of dolostone has been determined just after 20 days of consolidation with these nanoparticles under a dry and a humid environment, and after 18 months later under room temperature and humidity conditions.

2 MATERIALS AND METHODS

2.1 Materials and Sample Preparation

The Ca(OH)$_2$ dispersion used in this study is a commercial product (Nanorestore®) developed at the University of Florence (CSGI Consortium) [Dei & Salvadori 2006]. It is based on a colloidal suspension of nanoparticles of slaked lime (Ca(OH)$_2$) dispersed in isopropyl alcohol (5 g/l). The nanoparticles were exposed to 33% and 75% relative humidity (RH) at 20°C during 20 days and then left in the laboratory during 18 months under room temperature (RT) and RH conditions (20°C±5 and 50±10% RH). The room CO$_2$ concentration can oscillate in the laboratory between 500 and 800 ppm. The equilibrium relative humidity (RHeq) of specific supersaturated salt solutions inside closed
desiccators used as climatic chambers was used to keep the humidity constant at 20ºC: NaCl (RHeq 75%) to simulate a humid environment and MgCl₂ (RHeq 33%) to simulate a drier environment. Inside the chambers there was no additional CO₂ flux and no air in circulation.

Additionally, (Ca(OH)₂) nanoparticles were applied as a direct preventive treatment to a cream color dolostone of a high open porosity and prone to decay. One specimen was a fresh sample (33RH) that came from an ancient quarry (Redueña) where in the past the stone had been extracted to be broadly used in the construction of several historical buildings located in Madrid (Spain). The other specimen (75RH) also came from the same quarry, but it was submitted to freezing-thawing cycles by artificially accelerated aging tests [Fort et al. 2008]. These two dolostone specimens (2.5 x 2.5 x 1.5 cm) were impregnated with the Nanorestore® product with no dilution drop-by-drop through a capillary tube (1.3 ml) in two applications within an interval of five days. These stone specimens were analyzed before and after being placed inside the climatic chambers for 20 days of consolidation at 33%RH (specimen 33RH-20d) and 75% RH (specimen 75RH-20d). A detailed description of the NDT used in their characterization and the results obtained were reported in a previous work [López-Arce et al. 2010]. These stone specimens were again analyzed 18 months later (specimen 33RH-18m and 75RH-18m) after being exposed to room temperature (RT) and RH conditions (20ºC±5 and 50±10% RH) and using some of the same NDT methods as were previously used combined with some destructive techniques.

2.2 Analytical Techniques and Experimental Procedure

The characterization of the (Ca(OH)₂) nanoparticles exposed to 33% and 75% relative humidity (RH) has been studied by Environmental Scanning Electron Microscopy (ESEM) and X-ray Diffraction (XRD) after 20 days exposure to these RH conditions and as well, after 18 months of exposure under room T and RH conditions. ESEM was performed to study the morphology, size and distribution of the particles disposed on plastic cups using a Quanta 200 FEI microscope. XRD were performed to determine the mineralogy and crystallinity of the product. XRD patterns were recorded in an X’Pert Pro MPD Panalytical X’Celerator diffractometer.

The stone specimens incorporating the consolidating product and exposed at 33% RH and 75%RH were analyzed with several NDT, before, after 20 days and after 18 months treatment, in the following order: spectrophotometry, mobile Optical Surface Roughness (OSR) analyses, propagation of ultrasound velocity and determination of water absorption under vacuum and by capillarity at atmospheric pressure. Spectrophotometry was used to measure the chromatic parameters on the surface of the stone specimens, by means of a spectrophotometer (MINOLTA CM-700d) using the Lab color space or CIELAB. The Standard illuminant was D65 and observer 10° and the measured parameters were L*, which accounts for luminosity, a* and b* coordinates (a* being the red-green parameter and b* the blue-yellow) and YI for yellow index (measured according to ASTM 313-73). The total color difference ΔE* is given by the formula ΔE* = (∆L*)² + (∆a*)² + (∆b*)²)₁/² and the total chroma difference ΔC* is provided by the formula ΔC* = (∆a*)² + (∆b*)²)₁/². OSR analyses were performed on the surface of the specimens to evaluate the change in surface roughness. The equipment used was a contact-free surface profilometer (white light), TRACEiT, patented by Innoweep GmbH. The OSR analyses included 3D-topography maps (25 mm²) and some surface roughness profiles (5mm length, ±1mm height) displaying the average roughness parameters according to the DIN EN ISO 4287 standard: Ra (arithmetic mean of the absolute values of profile deviations from the mean line) and Rz (sum of the vertical distances between the five highest peaks and the five deepest valleys within the sampling length). The cut off λc(λc) used for calculations is 0.80 mm.

Propagation of ultrasound velocity was measured to evaluate the increase in effective porosity and the distribution of the consolidating product that is related to the durability. P-wave propagation time was measured to a precision of 0.1 µs with a PUNDIT CNS Electronics instrument. Standard recommendations were followed according to the Spanish and European standard UNE-EN 14579 [2005]. The frequency of the transducers used was 1 MHz. Measurements were taken in direct
transmission/reception mode, across opposite parallel sides of the cubic specimens in the three spatial directions. Water absorption by capillarity was carried out to study the hydric behavior through the stone using a continuous data-recording ACUASOR. The balance device was linked to a computer which automatically records weight gain in the tested specimen at specified intervals (every \(1/f\) seconds)\(^{1/2}\), in the current study \(f=2\). Water absorption under vacuum was performed to determine the bulk density, open porosity and to quantify the amount of water absorbed by the specimens once they reach saturation, as described in the Spanish and European standard UNE-EN 1936 [1999].

The stone specimens were also analyzed through destructive and micro-destructive techniques. Mercury Intrusion porosimetry (MIP) was applied to assess sample pore structure, i.e., total porosity (P) and pore size distribution (PSD). Readings were taken in pore diameters of 0.005 to 400 \(\mu\)m under measuring conditions ranging from atmospheric pressure to 60,000 psia (228 MPa) with a Micromeritics Autopore IV 9500 MIP. Drilling resistance measurement (DRMS-Sint Technology) was used to measure the penetration depth of the consolidating product and to determine if this resistance increases in the treated samples. The measurements were done with a hard widia drill bit with 5mm diameter and the drilling conditions used in this study were: penetration depth, 15 mm (the thickness of the specimen); penetration speed, 10 mm/min and speed rotation, 400 rpm.

3 RESULTS AND DISCUSSION

3.1 Characterization of Nanoparticles

The results of the ESEM and XRD analyses of the particles exposed to 75% RH and 33% RH after 20 days and 18 months are shown in ‘Fig.1’. As a result of the respective RH conditioning several differences in the crystallinity, agglomeration and mineralogy of the particles are observed. When nanoparticles were exposed to 75% RH, after 20 days (‘Fig 1a’) needle-like habits of vaterite microcrystal (1.98-6µm) are observed. The XRD pattern (‘Fig 1c’) confirms the carbonation process with the presence of vaterite, calcite and traces of monohydrocalcite. After 18 months (‘Fig 1b’), these microparticles (3-5µm and 8-10 µm) of vaterite and aragonite are associated to calcite (2.5-3.5µm) which is confirmed by XRD (‘Fig 1c’).

Figure 1. ESEM images and XRD patterns of nanoparticles: (a) ESEM after 20 days exposed to 75%RH; (b) same sample after 18 months exposed to room T and RH conditions; (c) XRD patterns of both samples (NR-75RH-20d and NR-75RH-18m); (d) ESEM after 20 days exposed to 33%RH; (e) same sample after 18 months; (f) XRD patterns of both samples (NR-33RH-20d and NR-33RH-18m).
The sample exposed to 33%RH after 20 days is shown in the ESEM image (‘Fig 1d’) where submicron clusters of portlandite with poor crystallinity (540nm to 5.16µm) can be observed. The XRD pattern (‘Fig 1f’) confirms the portlandite phase and displays a small signal of calcite. After 18 months, the carbonation process has not yet been completed, as is shown in the XRD (‘Fig 1f’) indicating the presence of portlandite and traces of calcite. The ESEM image (‘Fig 1e’) only reveals an increase in the particle size reaching values up to 8µm.

3.2 Characterization of Stone Specimens

3.2.1 Spectrophotometry

The results of spectrophotometric measurements are shown in Table 1. Color variations stabilized after 18 months of consolidation, being the differences between the fresh samples and the treated samples after 18 months smaller than the differences between the fresh samples and the samples after 20 days treatment. The greatest differences in color variation was for the 33RH-18m specimen, especially for values of ΔC*, ΔE* and ΔYI. On both specimens there is an increase of the chroma difference (ΔC*), this difference being greater for the 33RH-18m specimen due to the larger yellowing (ΔYI) effect.

Table 1. Color variation promoted on dolostone specimens after 20 days (75RH-20d and 33RH-20d) and 18 months (75RH-18m and 33RH-18m) treatment with Nanorestore®.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>ΔL*</th>
<th>Δa*</th>
<th>Δb*</th>
<th>ΔC*</th>
<th>ΔE*</th>
<th>ΔYI</th>
</tr>
</thead>
<tbody>
<tr>
<td>75RH-20d</td>
<td>1.81</td>
<td>-0.65</td>
<td>-1.77</td>
<td>1.89</td>
<td>2.61</td>
<td>-4.57</td>
</tr>
<tr>
<td>75RH-18m</td>
<td>1.01</td>
<td>0.05</td>
<td>-0.31</td>
<td>0.31</td>
<td>1.06</td>
<td>-0.75</td>
</tr>
<tr>
<td>33RH-20d</td>
<td>1.33</td>
<td>-1.53</td>
<td>-3.99</td>
<td>4.27</td>
<td>4.48</td>
<td>-9.36</td>
</tr>
<tr>
<td>33RH-18m</td>
<td>-1.68</td>
<td>-0.25</td>
<td>1.49</td>
<td>1.51</td>
<td>2.26</td>
<td>2.63</td>
</tr>
</tbody>
</table>

However, most of the chromatic parameters decrease after 18 months reaching much lower values than those obtained after 20 days treatment. The 75RH-18m specimen has a lower total color difference (ΔE*) as compared to the 33RH-18m specimen and this ΔE* also becomes lower after 18 months. Therefore, in both specimens the consolidating product does not significantly affect the color parameters of the stone after 20 days and even less so after 18 months; this result is based on considering the criteria for compatibility indicators that are available in the literature. When, for example, ΔE* (total color difference) is less than 3 the risk of incompatibility is 0 and when ΔE* is between 3 and 5 the risk is 5 (on a 5 to 10 scale) [Benavente et al. 2003, Delgado et al. 2007, Grossi et al. 2007]. Since ΔE* is lower than 3 for specimen 75RH and between 3 and 5 for specimen 33RH, the consolidation product does not affect stone color.

3.2.2 Optical Surface Roughness (OSR)

The results from OSR measurement are shown in Table 2. In specimen 75RH, values of Ra and Rz decrease after 20 days and 18 months. The decrease in Rz parameter is much greater after 18 months and this may be due to the penetration of nanoparticles through the pore network reducing the pore sizes and hence the depth of surface roughness giving rise to a shorter distance between the highest and lowest peaks of the roughness profiles (‘Fig. 4a’). The decrease in Rz value could also be explained due to changes and transformations of the vaterite polymorph, increasing the density of the consolidating product during its transformation into calcite as is observed in ‘Fig.1a-c’.

On other hand, in specimen 33RH, the roughness parameters increase slightly (Table 2). This may be because in a reduced humidity and drier environment the Ca(OH)₂ nanoparticles tend to agglomerate without penetrating the pores, thus covering the surface of the specimens and giving rise to longer distances between the highest and lowest peaks of roughness profiles, and thereby increasing the Rz parameter (‘Fig. 4a’). This change is greater in the specimen after 20 days, since after 18 months it decreases slightly, whereas Ra increases slightly. Even although, the transformations of Ca(OH)₂
nanoparticles are less important in this latter specimen as observed in ‘Fig.1d-f’, these produce a greater increase in Ra parameter with time as compared to the other specimen.

### Table 2. Optical Surface Roughness parameters: variation promoted on the dolostone specimens before consolidation (75RH-0d and 33RH-0d), after 20 days (75RH-20d and 33RH-20d) and 18 months (75RH-18m and 33RH-18m) treatment with Nanorestore®.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>75RH-0d</th>
<th>75RH-20d</th>
<th>75RH-18m</th>
<th>33RH-0d *</th>
<th>33RH-20d *</th>
<th>33RH-18m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ra (µm)</td>
<td>7.95±2.08</td>
<td>7.89±2.07</td>
<td>7.32±2.10</td>
<td>6.61±1.63</td>
<td>6.64±1.76</td>
<td>6.76±1.67</td>
</tr>
<tr>
<td>∆Ra (%)</td>
<td>-0.86/-0.7</td>
<td>-12.45/-6.48</td>
<td>-2/1.9</td>
<td>2.16/2.25</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Rz (µm)</td>
<td>32.24±7.74</td>
<td>31.98±7.54</td>
<td>28.85±7.66</td>
<td>28.17±6.30</td>
<td>28.47±6.68</td>
<td>28.03±6.10</td>
</tr>
<tr>
<td>∆Rz (%)</td>
<td>-0.25/-1.16</td>
<td>-15.62/-9.5</td>
<td>-0.3/1.93</td>
<td>0.27/-1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### 3.2.3 Propagation of ultrasound velocity (UV)

The propagation of UV of the specimens is shown in Table 3. In both specimens there is an increase in UV, but this increase is greater in specimen 75RH as compared to 33RH. In the former specimen, after 20 days of consolidation there is a significant increase (15%) and after 18 months this is stabilized, thus slightly decreasing in value, although reaching values above of those obtained in the specimen before treatment (6%). In specimen 33RH the increase in UV values after 20 days is lower than in the other specimen (2.5%) and after 18 months it reaches a similar value than that before consolidation.

#### 3.2.4 Hydric behavior

The results of hydric tests are shown in Table 3. These results show that both the open porosity and water absorption saturation under vacuum slightly change after consolidation in both specimens. However, the most significant result corresponds to the capillarity coefficient (C). In the case of specimen 75RH, the value of C decreases (38%) after 20 days and this decrease continues up to 58% in the specimen after 18 months. In specimen 33RH, the value of C also decreases (16%). However, after 18 months this value shows a slight decrease to 7%.

The nanoparticles introduced in the pore system of the specimens, gave rise to a “nano-roughness” that in turn made capillary water absorption difficult. Calcite has a greater degree of water repellency as compared to dolomite and this could be one of the reasons for the reduction of the value of the C coefficient that was even higher in specimen 75RH in which all the portlandite was transformed into calcite, especially after 18 months. In specimen 33RH the penetration of nanoparticles inside the pore system was less significant; there was also reduced transformation of portlandite into calcite as shown by the decrease in C value and lower than in the other specimen. In this latter specimen after 18 months, the nanoparticles increased in size but did not totally transform into calcite.

### Table 3. Values of ultrasound velocity (Vp), water absorption under vacuum and by capillarity for dolostone specimens before consolidation (75RH-0d and 33RH-0d), after 20 days (75RH-20d and 33RH-20d) and 18 months (75RH-18m and 33RH-18m).

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Average Vp for 3 axes (m/s)</th>
<th>∆Vp (%)</th>
<th>Saturation (S) (%)</th>
<th>∆S (%)</th>
<th>Open porosity (Op) (%)</th>
<th>∆Op (%)</th>
<th>Capillary coefficient (C) (g/m²s)</th>
<th>∆C (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>75RH-0d</td>
<td>2187±91</td>
<td>8.30</td>
<td>18.95</td>
<td></td>
<td>172.5±4.6</td>
<td>124.9±2.5</td>
<td>-38</td>
<td></td>
</tr>
<tr>
<td>75RH-20d</td>
<td>2585±145</td>
<td>15.33</td>
<td>7.95</td>
<td>-0.35</td>
<td>18.20</td>
<td>-0.75</td>
<td>123.9±2.5</td>
<td>-38</td>
</tr>
<tr>
<td>75RH-18m</td>
<td>2336±58</td>
<td>6.42</td>
<td>8.24</td>
<td>-0.06</td>
<td>18.88</td>
<td>-0.07</td>
<td>72.06±0.3</td>
<td>-58</td>
</tr>
<tr>
<td>33RH-0d</td>
<td>2674±113</td>
<td>7.06</td>
<td>16.60</td>
<td></td>
<td>148.02±3.9</td>
<td>123.9±1.3</td>
<td>-16</td>
<td></td>
</tr>
<tr>
<td>33RH-20d</td>
<td>2747±163</td>
<td>2.55</td>
<td>6.91</td>
<td>-0.15</td>
<td>16.30</td>
<td>-0.3</td>
<td>137.43±3.3</td>
<td>-7</td>
</tr>
<tr>
<td>33RH-18m</td>
<td>2659±220</td>
<td>-0.5</td>
<td>7.01</td>
<td>-0.05</td>
<td>16.55</td>
<td>-0.05</td>
<td>137.43±3.3</td>
<td>-7</td>
</tr>
</tbody>
</table>
3.2.5 Mercury Intrusion porosimetry (MIP)

The MIP results are shown in Table 4. These show that both total porosity and pore size distribution changed slightly in specimen 33RH. There is also a slight decrease in the total porosity and a slight increase of pore diameters in the range between 1 and 100 µm (‘Fig. 4b’).

**Table 4.** Surface area, total porosity and pore size distribution of samples treated with Ca(OH)$_2$ nanoparticles as obtained by mercury intrusion porosimetry.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>75RH-0d</th>
<th>75RH-18m</th>
<th>33RH-0d</th>
<th>33RH-18m</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific surface area (m$^2$/g)</td>
<td>0.30±0.02</td>
<td>0.26±0.05</td>
<td>0.37±0.05</td>
<td>0.27±0.01</td>
</tr>
<tr>
<td>Total connected porosity (%)</td>
<td>17.65±3.43</td>
<td>13.04±2.46</td>
<td>14.63±2.55</td>
<td>13.62±0.19</td>
</tr>
<tr>
<td>&lt; 0.01 µm</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>0.01 - 0.1 µm</td>
<td>1.30</td>
<td>1.63</td>
<td>2.49</td>
<td>1.59</td>
</tr>
<tr>
<td>0.1 - 1 µm</td>
<td>18.05</td>
<td>21.26</td>
<td>23.45</td>
<td>22.29</td>
</tr>
<tr>
<td>1-10 µm</td>
<td>62.61</td>
<td>62.81</td>
<td>66.15</td>
<td>67.77</td>
</tr>
<tr>
<td>10 - 100 µm</td>
<td>14.13</td>
<td>12.08</td>
<td>4.76</td>
<td>5.75</td>
</tr>
<tr>
<td>&gt;100 µm</td>
<td>3.90</td>
<td>2.23</td>
<td>3.15</td>
<td>2.58</td>
</tr>
</tbody>
</table>

The modification of the pore system in specimen 75RH is much greater. This is observed by the greater decrease in total porosity and a decrease of pore diameters in the range between 10 and 100 µm and an increase in diameters for the 1 to 10 µm pore size range (Table 4 and ‘Fig.2b’).

**Figure 2.** (a) OSR profiles before and after 20 days and 18 months consolidation at 33%RH and 75%RH; (b) Pore size distribution curves obtained with MIP in these stone specimens; (c) Drilling resistance graphs of same samples; drilling conditions: 10mm depth, 15 mm/min and 400 rpm.

3.2.6 Drilling resistance measurement (DRMS)

The results of the drilling resistance measurements (‘Fig.4c’) show that before consolidation the stone specimens display lower resistance values compared to the specimens after 18 months consolidation. Initially, in the specimens before consolidation the value for drilling resistance is slightly lower in the stone specimen 75RH-0d (3.98±2.00N) compared to the stone specimen 33RH-0d (4.11±1.08N). However, the increase in this value after 18 months consolidation is higher in the former specimen (75RH-18m), reaching values of 5.70±1.07N that are above the values attained by specimen 33RH-18m (4.74±1.47N). The highest increase in 33RH-18m is produced in the first 2 mm which is in agreement with the greatest number of particles located at the surface of this specimen as determined by ESEM and OSR analysis.

4 CONCLUSIONS

According to the results obtained in this study, the resistance to weathering effects of dolostone treated with Ca(OH)$_2$ nanoparticles increases, and this is greater, both in the short and long term, when the treatment is applied at higher RH (75%) as compared to an application at a lower RH (33%). For treatments at the higher RH, a complete transformation from portlandite (Ca(OH)$_2$) to calcite (CaCO$_3$) is achieved, giving rise to lower color variations, greater reduction in surface roughness and
a higher increase in the propagation of ultrasound velocity as compared to treatments at the lower RH. This is explained by a greater depth of penetration of the nanoparticle’s product and the total carbonation of the particles and their transformation from nano to micron-scale within the pore system, this effectively reduced pore sizes as was reflected by a corresponding reduction in the capillarity coefficient, and increased drilling resistance, thus providing a higher resistance to water penetration and hence, a greater resistance of dolostone to the effects of weathering agents.

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REFERENCES