STONE DURABILITY OF A SURFACTANT-SYNTHESISED ALKOSYLANE CONSOLIDANT ON GRANITES WITH DIFFERENT MINERALOGY AND TEXTURE

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Abstract:
The aim of this study was to evaluate the durability of the surfactant-synthesised alkosylane consolidant UCA-2o, applied in two granites from the NW Iberian Peninsula (Albero and Rosa Porriño) with different mineralogy and texture. The consolidated samples were subjected to 20 wetting/drying cycles. Then, results obtained in the consolidated samples by a multi analytical approach (peeling test, optical microscopy, colour measurements in CIELAB colour space, static contact angle, roughness measurements and scanning electron microscopy) were compared with those from unconsolidated samples also subjected to the same number of cycles. In summary, after aging, satisfactory results were still identified in terms of surface cohesion. Moreover, both granites showed hydrophobic behaviours. Colour variations in comparison to unconsolidated surfaces showed different trends depending on the texture of each granite: Rosa Porriño with narrower surface fissures has experienced a higher global colour change in comparison to the most porous Albero, due to the yellowing of the consolidant layer, which was more extensive on the surface of the former.

1. Introduction

Granite as sedimentary carbonate stones and marbles is susceptible to the alterations caused by salts crystallizations, such as granular disintegration or sanding associated with sodium chloride and scaling due to the action of soluble sulphates [1-4]. Consolidation is based on the restoration of the surface cohesion by applying polymers with organic compounds or inorganic products [5]. Synthetic organic materials such as acrylic, epoxy and vinyl resins were intensively used in the end of the 20th century, but several drawbacks such as colour modifications, changes of porosity, capillary, behaviour against water, etc. have been reported in previous researches [6,7]. Inorganic products such as ethyl silicate, calcium hydroxide, barium hydroxide, etc. have been also applied in the recent years in order to avoid the drawbacks cited. Due to their chemical compatibility, ethyl silicate is usually applied in silicate stones such as granite. Ethyl silicate-based consolidants are mainly composed by alkosylanes, which are well known for their polymerisation inside the pore of the stone, through a sol-gel process [8], increasing the surface cohesion of the stone. The low viscosity of the alkosylanes prevents the dilution in organic solvents and facilitates the penetration through the substrate in order to get a high consolidant dry matter. During the polymerization giving a xerogel, the consolidant with alkosylanes into fissures
start to show cracks due to the stresses caused by the existence of a meniscus at the liquid-vapour interface [9,10]. This fact generates a differential capillary pressure within the gels which induces cracking in the consolidant layer [9,10]. In addition, Scherer and Wheeler [11] reported that pore size of the xerogel around 3.5 nm rises high capillary pressure inducing cracking. Therefore, in order to develop free cracking xerogel, Mosquera et al. [12] develop a sol-gel route for producing nanomaterials avoiding porous with diameters below 3 nm and then, reducing the capillary pressure. They worked with a hybrid organic-inorganic polymer of ethyl-silicate and an organosiloxane, polydimethylsiloxane (PDMS), with an amine primary surfactant (n-octylamine) as a template for the pores coarsening the pore structure of the gel network. As was reported in [12], the sol with low viscosity penetrates into the stone and after being transformed into gel, the surfactant is spontaneously removed. Moreover, this consolidant is an environment-friendly product because volatile organic compounds (VOC) are not included in the formula. In addition, the absence of VOC increases the dry matter once the product is polymerized inside the stone through the porous system, and then, the consolidating effectiveness is enhanced [13]. This product shows a double function, because after polymerization, the material shows hydrophobicity and consolidation indexes [12,14]. This new surfactant (n-octylamine)-synthesised alkosylane consolidant has been tested on granite in two previous works [12,14]. Both researches reported satisfactory results in terms of granite consolidation although slight visible colorimetric changes after its application were highlighted. Moreover, in [14], the effectiveness of this product was confirmed in laboratory and in situ studies. The addition of n-octylamine contributes to obtain a crack-free xerogel layer and the absence of solvent allowed higher ratios of dry matter/uptake due to the great penetration avoiding the gel migration to the surface during the solvent evaporation [14]. Although satisfactory results were identified once this new surfactant (n-octylamine)-synthesised alkosylane consolidant was applied on granite types with different mineralogy and texture [12-14], scientific information about the durability of this treatment was not found. Therefore, the aim of this article was centred on the evaluation of the durability of the strengthening effects caused for a surfactant (n-octylamine)-synthesised alkosylane consolidant on two granite types with different mineralogy and texture, once samples were exposed to 20 wetting/drying cycles. Moreover, some features such as appearance, colour, hydrophobicity, roughness and micro texture of the consolidated surfaces were evaluated by comparison with untreated samples also exposed to the same artificial aging process.

2. Materials and methods

2.1. Granites

Two commercial quality ornamental granites from quarries in the NW Iberian Peninsula were selected, called Albero, fig. (1-a) and Rosa Porriño, fig. (1-b). Albero is an equigranular medium to coarse grained granite [15] composed of k-feldspar (42.6%), plagioclase (22.6%), quartz (21.9%), biotite (7%), muscovite (5.8%), and accessories minerals (apatite, zircon, rutile, chloride and sillimanite). The main grain size is 5 mm. Open porosity following [16] is 3.87 %. Rosa Porriño is a two-mica coarse-grained granite with a panallotriomorphic hetero granular texture [15], composed of quartz (40%), potassium feldspar (27%), plagioclase (14%), biotite (8%), muscovite (2%) and chlorite and opaques as accessories (5%). Grain sizes range through 10 mm (potassium feldspar grains), 3.8-1.2 mm (quartz grains) and 2.0-0.3 mm (biotite grains). Open porosity, according to RILEM [16] is 0.84 %, considerably lower than that for the Albero granite. From commercial 50 cm × 50 cm × 2 cm slabs of each granite, ten 4 cm × 4 cm
×2 cm-slabs were cut. Albero samples were identified as AL and Rosa Porriño samples as RP.

Figure (1) Shows micrographs taken with optical microscopy of the granitic samples; a. Albero, b. Rosa Porriño.

2.2. Consolidants

UCA-2o, a sol consists of a mix of Dynasilan 40 (from Evonik) and the surfactant n-octylamine (from Aldrich). According to its technical data sheet, Dynasilan 40 is a mixture of monomeric and oligomeric ethoxysilanes with a SiO$_2$ content of 40%. This consolidant was also used in [14]. The synthesis route of UCA-2o was firstly composed by an aqueous solution of n-octylamine with a concentration of the surfactant significantly higher than that corresponding to its critical micellar concentration (CMC), which is 0.010 M [17]. It was obtained by a vigorous stirring. More in detail, a 1.57 M aqueous solution of n-octylamine was used. Solution turbidity due to the formation of micelles was clearly observed. Then, the aqueous solution of n-octylamine was mixed with Dynasilan 40 under stirring, in a mole ratio of Dynasilan to n-octylamine of 1:5.10$^{-4}$. The sol was homogenised by high-power ultrasonic agitation (60 Wcm$^{-3}$) during 10 min. Finally, it was ready to be applied on the surfaces without addition of any solvent. Previously to the application and following De Rosario, et al. [14], samples were dried in an oven at 40 °C until constant weight. Then, on one side of five slabs for each granite, the product was applied. Two successive applications were made at a one-minute interval. Samples consolidated were identified with UCA following to AL or RP, i.e. AL-UCA and RP-UCA. After consolidant application, samples were left under laboratory conditions (18±5°C and 60±10% RH) until constant mass.

2.3. Artificial aging tests (wetting/drying cycles)

Wetting/drying experiments were performed following Venieale, et al. [18]. Each samples pack (AL, AL-UCA, RP and RP-UCA) were subjected to 20 wetting/drying cycles; each cycle (24 hours) consisted in 17 hours where samples placed in a plastic box were submerged in distilled water and then, 6 hours of drying in an oven at 40 °C and 1 hour at laboratory conditions (18±5 °C and 60±10% RH).

2.4. Analytical techniques

Before the wetting/drying cycles, the uptake of the consolidant on both granite samples was calculated by the difference of weight after and immediately before the treatment, expressed in g. Once the samples achieved constant mass, the content of dry matter was determined, also by difference of weight, expressed in g. This allowed to determine the dry matter/uptake ratio. After the 20 wetting/drying cycles, mass loss of the samples was measured in relation to the original mass of the samples. Moreover, in order to assess the consolidant effect, peeling test was applied following [19] using a double-sided Tesa Power bond adhesive tape, applied and removed 3 times consecutively to each slab. Peeled-off material was dete-
rmended as the tape weight differences per sample. Then, optical microscopy (SMZ 800 Nikon) was used in order to identify differences between the unconsolidated and consolidated surfaces. Colour was determined using a Minolta CM-700d spectrophotometer. A total of 15 random measurements were made for each stone surface, before the 20 wetting/drying cycles and after those for the unconsolidated samples and before the consolidant application and after the cycles for the consolidated samples. This number of measurements per surface has been taken following the recommendation for granitic stones proposed in [20]. Colour was expressed in the CIELAB colour spaces [21]. The measurements were made including the specular component (SCI mode), for a spot diameter of 8 mm, using illuminant D65 at observer angle 10°. The following parameters were measured: lightness (L*), which varies from 0 (absolute black) to 100 (absolute white); (a*), representing the redness-greenness range (+a*: red and -a*: green) where, (b*), associated with yellowness-blueness spectrum (+b*: yellow and - b*: blue), C*ab, chroma or saturation and h*ab, hue or tone. C*ab was calculated based on a* and b* values as C*ab = (a*² + b*²)^(1/2) and h*ab was computed as h*ab = tan^-1(b*/a*). CIELAB ΔL*, Δa*, Δb*, Δc*, Δh*ab and ΔH*ab colour differences and the global colour change (ΔE*ab) were calculated, taking as reference the same sample before the cycles for the unconsolidated ones and the same samples without consolidant for the consolidated samples. ΔE*ab was obtained as follows [21] ΔE*ab = \sqrt{(ΔL*)² + (Δa*)² + (Δb*)²}

The hydrophobicity of the surfaces was evaluated using a Phoenix-300 Touch SEO contact angle analyser, with an outer diameter of 0.012” (0.3048 mm) and an inner diameter needle of 0.005” (0.127 mm). Measured were 3 drops of 8 µL per mock-up following Spanish standards [22]. The roughness was measured by means of a profilometer Mitutoyo SJ400 (Mitutoyo) through the arithmetic average roughness (Ra, µm) and average maximum profile height (Rz, µm) described in [23]. The equipment traced a scan length of 2 cm, and three profiles per sample were obtained. A micro morphological analysis of the surfaces after being exposed to the wetting/drying cycles was performed. Superficial 1 cm × 1 cm, subsamples were extracted from the surfaces and after being C-coated, were visualized using scanning electron microscopy (SEM) in backscattered electron (BSE) and secondary electrons (SE) modes with energy dispersive x-ray (EDX) spectroscopy (using a Philips XL30). Optimum conditions of observation were obtained for an accelerating potential of 20 kV, a working distance of 9-11 mm and a specimen current of ~60 mA.

3. Results

Table (1) depicts the values for uptake and dry matter obtained after the treatment on both stones. Also, the relation between the dry matter and the uptake is also shown. The results of the uptake and dry matter were higher in Albero than those in Rosa Porriño and the dry matter/uptake ratio was higher also in Albero. After 20 wetting/drying cycles, it was detected that regardless of the stone, consolidated samples showed mass losses lower than those registered for the unconsolidated samples. The highest mass losses were detected for Albero. Attending to the mass loss reduction due to the consolidation, Albero experimented a reduction of the mass loss of 43.7% while Rosa Porriño, 51.5%. After the wetting/drying cycles, regarding the material peeled off shown in tab. (2), it was observed, as expected, that more material was extracted from the unconsolidated surfaces. Therefore, consolidated samples kept their effectiveness after the 20 cycles. Slightly more material was peeled off from Albero. After the consolidation, it was detected a reduction of the peeled off material, which was higher in Albero.
Table (1) Uptake (g), dry matter (g) and dry matter/uptake ratio after the application in the laboratory conditions of the UCA-2o consolidant in both granites: Albero (AL) and Rosa Porriño (RP). Moreover, mass loss of the unconsolidated and consolidated samples after 20 cycles of wetting/drying and the corresponding mass loss reduction (%) of the samples after being consolidated with UCA-2o in relation to the unconsolidated ones. AL: Albero samples. AL-UCA: Albero samples consolidated with UCA-2o. RP: Rosa Porriño samples. RP-UCA: Rosa Porriño samples consolidated with UCA-2o.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Uptake (g)</th>
<th>Dry matter (g)</th>
<th>Dry matter/uptake ratio</th>
<th>Mass loss in 20 cycles</th>
<th>Mass loss reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>1.080±0.150</td>
<td>0.740±0.068</td>
<td>0.685</td>
<td>0.107±0.021</td>
<td>43.7</td>
</tr>
<tr>
<td>AL-UCA</td>
<td>0.245±0.048</td>
<td>0.097±0.012</td>
<td>0.685</td>
<td>0.050±0.010</td>
<td>51.5</td>
</tr>
<tr>
<td>RP</td>
<td>0.910±0.110</td>
<td>0.403±0.032</td>
<td>0.443</td>
<td>0.050±0.010</td>
<td></td>
</tr>
</tbody>
</table>

Table (2) Peeled off material (mg) of the Albero and Rosa Porriño granites for the unconsolidated (AL and RP) and consolidated samples (AL-UCA and RP-UCA) after 20 wetting/drying cycles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peeled off material (mg)</th>
<th>Peeled off material reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>1.40±0.18</td>
<td></td>
</tr>
<tr>
<td>AL-UCA</td>
<td>0.47±0.03</td>
<td>33.6%</td>
</tr>
<tr>
<td>RP</td>
<td>1.13±0.16</td>
<td></td>
</tr>
<tr>
<td>RP-UCA</td>
<td>0.21±0.08</td>
<td>18.5%</td>
</tr>
</tbody>
</table>

Attending to the effect of the consolidant on the appearance of the granite surfaces, it was observed that comparing the surfaces of the unconsolidated stones, figs. (2-a, b, c & g, h, i) with the consolidated ones, figs. (2-d, e, f & j, k, l), in the former it was possible to identify the typical structure of the granite forming minerals (Qz: quartz, Kfs: potassium feldspar, Bt: biotite) while in the latter, these minerals were slightly covered by white deposits. Differences were identified regarding the granite: i) for Albero, the coated surfaces appeared less irregular than the uncoated samples, mainly due to the consolidant filling the fissures and voids of the feldspar grains, fig. (2-d). Moreover, white deposits were detected on the quartz surfaces, figs. (2-e, f). Moreover, these white deposits were found filling fissures around minerals, being remarkable this colour modification around biotite grains, because this granite is characterized by the yellow colour associated to the brown deposits filling fissures around biotite grains, staining the felsic minerals (feldspar and plagioclase). Following Escuder, et al [24] and Pozo-Antonio [25], these brown deposits are composed of oxyhydroxylated iron forms (traces) of low or no crystallinity. The weathering of the biotite grains entails a loss of iron which is transported by fluids through the fissures and accumulated into these as oxyhydroxylated iron forms [24]. For Rosa Porriño, the effect of the consolidant on the surface was not as clear as that found in the Alberto, since the rough disc cutting resulted in a very irregular surface with whitish hues for all the minerals, figs. (2-g, i). This tone made it difficult to identify consolidant deposits on the surface. In certain areas it was possible to identify a plastic appearance deposit on the feldspar grains, fig. (2-j).
Regarding colour characterization, tab. (3), the most affected parameter by the 20 wetting/drying cycles, regardless of the application of consolidant, was the L*, showing decreases, i.e. a darkening of the surfaces. The consolidated samples showed the highest L* decreases, being the most intense one for the RP-UCA sample. Moreover, a reddish effect was also detected on all the samples as was reflected by the a* increases. This a* increase was highest for the RP-UCA sample. On the other hand, b* showed decreases for the unconsolidated samples (AL and RP) due to the loose of yellow coloration and increases for the consolidated ones (AL-UCA and RP-UCA) due to the yellowing, mainly for Rosa Porriño sample. As result of this colour change, the C*\textsubscript{ab} and h\textsubscript{ab} also experimented changes. With exception of the AL sample, the colour of the remaining samples was more vivid after the cycles since C*\textsubscript{ab} increased, being the highest increase in RP-UCA. The h\textsubscript{ab} experimented decreases in all the samples, being the highest change detected again in RP-UCA. Considering the ΔE*\textsubscript{ab} as the quantitative parameter to identify a visible colour change, since [26] stated that a ΔE*\textsubscript{ab} higher than 3.5 CIELAB units corresponds to a colour change perceptible to an inexperienced observer, the consolidated samples experimented visible colour changes after the wetting/drying cycles, because for the AL-UCA, the ΔE*\textsubscript{ab} was 4.84 CIELAB units and for the RP-UCA it was 9.17 CIELAB units. In the current research, after 20 wetting/drying cycles, the consolidated surfaces experimented visible colour changes in comparison to those without consolidant, which although low intense (ΔE*\textsubscript{ab} lower than 2.5 CIELAB) also experimented slight ΔE*\textsubscript{ab}. The ΔE*\textsubscript{ab}
for the consolidated Rosa Porriño sample was around 4 CIELAB units higher than that for the consolidated Albero. Attending to the hydrophobicity of the surfaces after the 20 wetting/drying cycles, tab. (4), for the consolidated ones, $\theta^0$ were higher than 90º, which is the threshold above that a surface can be considered hydrophobic [27]. Both consolidated granites showed similar $\theta^0$, around 124º. However, for the unconsolidated surfaces, only the Rosa Porriño sample showed $\theta^0$ around 90º (hydrophobic behaviour). The unconsolidated Albero sample showed a $\theta^0$ of 78.42±2.89º. In the tab. (5), the roughness parameters measured in this research are detailed. It was detected that after the cycles, the consolidated surfaces showed lower Ra and Rz values than their unconsolidated counterparts being these differences statistically significant expect for the Ra registered in the Rosa Porriño samples. Therefore, the reduction of the roughness due to consolidant application was kept after the artificial aging.

Table (3) Colorimetric differences ($\Delta L^*$, $\Delta a^*$, $\Delta b^*$, $\Delta C^*_{ab}$ and $\Delta H^*_{ab}$) and global colour changes ($\Delta E^*_{ab}$) of the Albero and Rosa Porriño granites for the unconsolidated (AL and RP) and consolidated samples (AL-UCA and RP-UCA) after 20 wetting/drying. The differences were computed taking as reference the same sample before the cycles for the unconsolidated ones and the same samples without consolidant for the consolidated samples. Mean values ($n = 75$).

<table>
<thead>
<tr>
<th>Samples</th>
<th>$\Delta L^*$</th>
<th>$\Delta a^*$</th>
<th>$\Delta b^*$</th>
<th>$\Delta C^*_{ab}$</th>
<th>$\Delta H^*_{ab}$</th>
<th>$\Delta E^*_{ab}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>-2.04</td>
<td>1.33</td>
<td>-0.44</td>
<td>-0.05</td>
<td>-1.43</td>
<td>2.48</td>
</tr>
<tr>
<td>AL-UCA</td>
<td>-4.54</td>
<td>1.66</td>
<td>0.28</td>
<td>0.74</td>
<td>-1.53</td>
<td>4.84</td>
</tr>
<tr>
<td>RP</td>
<td>-1.63</td>
<td>1.41</td>
<td>-0.88</td>
<td>0.37</td>
<td>-2.29</td>
<td>2.33</td>
</tr>
<tr>
<td>RP-UCA</td>
<td>-8.25</td>
<td>3.29</td>
<td>2.25</td>
<td>3.72</td>
<td>-4.49</td>
<td>9.17</td>
</tr>
</tbody>
</table>

Table (4) Static contact angle ($\theta^0$) measured of Albero and Rosa Porriño granites for the unconsolidated (AL and RP) and consolidated samples (AL-UCA and RP-UCA) after 20 wetting/drying.

<table>
<thead>
<tr>
<th>Sample</th>
<th>($\theta^0$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>78.42±2.89</td>
</tr>
<tr>
<td>AL-UCA</td>
<td>123.40±2.00</td>
</tr>
<tr>
<td>RP</td>
<td>90.37±2.17</td>
</tr>
<tr>
<td>RP-UCA</td>
<td>126.01±1.44</td>
</tr>
</tbody>
</table>

Table (5) Roughness parameters: the arithmetic average roughness (Ra, µm) and average maximum profile height (Rz, µm) of Albero and Rosa Porriño granites for the unconsolidated (AL and RP) and consolidated samples (AL-UCA and RP-UCA) after 20 wetting/drying.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ra (µm)</th>
<th>Rz (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AL</td>
<td>3.40±0.19</td>
<td>17.87±0.78</td>
</tr>
<tr>
<td>AL-UCA</td>
<td>2.42±0.24</td>
<td>13.18±0.90</td>
</tr>
<tr>
<td>RP</td>
<td>2.54±0.15</td>
<td>13.44±0.98</td>
</tr>
<tr>
<td>RP-UCA</td>
<td>2.13±0.39</td>
<td>11.08±1.02</td>
</tr>
</tbody>
</table>

SEM observations allowed the identification of consolidant deposits on the surfaces of both stones, figs. (3-c,d). On the unconsolidated samples, figs. (3-a,b), it was identified the typical fissural system of granitic stones consisted of three kinds of fissures: transgranular (fissures that cut across a grain boundary), intergranular (between grains), and intragranular (within grains, mainly in feldspar crystals) as was identified with fluorescence microscopy of thin sections on other granites also from the northwest Iberian Peninsula [28]. It was also possible to identify that Albero was most irregular than Rosa Porriño where a higher compactness level was detected, figs. (3-a,b). Attending to the consolidated samples, it was found that the consolidant was retained on the surfaces through different patterns regarding the stone: on Albero,
the consolidant accumulation was mainly filling fissures, fig.(3-c) while on Rosa Porriño, it was found covering the surfaces, fig.(3-f). Therefore, superficially, higher extension of consolidant was detected on the Rosa Porriño than that on Albero. Regarding the consolidant deposits, fig. (3-e), it was possible to identify the polymerized xerogel rich in Si with fissures [29], showing well-formed cracks, mainly in the fissures of Albero. In Rosa Porriño, the consolidant coating did not show cracking as intense as that detected in Albero.

Figure (3) Shows SEM micrographs a, c, e, of the Albero and b, d, of Rosa after 20 wetting/drying cycles, a: unconsolidated Albero (AL), b: unconsolidated Rosa Porriño (RP), c, e: consolidated Albero (AL-UCA), d, consolidated Rosa Porriño (RP-UCA), e, is accompanied by a EDS spectrum of the consolidant product detected on AL-UCA.
4. Discussion

The highest values of the uptake and the dry matter in Albero comparatively to Rosa Porriño granite may be related to the pores distribution found in these stones. As was obtained in [30], attending to the Mercury Intrusion Porosity (MIP), Albero has a bimodal pore distribution, i.e. a range of pores with wider access (pore diameter around 10 µm) and a range with narrower access (pore diameter less than 1µm), while Rosa Porriño, showed a pores distribution without narrower access. Therefore, considering [28], who reported a direct relationship between the percentage of pores with an access radius less than 1 µm and the capillary suction, Albero was affected by a consolidant penetration by capillary processes much more easily than that found in Rosa Porriño, with low or null percentages of narrow access pores (pore diameter lower than 1µm), which would imply a low capillary suction coefficient. Comparing with [14] where a successful performance of the UCA-2o on a Spanish leuco granite was described, for Rosa Porriño, the dry matter/uptake ratio were notable lower than that obtained by them (i.e. 0.84), while for Albero the dry matter/uptake ratio was closer to that. This is related to the open porosity and pores distribution for both stones; Rosa Porriño shows an open porosity of 0.84% and low or null percentages of pore diameter lower than 1µm, while Albero shows an open porosity of 3.87% and pores with narrower access (pore diameter less than 1µm). The granite used in [14] showed an open porosity of 3.18% and about 30% of the total porous volume corresponded to pores with a diameter less than 1µm. The higher dry matter/uptake ratio found for the consolidated granite with UCA-2o comparing to those obtained with the common consolidants Paraloid-B82 and Estel 1000 in [14] was assigned to the absence of volatile organic components in UCA-2o that would be evaporated during the polymerization, dragging active matter towards the surface.

The consolidants Paraloid B-82 and Estel 1000 contain an organic solvent that, when it evaporates, could reduce the final dry matter. After the artificial aging, mass losses were lower in consolidated samples than those found in the unconsolidated ones. In [14], satisfactory consolidation performance was detected applying the same consolidant in situ in a granitic church. As expected, these losses were higher for Albero since for the unconsolidated sample, higher mass losses were also detected. This was also confirmed by peeling test, because more peeled material was identified for Albero. Rosa Porriño exhibited the highest surface strengthen enhancement, since its mass loss reduction percentage was slightly higher and the amount of material peeled off using the peeling test was lower. This is related to the fact that this stone already has a greater surface cohesion, which contributes to the consolidant accumulation on the surface as it was reflected by SEM. In addition, this consolidant accumulation in Rosa Porriño induced perceptible colorimetric changes for an inexperienced observer [26] due to a yellowing effect, which was also detected at lesser extent in Albero (ΔE*ab for the consolidated of Rosa Porriño around 4 CIELAB units higher than that for the consolidated Albero). It is important to highlight that a slight yellowing was also reported in a previous article working also with this consolidant [14]. La Russa et al. [31] also reported a yellowing and darkening of a tuff surface coated with either a suspension of nano-sized silica in water or a tetraethyl orthosilicate diluted in white spirit and exposed to a salt weathering test. SEM allowed the identification of a higher consolidant extension on Rosa Porriño than that on Albero; in the latter an intense cracking was detected by SEM. This disagrees with [14] because they found a continuous and non-fractured film on the granite without pores. This mismatching may be related to the uptake and the
consequent dry matter retained into the stones, because in the most porous granite of the current research (Albero) with an open porosity of 3.87%, a 0.69 dry matter/uptake ratio was obtained while in the granite used in [14] with an open porosity of 3.18%, a 0.84 dry matter/uptake ratio was reported. Greater consolidant amounts could improve the coating performance in terms of homogeneity. This lower consolidant amount could limit the role played by the n-octylamine to reduce the capillary pressure during the drying [13]. The presence of consolidant filling fissures in Albero and covering the surface for Rosa Porriño, identified by means of SEM, induced a smoothing effect of the surface as was identified through the decrease of the roughness parameters. In addition, the consolidant retained on the surface allowed the enhancement of the hydrophobicity, since 0 were higher than 90° [27]. Therefore, the UCA-2o exhibited a double function: improvement of the superficial cohesion of the granite and achievement of the hydrophobicity, which are durable even after 20 wetting/drying cycles.

5. Conclusion
The durability of a surfactant-synthesised alkylsilane consolidant applied on two granites with different mineralogy and texture was assessed after their exposure to 20 wetting/drying cycles. In addition to the measurement of the surface cohesion by means of the peeling test, other physical properties were evaluated (appearance, colour, hydrophobicity and roughness). The most porous granite Albero experimented the highest uptake and dry matter of consolidant due to its bimodal pore distribution. After the artificial aging due to 20 wetting/drying cycles, Albero showed the lowest mass loss reduction considering the weights for the unconsolidated and consolidated samples and the highest peeled material for the consolidated samples, because Rosa Porriño without consolidant already showed a more cohesive surface due to its lower weathering. After the artificial aging due to 20 wetting/drying cycles, consolidated samples, regardless of the granite, still kept their hydrophobic behaviours, conversely to their unconsolidated counterparts. The increase of static contact angle was attributed to the filling of the fissures. Although consolidant penetrated through the fissures, also product was retained on the surface following different patterns according to the texture of the stone. In Albero, consolidant filled fissures while in Rosa Porriño due to the compactness of the stone with narrower fissures; the retained consolidant was distributed more homogeneously on the surface. Therefore, the extent of the consolidant on the surface influenced on the colour, because the yellowing due to the aging of the consolidant affected greater to the colour change experimented by these samples. The higher consolidant extent on the surface induced higher colorimetric modification of the surface after aging.

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References


[16] RILEM (1980) Recommended tests to measure the deterioration of stone and to assess the effectiveness of treatment methods, Test V.1a—crystallization test by total immersion (for untreated stone); Test V.1b—crystallization test by total immersion (for treated stone); Test V.2—crystallization test by partial immersion, Materials and Structures, Vol. 13 (75), pp. 175-253.


