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OTERO, Jorge, STARINIERI, Vincenzo <<http://orcid.org/0000-0002-7556-0702>> and CHAROLA, AE

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Influence of substrate pore structure and nanolime particle size on the effectiveness of nanolime treatments

J. Otero^{a,b*}, V. Starinieri^a, A. E. Charola^c

^a *Materials and Engineering Research Institute, Sheffield Hallam University, Sheffield, S1 1WB, UK*

^b *Getty Conservation Institute, The J. Paul Getty Trust, Los Angeles, CA 90049, US*

^c *Museum Conservation Institute, Smithsonian Institution, Washington DC, USA*

* corresponding author: Tel: +44 1142253500; Fax: +44 114 225 3501; Jotero@getty.edu;
jorge.otero.h@gmail.com

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Abstract. Nanolime is a promising consolidation treatment for the conservation of historic structures thanks to its high compatibility with carbonate-based substrates. Nanolime products can effectively reduce the porosity and restore the mechanical properties of treated surfaces. Whilst the popularity of nanolime has been growing, its consolidation mechanism still needs to be fully understood when applied to porous substrates. The aim of this paper is to determine the influence of nanolime particle size and substrate pore structure on the effectiveness of nanolime treatments. Results suggest that nanolime products with larger particle size tend to close predominantly large sized pores, while nanolime with smaller particle size tends to fill both large and small pores equally. These results suggest that for a consolidation treatment, the nanolime product must be chosen taking into consideration the substrate pore structure.

1. Introduction

One of the most relevant conservation principles, promulgated by the Athens Charter for the Restoration of Historic Monuments in 1931 [ICOMOS 1931], states that historic objects or structures with significant value (artistic, cultural or historical) must be, whenever possible, restored and preserved. Calcareous limestones are important construction materials used in Cultural Heritage around the world throughout history. These substrates are

28 susceptible to several weathering processes (e.g. freeze-thaw, salt damage, dissolution, acidic attack, etc) which
29 lead structures to lose some of their original properties [Doehne and Price, 2009].

30

31 Consolidation products are used to restore the materials original properties. These consolidants must be physico-
32 chemically compatible with the matrix and should restore its mechanical properties [ICOMOS, 1964]. In recent
33 years the most used consolidating products are silica-precursor consolidants (e.g. TEOS or MTMOS). These
34 products are used in restoration treatments thanks to their ease of application, good penetration and immediate
35 strength enhancement [Wheeler, 2005]. However, in the case of calcareous substrates, the low physical and
36 mechanical compatibility of silica-precursor consolidants with the mineral substrate can cause cracks and
37 significant damage in the long-term [Wheeler, 2005; Wheeler, 2008; Ferreira-Pinto and Delgado-Rodrigues, 2008].
38 For that reason, a lime-based consolidant (i.e. lime-water) has been traditionally preferred due to its high
39 compatibility and durability [Brajer and Kalsbeek, 1999; Baglioni et. al., 2014]. The consolidation of limewater
40 ($\text{Ca}(\text{OH})_2$ aqueous solution) is based on the carbonation reaction produced when portlandite ($\text{Ca}(\text{OH})_2$) is exposed
41 to open environments with CO_2 and H_2O giving rise to CaCO_3 , which is the matrix of calcareous materials.
42 However, this technique presents some important limitations such as the reduced impregnation depth and the very
43 slow carbonation process, which in many cases leads to unsatisfactory treatments [Price et. al., 1988].

44

45 Nanolime dispersions were created to overcome the limitations of the lime-water technique. The consolidation
46 effect of nanolime occurs by carbonation reaction in the same way as for lime-water. However, the smaller size of
47 the lime particles improves the consolidation effectiveness as these are more reactive and reach **greater** penetration
48 depths. The popularity of nanolime has been growing since its first synthesis in 2001. Both commercial nanolime
49 products (Calosil® and Nanorestore®) have proven to be effective products for superficial consolidations (e.g.
50 wall-paintings, stuccoes or plasters) [Otero et al, 2017; Baglioni et al, 2014]. In contrast, the results for
51 consolidations deeper than a few millimetres of highly porous substrates are fewer and often controversial with
52 some unsatisfactory results [Costa and Delgado-Rodrigues, 2012].

53

54 Nanolime effectiveness depends on several factors: i) external factors such as high Relative Humidity (~75%RH)
55 clearly enhance the carbonation process of nanolime [Lopez-Arce et al, 2010]; ii) type of solvent can influence the
56 deposition of the nanoparticles in the pores reducing the migration of the nanoparticles toward the surface during

57 solvent evaporation [Borsoi et al, 2016]; iii) concentration of nanolime can increase the deposition of particles in
58 the pores [Arizzi et al, 2015] v) repetition of applications of low concentrated nanolime can increase the
59 consolidation effectiveness of the treatment [Slikova et al, 2012]; vi) a content of water in the alcoholic solvent
60 increases the carbonation process [Dei and Salvatori 2006; Daniele and Taglieri 2010; Daniele et al, 2018; Taglieri
61 et al, 2017]; and vii) storage conditions of nanolime prior to application (low temperatures for short periods of time)
62 reduces the conversion of calcium hydroxide into calcium alkoxides which clearly enhances the carbonation of
63 nanolime [Rodriguez-Navarro et al, 2016].

64

65 Nanolime has been successfully synthesized by diols [Salvadori and Dei, 2001, Samanta et al., 2016], w/o
66 microemulsions [Nanni and Dei, 2003], aqueous solutions [Sequeira et al, 2006, Daniele et al, 2012], solvothermal
67 reactions [Poggi et al, 2016, Borsoi et al, 2016], plasma metal reaction method [Liu et al, 2010], or anion exchange
68 kinetics [Volpe et al, 2016; Taglieri et al, 2015]. Synthesized nanoparticles present slightly different features in
69 terms of reactivity and particle size depending on the synthesis route [Otero et al, 2018]. Nanolimes synthesized by
70 solvothermal reactions present nanoparticles with sizes ranging from 100 to 300 nm, which usually form clusters of
71 approximately 600 nm [Borsoi et al, 2016, Rodriguez-Navarro et al, 2013]. Conversely, nanolimes synthesized by
72 anion exchange processes present nanoparticles with sizes ranging from 20 to 80 nm, which usually form clusters
73 of approximately 200 nm [Taglieri et al, 2018].

74

75 The aim of this paper is to determine the influence of two nanolime products with different nanolime particle size
76 and two substrates with different pore structure on the effectiveness of nanolime treatments. In this experiment, the
77 consolidation effectiveness of two nanolimes with large difference in particle size onto two limestones with
78 different pore size distribution have been investigated. The consolidation effectiveness was assessed by studying
79 changes in porosity (MIP), water absorption capillarity (WAC), drying kinetics, drilling resistance (DRMS),
80 superficial cohesion (STT) and aesthetic changes (colorimeter). The approach mimics that of a conservator faced
81 with the conservation/restoration of a cultural heritage building/monument who needs to determine, with a
82 minimum of testing, the most appropriate consolidation method [Rodriguez Delgado and Grossi, 2007].

83

84 **2. Materials and methods**

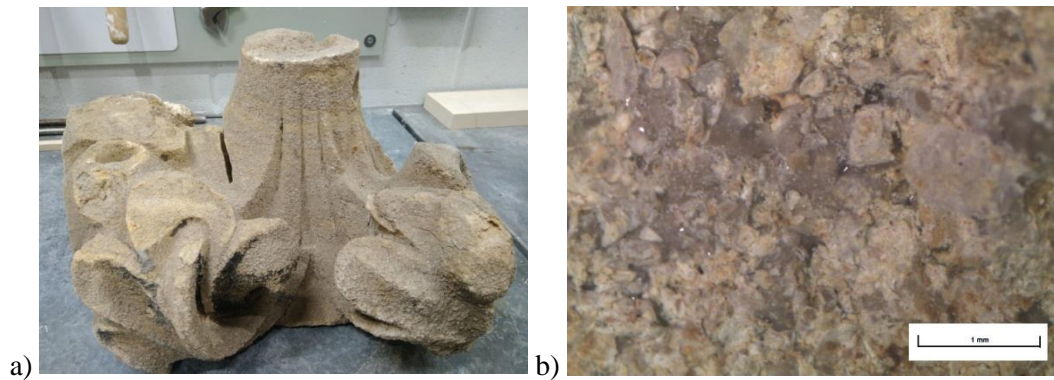
85 *2.1 Limestone samples*

86 Two limestones were used for the test:

87 - **Weathered limestone 1:** This sample, shown in Figure 1, is a weathered Doulling stone capital from the
88 Wells Cathedral (Somerset, UK), a building listed as Grade I in the National Heritage List for England
89 (NHLE) [Historic England, 2011]. This capital was removed from the Cathedral during a restoration
90 intervention and was used by Prof. Clifford Price for a research experiment in the 1980s [Price, 1989;
91 Doehne and Price, 2009]. In Price's experiment, the left-hand side (Fig. 1a) was treated with Brethane (a
92 MTMOS based product) whilst the right-hand side was left untreated [Price, 1989]. After the experiment,
93 the capital was stored in the Building Research Establishment (BRE) outdoor historic stone deposit
94 (Watford, UK). In this research, only the untreated area which had not been treated with the Brethane was
95 used. Doulling limestone is a clastic sedimentary rock composed of fragments of older Carboniferous
96 limestones which were eroded and later re-deposited and cemented together [Price, 1989]. The rock can be
97 classified as intramicrite [Folk, 1959] or grainstone [Dunham 1962]. This stone is referred to as CP. The
98 capital was cut into 35 x 35 x 35 mm cubes for testing.

99

100



101 Figure 1. Weathered capital of Doulling stone (referred as CP) from the Wells Cathedral (UK). a) capital; b)
102 stereomicroscope image of a fragment of Doulling stone

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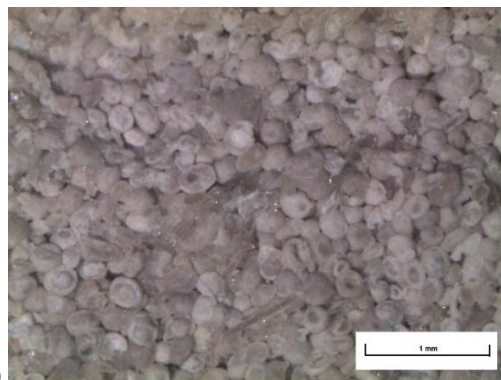
104 The elemental composition of this stone was determined by XRF (Philips PW2400) on pressed powder
105 samples (Retsch PP-40 pellet press). XRF results shows that CP stone is composed of 93.4 (± 0.2) of Ca,
106 2.00 (± 0.09) of Si, 1.7 (± 0.03) of S, 1.3 (± 0.04) of P, 0.7 (± 0.004) of Fe and 0.3 (± 0.01) of K.

107

108 The mineralogical composition was determined by X-Ray Diffraction (PANalytical XPert PRO) where
109 XRD patterns were recorded with a step size of $0.026^{\circ}2\theta$, in the angular range $20-70^{\circ}2\theta$. The samples were
110 ground and sieved through an $80\ \mu\text{m}$ sieve mesh and placed over an XRD zero-background sample holder.
111 X-ray data were fitted using the pseudo-Voigt profile function. Specimen displacement, polynomial
112 coefficients for the background function, lattice parameters, profile parameters, and Gaussian and
113 Lorentzian profile coefficients were refined [Bish and Post, 1989]. XRD refinement shows that Calcite
114 (CaCO_3 , ICSD #01-086-2334) is the only detected mineral in the stone, suggesting that other mineral
115 phases (e.g. feldspar containing P, Si, Fe, K, Al and S, which were elements detected by XRF) could be
116 present in amorphous or poorly crystallised phases or in amounts below the instrument detection limit ($<$
117 1%).

118
119 The pore structure was determined by Mercury Intrusion Porosimetry (MIP) by means of a PASCAL
120 140/240 instrument. The contact angle was taken to be 140° . Samples for MIP consisted of stone fragments
121 measuring approximately $8 \times 15\ \text{mm}$ which were dried in a fan-assisted oven at $60\ ^{\circ}\text{C}$ until constant weight.
122 MIP results shows that the porosity of this stone is $14.10 (\pm 0.42)\%$ and the density is $2.0801 (\pm 0.03)\ \text{g/cm}^3$.

- 123
124 – **Weathered limestone 2** (Fig. 2): The origin of this piece is unknown. The specimen was stored in the
125 Building Research Establishment (BRE) outdoor historic stone deposit. It is a sedimentary rock composed
126 of ooids cemented by sparry calcite. The rock can be classified as an intrasparite [Folk, 1959] or
127 Grainstone [Dunham 1962]. The surface of the stone is covered by a dark grey patina (Fig. 2a). This stone
128 is referred to as LS. This stone was also cut into $35 \times 35 \times 35\ \text{mm}$ cubes for testing making sure that their
129 surface was free of the dark grey patina.



131 **Figure 2.** Weathered limestone (referred to as LS). a) Studied limestone showing a black patina on the surface; b)
132 stereomicroscope image of the limestone.
133

134 The elemental composition of this stone was calculated by XRF which shows that LS stone is composed of
135 95.2 (± 0.2) of Ca, 1.15 (± 0.07) of Si, 1.3 (± 0.03) of P, 0.9 (± 0.03) of Fe, 0.5 (± 0.2) of Al, 0.3 (± 0.01) of S
136 and 0.2 (± 0.01) of K.
137

138 XRD refinement shows that Calcite (CaCO_3 , ICSD #01-086-2334) is the only detected mineral in this
139 stone, suggesting that any other mineral phases (e.g. feldspar containing P, Si, Fe, K, Al and S, which were
140 elements detected by XRF) could be present in amorphous or poorly crystallised phases or in amounts
141 below the instrument detection level ($< 1\%$).
142

143 The pore structure was determined by Mercury Intrusion Porosimetry (MIP) which showed that the
144 porosity of this stone is 16.30 (± 0.22) % and the density is 2.0354 (± 0.05) g/cm^3 . Due to the nature of its
145 allochems (sub-spherical grains, i.e. ooids) and due to the sparitic cement not filling completely the
146 intergranular spaces, this limestone is characterised by a higher amount of larger pores than the CP
147 limestone (see section 3.1).
148

149 2.2 Nanolimes

150 Two nanolime dispersions were used for this test:

- 151 - Nanorestore Plus Propanol 5® (CSGI Consortium - University of Florence, Italy) [Nanorestore® Italian
152 Patent No. FI/96/A/000255]: 5 g/L nanoparticles in 2-propanol. Particles are plate-like hexagonal $\text{Ca}(\text{OH})_2$
153 nanoparticles regularly shaped with a particle size ranging from 100 to 300 nm [Baglioni et al, 2014]. This
154 dispersion is referred to as NAN.
155
- 156 - Nanolime synthesised through the method developed by the University of L'Aquila [Taglieri et al, 2015]: 5
157 g/L nanoparticles in 50-50% W/A (water - 2-propanol). Particles are plate-like hexagonal $\text{Ca}(\text{OH})_2$
158 nanoparticles regularly shaped with a particle size ranging from 20 to 80 nm [Taglieri et al, 2017]. This
159 dispersion is referred to as LAQ.

160

161 LAQ was synthesized through an anionic exchanges process carried out at room temperature and ambient pressure
162 by mixing under moderate stirring an anion exchange resin (Dowex Monosphere 550A OH by Dow Chemical) with
163 an aqueous calcium chloride solution (CaCl_2 by Sigma-Aldrich), as described in literature [Taglieri et al, 2015,
164 2017]. The concentration of chlorides was monitored during the process using a Vernier Chloride Ion-selective
165 Electrode CL-BTA. The decrease of chloride content during the synthesis was very rapid and the synthesis was
166 stopped when the ion exchange process was completed (zero kinetic exchange), with a total reduction of chloride
167 content of 99.82% and a residual chloride content of 29.4 mg/L. After the synthesis, 50% vol. of the supernatant
168 water of the produced nanolime (W) was extracted through a pipette and replaced by 50% vol. of isopropanol,
169 maintaining the concentration at 5 g/L. A characterization of morphology, reactivity and colloidal stability of both
170 nanolimes can be found elsewhere [Otero et al, 2018].

171

172 *2.3 Nanolime treatments*

173 Four specimens of each stone (CP and LS) were treated with both nanolimes (NAN and LAQ). The treatment was
174 carried out by brush in outdoor conditions. Both nanolime suspensions were agitated before the treatment.
175 Treatments started two days after the nanolime synthesis of LAQ to increase their effectiveness [Rodriguez-
176 Navarro et al, 2016]. Each nanolime was applied by brush on just one dry and clean surface of each limestone cube
177 (35 x 35 x 35 mm), until the consolidant reached the opposite side of the sample. The application was stopped
178 when no further absorption was observed (surface remained wet for a period of at least one minute). Then the
179 samples were left to dry and retreated again after 24 hours. Samples were weighed before and after each application
180 to obtain the amount of nanolime absorbed by each cube. The treatment was considered complete when each cube
181 absorbed 500 mg of calcium hydroxide (approximately 100ml) which required approximately 30 consecutive days
182 of application for each nanolime. Upon treatment completion, the samples were stored outdoor in a sheltered area
183 for a period of 28 days ($\text{RH} \approx 60\text{-}80\%$, monitored by a humidistat). A set of untreated control samples was also
184 stored in the same conditions.

185

186 *2.4 Consolidation effectiveness*

187 Following 28-day outdoor exposure, the limestones cubes were dried to constant mass at 60 °C in a fan assisted
188 oven and subsequently stored in a desiccator until testing.

189

190 In order to assess the degree of carbonation of the nanolime after 28 days in the pores, one of the treated cubes was
191 split in half and a 1% phenolphthalein solution (70% ethanol - 30% water) [BRE, 1995] was immediately sprayed
192 onto one of the internal faces. Phenolphthalein is a chemical compound (C₂₀H₁₄O₄) which is a well-known pH
193 indicator which remain colourless for pH <8.2, while it turns to pink/purple colour in pH conditions higher than 9.8
194 [Lahdensivu, 2016]. For this application, due to the alkalinity of nanolime (pH ~ 12), it turns pink in basic solution
195 (nanolime) and colourless in non-basic medium (CaCO₃).

196

197 Pore size distribution and open porosity were measured by MIP. Tests were carried out on two samples taken from
198 the surface (up to a depth of 50 mm) of treated and compared to control samples.

199

200 Capillary absorption curves were obtained [EN 13755] and the water absorption coefficient (WAC) was calculated.
201 Upon completion of this test, samples were immersed in water for 24 hours and apparent porosity was calculated at
202 room atmosphere [ASTM C 67-00]. Their drying behaviour was also followed and the initial drying rate calculated
203 [EN 16322]. This sequence was carried out on three control and three treated samples per each stone.

204

205 The influence of nanolime treatment on surface cohesion was evaluated by the 'Scotch Tape Test' (STT) according
206 to ASTM, 2009 [ASTM D3359]. The test was carried out on treated and control samples with a mean of 9
207 measurements for each sample.

208

209 The resulting consolidation of both nanolimes was also evaluated by means of the Drilling Resistance
210 Measurement System (DRMS) from SINT-Technology, regularly used in the literature for assessing consolidation
211 effectiveness [Costa and Delgado-Rodrigues, 2012]. Tests were performed on both control and treated samples
212 using drill bits of 5 mm diameter, rotation speed of 600 rpm, rate of penetration of 15 mm/min and penetration
213 depth of 20 mm. Drilling resistance values were calculated as the mean of 6 tests per each treatment.

214

215 Any colour changes caused by treatments were evaluated with a spectrophotometer (Minolta CM508D
 216 Colorimeter) with the CIE-Lab system [Rodriguez-Navarro, 2013], using 30 readings taken in different areas per
 217 each treatment as well as of the control sample. Total colour variation (ΔE) is calculated by the formula:

$$\Delta E = \sqrt{\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2}}$$

218 where ΔL^* is the change in luminosity (white-black parameter), Δa^* (red-green parameters) and Δb^* (blue-yellow
 219 parameters).

220

221

222 3. Results and Discussions

223 3.1 Consolidation effectiveness

224

225 The phenolphthalein test carried out on one of the internal faces of the cut open treated cubes shows that there is no
 226 Portlandite present in the pores following 28-day outdoor exposure. This result suggests that both nanolimes (NAN
 227 and LAQ) have fully carbonated in the pores in both stones after a period of 28 days at RH \approx 60-80%.

228

229 The pore structure properties of treated and control samples for both stones are summarised in Table 1. MIP results
 230 show that all treated samples have lower porosity than the control. For the LS stone, both treatments obtained a
 231 similar porosity reduction. In the case of the CP stone, the NAN treatment yielded a higher porosity decrease than
 232 the LAQ. Both treatments also reduced the modal pore diameter while increasing the total pore surface area in both
 233 stones. LAQ treatments yielded a higher increase in total pore surface and decrease in modal pore diameter in both
 234 stones, which suggests that samples treated with LAQ present finer pore network than samples treated with NAN.

235

Table 1. Porosity properties of samples calculated by MIP

	Porosity (vol.%)	Modal Pore diameter (μm)	Total pore surface area (m^2/g)
LS-CO	17.90 (± 0.21)	32.88 (± 0.25)	0.801 (± 0.07)
LS-NAN	15.72 (± 0.23)	32.10 (± 0.21)	1.081 (± 0.03)
LS-LAQ	15.51 (± 0.19)	30.15 (± 0.18)	1.433 (± 0.05)
CP-CO	14.11 (± 0.19)	34.47 (± 0.27)	0.502 (± 0.09)
CP-NAN	10.22 (± 0.15)	13.52 (± 0.17)	0.703 (± 0.06)

CP-LAQ	12.83 (± 0.29)	13.14 (± 0.21)	1.867 (± 0.06)
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The pore size distributions of treated and control samples are shown in Figure 3. It is evident that both treatments affected the pore structure of the two stones. NAN appears to have filled the pores with larger diameters in both stones. In the case of the LS stone, which has a higher population of pores with diameter between 10 μm to 50 μm compared to CP, the NAN treatment also reduced the amount of pores with diameters between 10 and 40 μm (Fig 3a). Additionally, in this stone, MIP also recorded an increase of the pores with diameter between 40 to 100 μm . This is attributed to NAN reducing the number of pores with bigger diameters ($>100 \mu\text{m}$) which are outside of the measurement range of the used MIP technique. Moreover, as a result of this treatment, NAN caused a slight increase in the population of pores with diameters between 0.2 μm and 0.3 μm and between 0.01 μm and 0.03 μm . In the case of the CP stone, which presents a pore structure with large pores within the range 10-100 μm and intermediate pores between 0.1 to 6 μm , the treatment follows the same pattern. NAN treatment clearly closed the large pores with diameter between 20 and 100 μm , and in this case the treatment slightly reduced the amount of intermediate pores with diameters between 0.2 and 1 μm (Fig. 3b).

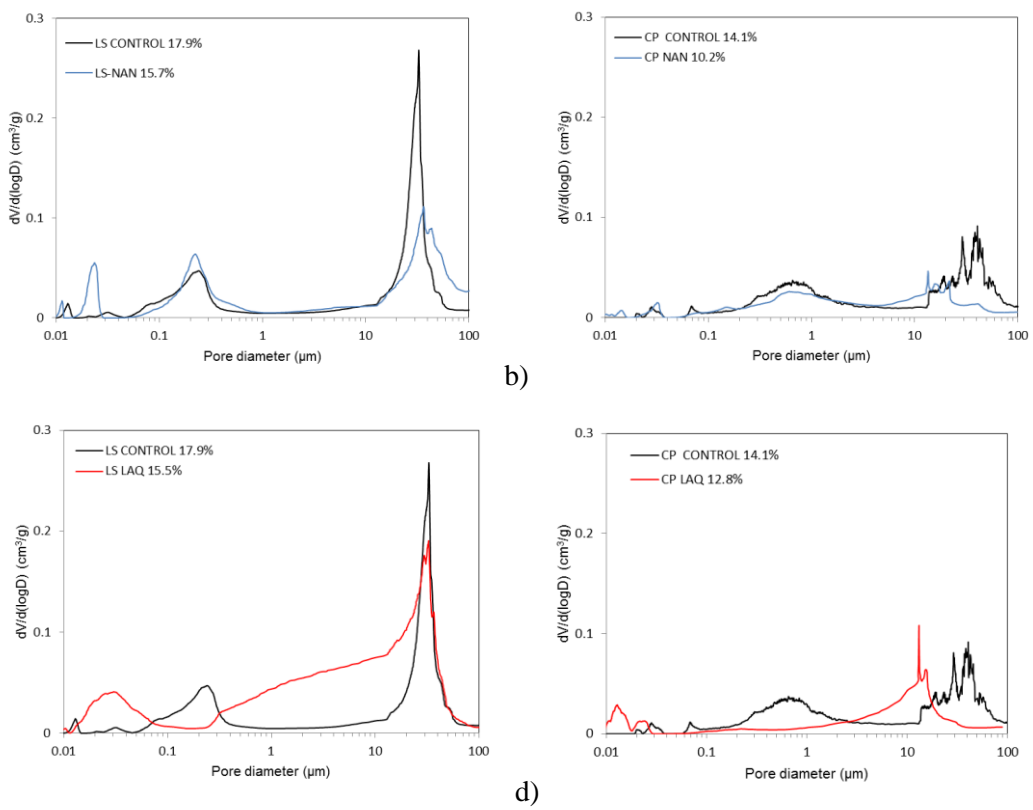
In contrast, MIP results show that LAQ treatment tends to fill both large and small pores alike. LAQ treatment appears to partially fill the pores causing in both stones an increase in the population of smaller pores. In the case of LS stone, LAQ treatment clearly closed large pores between 20 and 40 μm which is accompanied by an increase of the intermediate pores between 0.3 and 20 μm . This treatment also closed smaller sized diameter pores (0.06 to 0.3 μm) which is accompanied by an increase of the finer pores size distribution (0.01 to 0.06 μm) (Fig. 3c). In the case of CP stone, the treatment follows the same pattern. LAQ treatment filled the pores with large pore size distribution (11 to 100 μm) while increasing the amount of intermediate pores (2 to 11 μm) and closed the pores with diameter 0.1 to 2 μm while increasing the amount of finer pores (0.01 to 0.03 μm) (Fig. 3d).

These results suggest that the LAQ treatment could be more effective for consolidating fine pores in the range of 0.1 μm to 1 μm , especially those $< 0.6 \mu\text{m}$, than NAN. This is attributed to the small particle size of LAQ (particle size $\sim 20\text{-}80\text{nm}$), which may allow a better penetration into pores with smaller size diameters when compared to NAN (particle size $\sim 150\text{-}300\text{nm}$). Moreover, nanoparticles tend to agglomerate and form clusters [Rodriguez-

264 Navarro et al, 2013; Borsoi et al, 2016; Rodriguez-Navarro et al, 2016]. The clusters measure approximately
 265 600nm for NAN [Rodriguez-Navarro et al, 2013] and approximately 200nm for LAQ [Taglieri et al, 2017, 2018].
 266 Thus, in the case of NAN, the access of the nanolime particles seems to be restricted to pores with large size
 267 diameter (> 600nm) while in the case of LAQ particles the access is also noticeable in pores with smaller size
 268 diameters up to 100nm. These results suggest that nanolimes with smaller particle size (e.g. LAQ) could be more
 269 effective for consolidation treatments of fine porous substrates (<0.6 μm) than other nanolimes (e.g. NAN) due to
 270 the smaller particle size and clusters.

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 272

273



274

275 **Figure 3.** Pore size distribution of control and treated samples for: a) LS-NAN; b) CP-NAN; c) LS-LAQ; and d) CP-LAQ.

276
 277

278 The water absorption and drying curves are reported in Fig 4 and Fig 5 and apparent porosity by immersion, water
 279 absorption and drying characteristics are reported in Table 2.

280

281 Table 2 shows that both nanolime treatments slightly reduced the apparent porosity of both stones. It also shows
 282 that the NAN treatment yielded a significant 77% decrease in the capillary absorption coefficient (WAC) in the LS
 283 limestone while LAQ only yielded a 15.8 % decrease in the same stone. This is attributed to the higher reduction of

284 the large pores following the NAN treatment without increasing the intermediate pores, which clearly slows down
 285 the capillary rise [Charola and Wendler, 2015]. In the case of CP stone, both treatments slightly reduced the water
 286 absorption by capillary coefficient and both presented similar curves to each other. All treatments yielded similar
 287 reduction of the total water absorbed by capillarity in both stones.

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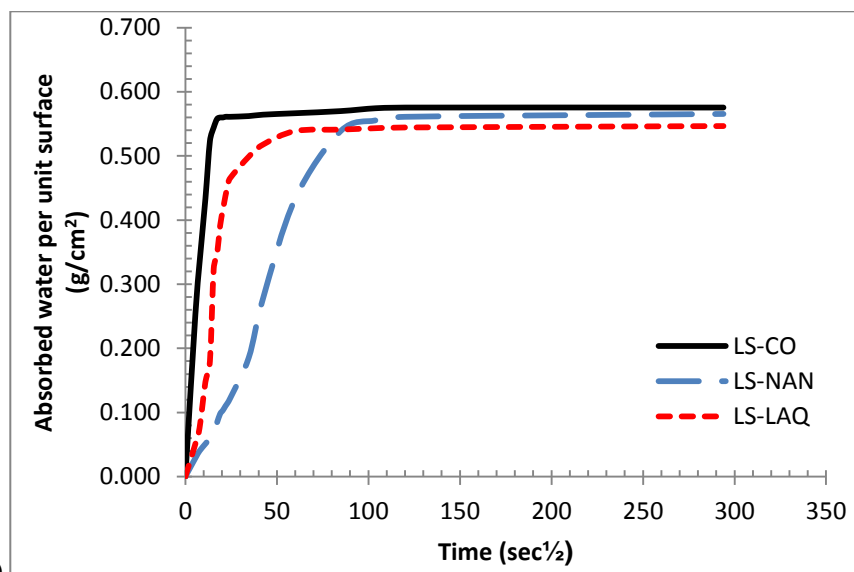
Table 2. Water absorption and drying characteristics

Parameter	LS- CO	LS- NAN	LS- LAQ	CP- CO	CP- NAN	CP- LAQ
Apparent Porosity (%)	7.48 (±0.13)	7.05 (±0.16)	6.96 (±0.21)	6.87 (±0.04)	5.99 (±0.13)	6.26 (±0.08)
W. absorption coefficient ($10^{-3}\text{g}/\text{cm}^2 \text{s}^{0.5}$)	27.4 (± 0.5)	6.1 (± 0.3)	23.1 (± 0.3)	13.9 (± 0.4)	13.2 (± 0.3)	13.8 (± 0.3)
W. absorbed at asymptotic value (g)	5.25 (±0.07)	5.17 (±0.08)	5.11 (±0.17)	4.12 (±0.11)	3.9 (±0.13)	4 (±0.09)
W. absorbed after 24-hour immersion (g)	5.55 ±0.13	5.16 (±0.15)	5.18 (±0.21)	4.51 (±0.04)	4.01 (±0.13)	4.01 (±0.08)
Drying rate ($10^{-3}\text{g}/\text{cm}^3 \text{h}$)	5.9 (±0.2)	5.8 (±0.4)	5.2 (±0.5)	4.4 (±0.10)	3.9 (±0.2)	3.7 (±0.3)
Time for total drying (h)	<50	<50	<50	<50	>50	>50

290

291 All treated stones took more time to reach the asymptotical values (Fig. 4). LS stone control samples reached the
 292 asymptotical values in the first 1.5 minutes of contact with water. In contrast, LS samples treated with LAQ needed
 293 7 minutes and NAN treated samples needed over 2 hours. For the CP stone, both treated samples reached the
 294 asymptotical value in about 1 hour, which was only slightly higher than for the control samples.

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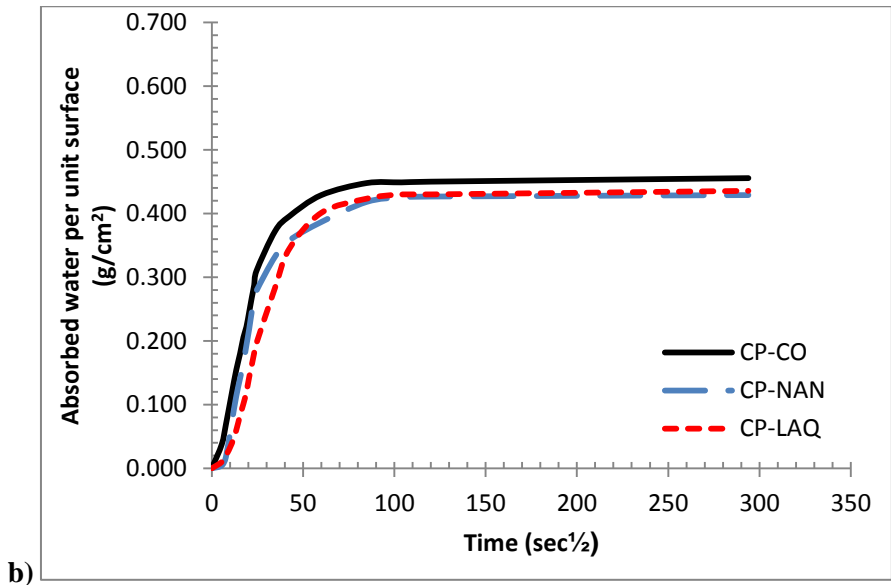
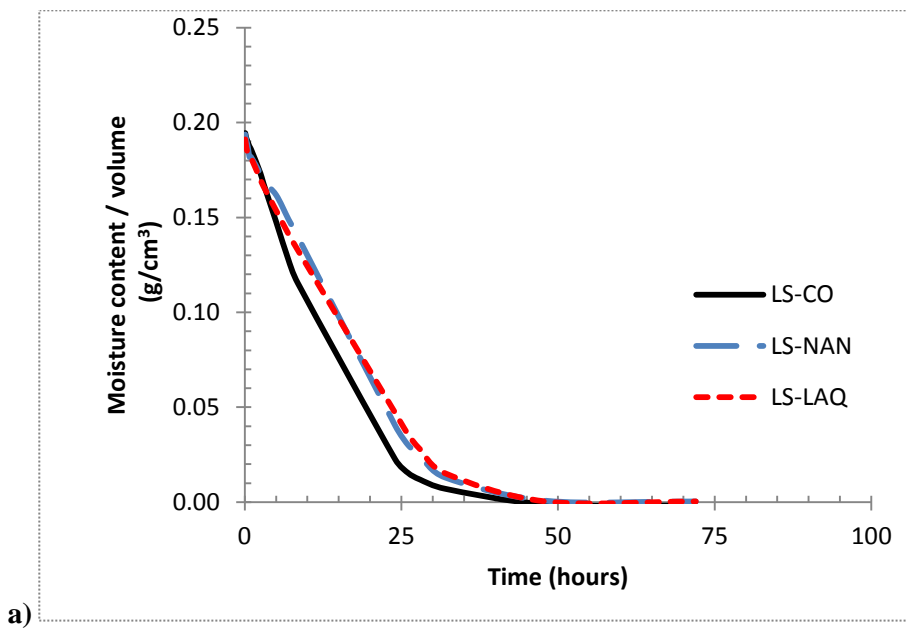
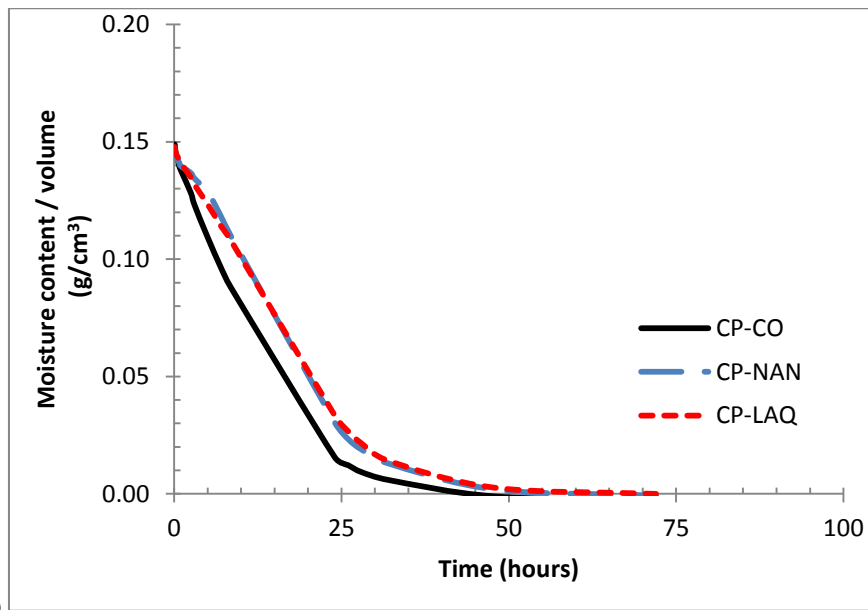


Figure 4. WAC curves for a) LS; b) CP.

The drying curves for both stones are shown in Fig 5. Drying curves for LS and CP show that the treated samples take slightly more time to dry than control samples (Table 2). This could be an undesirable behaviour should the difference increase as it would promote the risk of spalling when the stones are exposed to freeze-thaw cycles, or that of biological attack, etc [Charola et al, 2017]. The slower drying rate is attributed to the more compact pore structure in the weathered layer which has been consolidated after nanolime treatments. The denser structure reduces the liquid transport of water towards the surface hence slowing down the drying kinetics [Charola et al, 2017]. Both treatments present similar drying rate and total drying time to each other in both stones.





b)

Figure 5. Drying curves for treated samples of: a) LS limestone; b) CP limestone

The results of the Scotch Tape Test (STT) are shown in Table 3. All treatments obtained lower values of removed material after nanolime treatments ($\Delta W \approx 62 - 88\%$). These results confirm that all surfaces are more compact after nanolime treatments. STT results confirm that the NAN treatment yielded the highest increase of surface cohesion in LS samples, which is in line with WAC and MIP results that show that this treatment is more effective in this type of stone and can be attributed to the higher reduction of the large pores. In contrast, LAQ treatment yielded the highest increase in the surface cohesion in CP samples suggesting that the surface is more compact for this stone following this treatment.

Table 3. Scotch Tape Test (STT) results

Code ID	Released material (mg/cm ²)	ΔW (%)	SD
LS-CO	9.94	-	6.4
LS-NAN	1.64	83.5	0.5
LS-LAQ	3.28	67.0	2.1
CP-CO	17.74	-	6.6
CP-NAN	6.67	62.4	7.6
CP-LAQ	2.04	88.5	1.4

Scotch area: 3 x 1.5 cm; SD (Standard Deviation of released material)

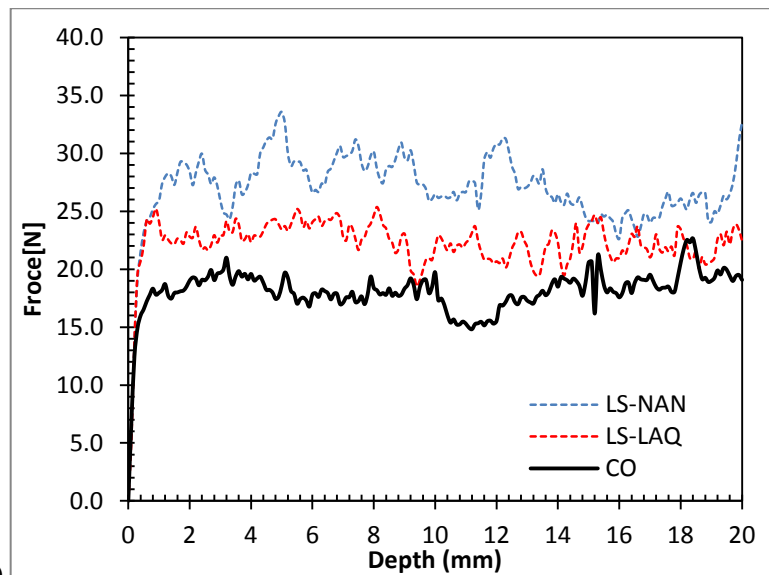
Drilling resistance results for both limestone samples are shown in Figure 6. The drilling resistance of LS limestone is constant throughout the drilling depth (20 mm). In contrast, the drilling resistance of CP limestone shows lower drilling resistance on the surface. This suggests that the external layer of this stone (Capital) has been affected by a

323 weathering process, which decreased the compactness of the stone at the surface. The average drilling resistance of
324 CP stone is $F \sim 12.5\text{N} (\pm 2.59)$, lower than LS stone ($F \sim 18\text{N} (\pm 1.47)$). Both treatments significantly increased the
325 drilling resistance in both stones. In the case of the LS stone (Fig 6a), the samples treated with NAN recorded the
326 highest increase in drilling resistance ($\Delta F \sim 50\%$), which was more pronounced in the outer 14 mm. This is in line
327 with STT, WAC results that shows this treatment is more effective reducing the superficial cohesion and reducing
328 the water absorption by capillarity. In the same stone, LAQ treatment also yielded an increase in the drilling
329 resistance ($\Delta F \sim 22.2\%$), which was constant throughout the drilling depth. The higher increase of strength of NAN
330 in this stone is attributed to the higher reduction of the large pores (20-40 μm), as the reduction of large pores
331 increases the mechanical strength more than in the case of a reduction in the number of small pores [Zhao et al,
332 2014]. In the case of CP stone (Fig. 6b), both treatments yielded similar drilling resistance which was constant
333 throughout the drilling depth (20 mm). Both NAN and LAQ treatments resulted in a strengthening of the weathered
334 layer, where the drilling resistance increases considerably in the outer 14 mm ($\Delta F \sim 20.8\%$ for NAN and $\Delta F \sim 18.4\%$
335 for LAQ).

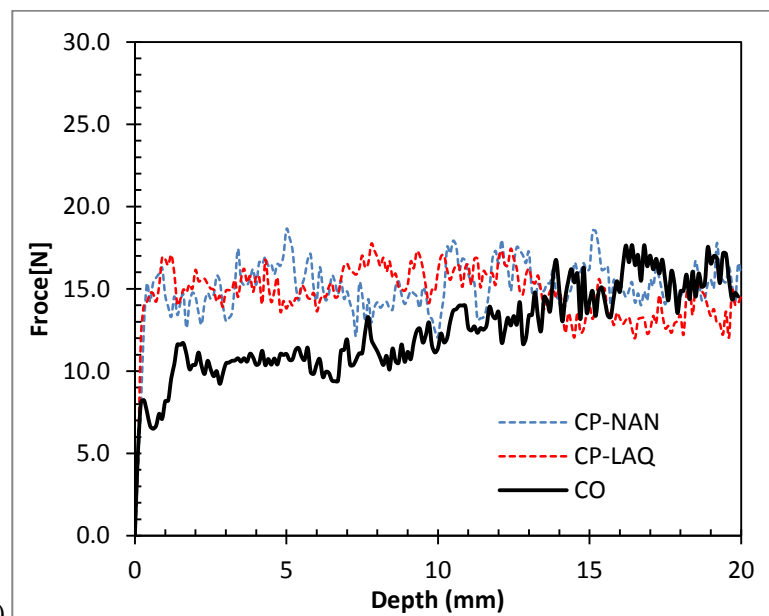
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337 DRMS results of both stones show that the penetration of the two nanolimes is significantly deeper in both
338 limestones (14 – 20 mm) than previous studies on lime-mortars (6 - 10 mm) [Otero et al, 2018]. Furthermore, the
339 increase in drilling resistance is significantly higher in pure calcite-based materials (both limestones, increase of
340 $\sim 10 - 20\text{N}$) than in lime-mortars (increase of $\sim 1\text{N}$), which were composed of 82.3% quartz and 17.7% calcite
341 [Otero et al, 2018]. The higher mechanical strength in lime-based substrates is attributed to the higher amount of
342 calcite facilitating the bonding of the newly formed calcite to the existing calcite crystals thus inducing a higher
343 resistance due to chemical compatibility [Lanas et al, 2004].

344



345 a)



346 b)

347 **Figure 6.** DRMS measurements of: a) limestone (LS); b) weathered capital (CP).

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349

350 Ideally a consolidation treatment should improve the physico-mechanical properties without affecting the aesthetic
 351 properties. A common side effect of nanolime treatments is the whitening of the surface following treatment.
 352 Spectrophotometric analyses were carried out to measure changes in L^* (white-black parameter) and ΔE^* (total
 353 colour variations) following the treatments. ΔE^* and ΔL^* values <5 are considered suitable for consolidations as
 354 they are imperceptible by naked eye [Rodríguez-Navarro et al, 2013]. Results (Table 4) show that the treatments
 355 caused a whitening of the surface. Both treatments in both stones caused variations of both ΔE^* and ΔL^* with
 356 values above 5 and both obtained similar values to each other. The whitening is attributed to the accumulation of
 357 carbonated nanolime particles on the surface following the treatment.

Table 4. Chromatic alterations for treated samples

	ΔL^*	Δa^*	Δb^*	ΔE^*
LS-NAN	8.23 (± 0.098)	-1.76 (± 0.67)	-6.79 (± 0.89)	10.81
LS-LAQ	9.78 (± 1.11)	-1.74 (± 0.88)	-4.95 (± 0.78)	11.09
-	-	-	-	-
CP-NAN	11.15 (± 1.40)	-2.56 (± 0.87)	-13.48 (± 1.21)	17.68
CP-LAQ	10.28 (± 1.52)	-0.61 (± 0.56)	-4.43 (± 0.87)	11.21

Mean Values determined on 30 measurements

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363 **4. Conclusions**

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365 The present study has shown that both nanolime products, NAN and LAQ applied by surface brushing, cause
 366 significant consolidation of two different types of limestones with diverse porosity structure. Both types of
 367 nanolime are considered acceptable for a potential in-situ consolidation treatment of weathered stone at the
 368 Cathedral of Wells or any historic structure built with Doulling stone. The consolidation effectiveness of both
 369 nanolimes present small differences depending on the substrate pore structure.

370

371 It has been shown that:

- 372 - Both treatments reduced the porosity of the two types of limestones. In the case of LS stone, both
 373 treatments obtained a similar porosity reduction. In the case of CP stone, the NAN treatment yielded a
 374 higher porosity decrease than the LAQ one. However, LAQ treatments yielded higher increase in total pore
 375 surface in both stones than NAN did, suggesting that LAQ treated samples present a finer pore network.
- 376
- 377 - The pore size distribution curves show that NAN treatment predominantly tends to close the pores with
 378 large pore sizes ($\sim 20 - 100\mu\text{m}$), while LAQ treatment tends to fill both large ($\sim 20 - 100\mu\text{m}$), and small
 379 pores ($\sim 0.07 - 2 \mu\text{m}$) equally. These results suggest that LAQ treatment could be more suitable to
 380 consolidate substrates with finer pores than NAN and can be attributed to the smaller particle size of LAQ
 381 ($\sim 20-80\text{nm}$) and smaller cluster formation ($\sim 200\text{nm}$), compared to NAN particle size ($\sim 150-300\text{nm}$) and
 382 clusters ($\sim 600\text{nm}$), that could facilitate the access of the nanoparticles to the finer pore structure (<0.6
 383 μm).

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- Both treatments reduce the water absorption by capillarity and drying rates due to the finer pore network in the stone's surface following treatment. NAN treatment yielded the largest decrease in capillary absorption rate for the LS limestone as this treatment yielded higher reduction of the large pores without increasing the intermediate pores. In the case of CP stone, both treatments reduced the water absorption by capillarity rate and both present similar water absorption curves.
- Scotch tape test confirms that both treatments successfully restore the surface cohesion of both limestones. NAN treatment yielded the highest increase in the surface cohesion in LS samples, where the treatment yielded higher reduction of the large pores.
- Both treatments clearly increase the drilling resistance of the stone after treatments. NAN treatment clearly yielded the highest increase of the drilling resistance ($\Delta F \sim 50\%$) in the LS stone, which is attributed to the increased filling of the large pores. However, in the CP stone, both treatments yielded a similar drilling resistance as both resulted in similar reduction of the large pores. Both treatments were able to consolidate the external weathered layer of the sample maintaining a constant drilling resistance throughout the stone. These results suggest that nanolime with larger particle size (e.g. NAN) could be more effective in coarse porous substrates as they yield higher reduction of the large pores (20-40 μm) and higher increase of mechanical properties than nanolimes with smaller particle size (e.g. LAQ).
- The penetration and increase of the drilling resistance due to nanolime treatments is significantly higher in pure calcite-based substrates (both limestones) than in lime-mortars composed of approximately 80% of quartz and 20% of calcite [Otero et al, 2018]. The higher mechanical strength can be attributed to the fact that the bonding between calcite-calcite delivers higher resistance due to its higher chemical compatibility [Lanas et al, 2004].
- Finally, colorimeter results show that both treatments caused a slight whitening of the surface of the limestones.

413 One conclusion of this study is that the selection of a nanolime product for a consolidation treatment must be done
414 in relation with the nanolime particle size and the substrate pore structure. Thus, Nanorestore Plus IP5® would be
415 more suitable for consolidating stones with large pore sizes and L'Aquila nanolime for stones with fine pore sizes.
416 Further studies are required to better understand the influence of the particle size in relation to the substrate
417 porosity.

418

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