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Preliminary investigations of compatible nanolime treatments on Indiana limestone and weathered marble stone

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Abstract. The conservation of historic structures must be carried out through treatments that use materials which are compatible with the originals. In recent years, nanolime has been considered one of the most promising products for the consolidation of calcareous substrates due to its characteristics of high compatibility with the treated susbstrate and durability. The effectiveness of nanolime products has been proven for superficial consolidation treatments (e.g. plasters and wall-paintings), and research nowadays is focused on the study of the in-depth consolidation effectiveness of porous substrates. The aim of this paper is to undertake preliminary investigations of compatible nanolime treatments for Indiana limestone (US) and a weathered marble. Nanolime was synthetized by anion exchange resins and dispersed in isopropanol and ethanol. The consolidation effectiveness was assessed by studying changes in porosity, drilling resistance, surface cohesion and aesthetic appearance (colour). Results showed that nanolime yielded the highest consolidation effectiveness when treated samples were kept in high relative humidity environments (~75%RH) or regularly sprayed with carbonated water in a laboratory environment (~50%RH). These results suggest that for an on-site consolidation treatment with nanolime in dry environments, treated surfaces could be regularly sprayed with carbonated water to increase consolidation effectiveness.

1. Introduction

In conservation work, there is a dictum that consolidation should be done using materials which are compatible with the original substrate [1]. This statement from the Venice Charter for the Restoration of Historic Monuments, sums up the importance of the compatibility of any treatments applied to Cultural Heritage structures with significant value (artistic, cultural or historical). Calcareous stones are important construction materials employed in Cultural Heritage and widely used around the world. These historic structures are susceptible to several weathering processes, which cause structures to lose some of their original properties [2].

The mechanical properties of weathered historic structures are aimed to be restored using consolidating products. One of the most important points is that the used consolidant must meet the "compatibility with the original substrate" condition, as stated by the 1972 Italian Carta del Restauro [3] and considered as one of the three conservation principles by Brandi [4]. In the last four decades, most of the consolidating products used for restoration treatments are silica-based precursors (e.g. TEOS or MTMOS) [5]. These products were originally developed for the consolidation of sandstone, and then extended to other types of stone thanks to their ease of application, good penetration capability, immediate strength enhancement and effectiveness for silica-based substrates [6]. However, in the case of calcareous substrates, these consolidants present low physical and mechanical compatibility with the treated material, which in many cases cause cracks and significant damage in the long term [5-7]. For this reason, lime-based consolidants such as lime-water were traditionally preferred due to their higher compatibility with the matrix and durability [8,9]. The consolidation effect of lime-water (aqueous suspension of lime particles) occurs by the carbonation reaction of lime particles (portlandite ($Ca(OH)_2$)) when exposed to atmospheric CO_2 and H_2O, producing new $CaCO_3$, which is obviously totally compatible with the matrix of calcareous materials. Thus, this method presents a high compatibility with the substrate as it "*adds more of its natural cementing materials to the substrate"*. However, the lime-water consolidation technique presents some important limitations such as a reduced impregnation depth (few millimetres), a very slow carbonation process, a low amount of lime particles applied in each application, and a limited access of lime particles to the pores with small diameters; which in many cases leads to unsatisfactory treatments [10].

Nanolime is based on the lime-water technique and keeps the same high compatibility with the substrate but presents higher consolidation properties due to the smaller size of the lime nanoparticles and especially the higher

amount of consolidant and a lower amount of water introduced to the stones [8, 11, 12]. Nanolime has been successfully synthetized by several methods: diols [13, 14], w/o microemulsions [15], aqueous solutions [16,17], solvothermal reactions [18, 19] plasma metal reaction method [20] or anion exchange kinetics [21, 22]. The latter method synthetized nanoparticles which present higher reactivity and smaller particle size [23, 24].

The consolidation effect of nanolime occurs by the same carbonation reaction as for lime-water; however, the smaller size of the lime particles improves the penetration providing access to smaller pores and faster carbonation process due to the higher specific surface of nanoparticles [12]. Since its development in 2001, nanolime has been effectively tested for the consolidation of several substrates such as wall-paintings [13], lime-mortars [24], limestones [25], biocalcarenites [23,26], and other historic materials such as paper [16], canvas [27], bones [28] or wood [18]. Recently this type of nanolime has been also applied successfully on in-situ and long-term applications [19, 29, 30, 31, 32].

2. Research Aim

This paper describes the preliminary investigations of compatible nanolime treatments for Indiana limestone, a stone that has been used in many buildings in the US, as well as for weathered marble, to test out its effectiveness prior to testing it in-situ on the weathered marble (from Texas, Md) sills of the west facade of the Reynolds Center, previously the Patent Office Building, which houses both the Smithsonian's National Portrait Gallery and the American Art Museum (Washington, D.C., USA). The consolidation effectiveness of two types of nanolime (dispersed in ethanol and isopropanol) was assessed by studying changes in porosity, drilling resistance, superficial cohesion and aesthetic appearance.

3. Materials and methods

3.1 Limestone and Marble Samples

- **Indiana limestone**: This stone, which is shown in Figure 1, is a limestone which is one of the most commonly used building materials in the USA [33]. The stone is a sedimentary rock composed of bioclasts and intraclasts cemented together by sparry calcite cement. The rock can be classified as a biointrasparite

[34] or Grainstone [35]. This stone was cut into 5 x 5 x 5 mm cubes for testing. This stone was referred to as "I".

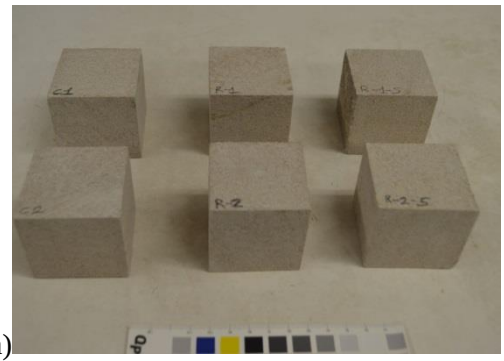
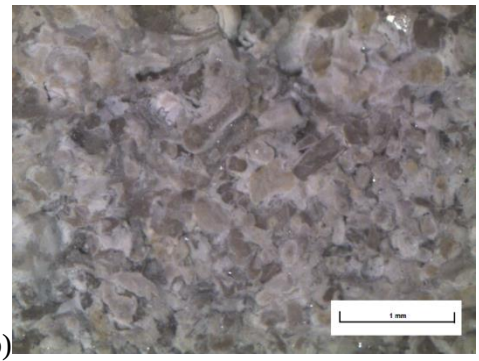
a)  b) 

Figure 1. a) Indiana limestone cubic samples; b) steromicroscope image of the limestone.

The elemental composition of this stone was calculated by XRF which shows that the stone is composed of 97.7 (±0.2) of Ca, 0.81 (±0.01) of Si, 0.45 (±0.003) of P, 0.18 (±0.001) of Fe, 0.61 (±0.02) of Mg, 0.19 (±0.001) of S and 0.03 (±0.001) of Sr.

The mineralogical composition was determined by X-Ray Diffraction (PANalytical XPert PRO) where XRD patterns were recorded with a step size of 0.026˚2θ, in the angular range 20-70°2θ. The samples were ground and sieved through an 80 µm sieve mesh and placed over an XRD zero-background sample holder. X-ray data were fitted using the pseudo-Voigt profile function. Specimen displacement, polynomial coefficients for the background function, lattice parameters, profile parameters, and Gaussian and Lorentzian profile coefficients were refined and XRD data was analysed by Rietveld refinements [36, 37]. XRD-Rietveld refinement shows that the only mineral detected is calcite ($CaCO_3$, ICSD #00-005-0586), suggesting that any other mineral phases (e.g. feldspar containing P, Si, Fe, Mg, Sr and S, which were elements detected by the XRF) could be present in amorphous or poorly crystallised phases or in amounts below the instrument detection level (< 1%).

The pore structure was determined by Mercury Intrusion Porosimetry (MIP) which shows that the porosity of this stone is 11.41 (±0.86) % and its density is 1.974 (±0.121) g/cm^3

- **Weathered marble**: This stone, which is shown in Figure 2, is a weathered marble which was probably part of a cornice from a building to be remodelled, in Washington D.C, USA. It was taken from a pile of architectural marble blocks stored in the stone deposit at the Smithsonian Garber facility (Suitland, Md.). This stone presents similar weathering conditions to the weathered marble sills of the west facade of the Smithsonian's National Portrait Gallery and the American Art Museum (Washington, D.C., USA). The stone is a fine-grained marble with two weathered surfaces (black crust). This cornice was cut into 50 x 50 x 50 mm cubes with one of the faces being curved as shown in Figure 1a. This stone is referred to as "M".

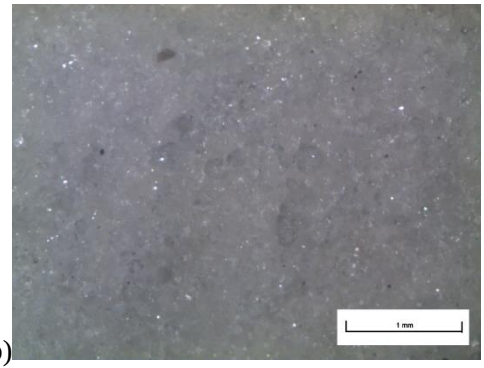
a)  b) 

Figure 2. a) marble samples; b) steromicroscope image of the marble sample

The elemental composition of this stone was determined by XRF (Philips PW2400) on pressed powder samples (Retsch PP-40 pellet press). XRF results for the superficial black crust and the core of this stone are reported in Table 1.

XRD-Rietveld refinement shows that the only detected mineral in the marble core is Calcite ($CaCO_3$, ICSD #00-005-0586). However, quantitative analysis by Rietveld refinement of the black crust shows the mineralogical composition of the black crust is 84.4% calcite ($CaCO_3$, ICSD #00-005-0586), ICSD# 980086161) and 15.6% gypsum (calcium sulphate, $CaSO_4$, ICSD# 01-076-1746). This result was confirmed by XRF (Table 2), which showed that the black crust consists mainly of gypsum ($CaSO_4$), probably resulting from the reaction of $CaCO_3$ with acidic rain [38].

Table 1. XRF analysis of the marble sample (wt %).

	Ca	P	Si	Al	S	Sr	Ti
Core	98.7	0.69	0.38	-	-	0.04	0.19

	(±0.3)	(±0.03)	(±0.1)			(±0.02)	(±0.002)
Black crust	96.4 (±0.3)	0.41 (±0.01)	0.45 (±0.06)	0.14 (±0.02)	2.4 (±0.03)	-	-

The pore structure of the weathered portion of the stone (outer 1 cm from the surface) was determined by Mercury Intrusion Porosimetry (MIP) by means of a PASCAL 140/240 instrument. The contact angle was taken to be 140°. Samples for MIP consisted of two stone fragments measuring approximately 8x8x15 mm which were dried in a fan-assisted oven at 60 ºC until constant weight. MIP results shows that the porosity of the weathered surface is 6.0 (±0.52) % and the density is 2.144 (±0.08) g/cm^3.

3.2 Nanolimes

Nanolime was synthesized through an anionic exchange process carried out at room conditions (± 50% RH, ± 20°C) by mixing under moderate stirring an anion exchange resin (Dowex Monosphere 550A OH by Dow Chemical) with an aqueous calcium chloride solution ($CaCl_2$ by Sigma-Aldrich), as described in the literature [21, 22, 39]. The concentration of chlorides was monitored during the process using a chloride strip (Fisherbrand® Chloride Strips). The decrease of chloride content during the synthesis was very rapid and the synthesis was stopped when the ion exchange process was completed (zero kinetic exchange), with a residual chloride content below 100 mg/L. Following the synthesis, the supernatant water of the produced nanolime was extracted through a pipette and substituted by an alcohol maintaining the concentration at 25 g/L. Two nanolime dispersions were prepared: i) 25 g/L nanoparticles in isopropanol (**IP25**); ii) 25 g/L nanoparticles in ethanol (**ET25**). The synthesized nanolime presents nanoparticles with size of approximately 20-80 nm, which are highly reactive to carbonation [11, 24, 25-27].

A small residual water (W = 5%) remained in the IP25 and ET25 dispersions, as this practice enhances the carbonation process [30]. Dispersions were kept in a refrigerator (T < 5 °C) prior to the application to minimize the $Ca(OH)_2$ particles conversion into Ca alkoxides [40].

3.3 Nanolime treatments

Samples were kept at laboratory conditions (50% (±5) RH) for 7 days before treatment. The treatments were carried out by brush in the same laboratory conditions. Treatments started two days after the nanolime synthesis to increase their effectiveness [40]. Prior to the treatment, both nanolime dispersions (**ET25** and **IP25**) were placed in an ultrasonic bath (60 Hz) for 30 minutes to minimize nanoparticle aggregation. Each nanolime was applied by brush on a dry and clean surface of the specimens. IP25 was applied by brushing on two of the weathered faces of 8 marble specimens (**M**), whereas E25 was applied by brushing on 4 Indiana limestone samples (**I**). Previous research showed that nanolime deposition in-depth within a substrate can be highly influenced by the nanolime evaporation rate, being nanolime products with slightly slower evaporation rate more suitable for coarse porous substrates and nanolime with faster evaporation rate more suitable for fine porous substrates [19]. Based on this findings, nanolime dispersed in ethanol was applied to the marble samples due to the higher evaporation rate, while nanolime in isopropanol, which is the most commonly used solvent for nanolime, was used for the Indiana limestone samples.

The application was stopped when no absorption was observed (surface remains wet for at least one minute). Following saturation, the samples were left to dry and then retreated again after 24 hours when samples were completely dry. The treatment was repeated twice for both nanolimes. Upon treatment completion, the marble samples (**M**) were stored in different environments to evaluate the influence of Relative Humidity on nanolime carbonation: i) two of the treated marble samples were placed in a desiccator with a saturated solution of $Mg(NO_3)_2$ (RH~55%), which were referred to as **M55**; ii) two of the treated marble samples were placed in a desiccator with a saturated solution of NaCl (RH~75%), which were referred to as **M75**; iii) two samples of treated marble were exposed to the room environment conditions (50±5% RH, T = 20±5°C), which were referred to as **MR**; and iv) two of each treated marble were exposed to room conditions and daily sprayed with carbonated water at room conditions, which were referred to as **MRS**. A set of 2 untreated marble control samples **(M-CO)** were stored in the same room.

For the Indiana limestone, treated samples were kept in two environments: i) two of the treated Indiana samples were exposed to the room environment conditions (50±5% RH, T = 20±5°C), which were referred to as **IR**; and ii) two other treated Indiana samples were exposed to room conditions and were sprayed daily with carbonated water (~10 mL of commercial carbonated sparkling water containing approximately 6-8 g/L CO_2 was daily used) at room conditions, which were referred to as **IRS**. A set of untreated control samples was also stored in the same room

environment conditions, **IR-CO** (control samples of Indiana). All samples were analysed after curing them for 28 days in the above conditions.

3.4 Consolidation effectiveness

For the Indiana samples (I), apparent porosity was measured, for each treatment, by immersing two cubic samples in water for 48 hours at room atmosphere as described in ASTM C 67-00 [41]. For the marble samples (M), pore size distribution and open porosity were measured by MIP. Tests were carried out on two samples taken from the treated surfaces (the outer section up to a depth of 50 mm) and on two control samples. MIP was only carried out on Marble samples due to the lack of availability of I samples.

The influence of nanolime treatments on both Indiana (I) and marble (M) surface cohesion was evaluated by 'Scotch Tape Test' (STT) according to ASTM, 2009 [42]. The test was carried out on treated and control samples with a mean of 9 measures for each sample.

The consolidation action of both nanolimes was also evaluated by means of a Drilling Resistance Measurement System (DRMS) from SINT-Technology, regularly used in the literature for assessing consolidation effectiveness [43]. Tests were performed on both control and treated samples using drill bits of 5 mm diameter, rotation speed of 600 rpm, rate of penetration of 15 mm/min and penetration depth of 20 mm. Drilling resistance values were calculated as the mean of 6 tests per each treatment.

The cross-section area of the surfaces of both Indiana and marble treated and control samples were observed under a Scanning Electron Microscope (Hitachi S-3700N). Micro-graphs were taken with an ETD detector and an accelerating voltage of 20 kV. Specimens were coated with a 20nm thick layer of gold using a Quorum Q150T coater unit to prevent surface charging.

Any colour changes in both stones caused by treatments were evaluated with a spectrophotometer (Minolta CM508D Colorimeter) with the CIE-Lab system [44], using 30 readings taken in different areas per each treated and control sample. Total colour variation (ΔE) was calculated by the formula:

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

where ΔL* is the change in luminosity (white-black parameter), Δa* (red-green parameters) and Δb* (blue-yellow parameters) where the difference is with respect to the treated and the control sample.

4. Results and Discussions

4.1 Consolidation effectiveness

The apparent porosity of cubic Indiana limestone samples treated with ET25 was obtained by immersing the samples for 24 hours in water at atmospheric pressure. Table 2 shows apparent porosity and open porosity of treated and untreated samples. Both treated samples, IR (stored in room condition) and IRS (stored in room condition and regularly sprayed with carbonated water), have slightly lower porosities than the control. This suggests that a certain amount of nanolime penetrated and carbonated in the Indiana limestones, although the high standard deviation makes this decrease not statistically significant.

Table 2. Calculated Apparent porosity (% g/g) and Open porosity (cm^3/cm^3)

Sample	**I-CO**	**IR**	**IRS**
Apparent Porosity % w/w	5.99 (±0.52)	5.75 (±0.44)	5.88 (±0.39)
Open Porosity % v/v	13.44 (±0.4)	12.96 (±0.21)	13.04 (±0.31)

The pore structure properties of the weathered marble treated with IP25 and control samples were obtained by MIP and are summarised in Table 3. It is evident that all treatments affected the pore structure of the weathered marble by reducing the open porosity. The highest porosity decrease was observed for the samples which have been treated and sprayed regularly with carbonated water, MRS (~60% decrease), followed by those treated and kept in a 75% RH environment, M75 (~50% decrease). This is in line with the literature, as is well-known that the carbonation process is strongly influenced by moisture and CO_2 exposure [2].

Table 3. Pore structure properties of treated and

control marble samples measured by MIP

Sample	Open porosity (%)	Total pore surface area (m^2/g)
M-CO	6.00 (±0.24)	3.49 (±0.11)
MR	3.85 (±0.33)	2.35 (±0.19)
MRS	2.44 (±0.12)	1.48 (±0.12)
M55	3.11 (±0.29)	1.38 (±0.09)
M75	3.00 (±0.30)	1.76 (±0.18)

The pore size distributions of treated and untreated marble samples are shown in Figure 3. All treatments yielded a reduction in the population of pores with diameters between 0.02 µm and 30 µm, and this reduction is more pronounced for the samples treated with MRS, M-75 and M-55. The pore size regions of 0.1-0.2 µm and 30-50 µm seem to have been less affected by the treatments.

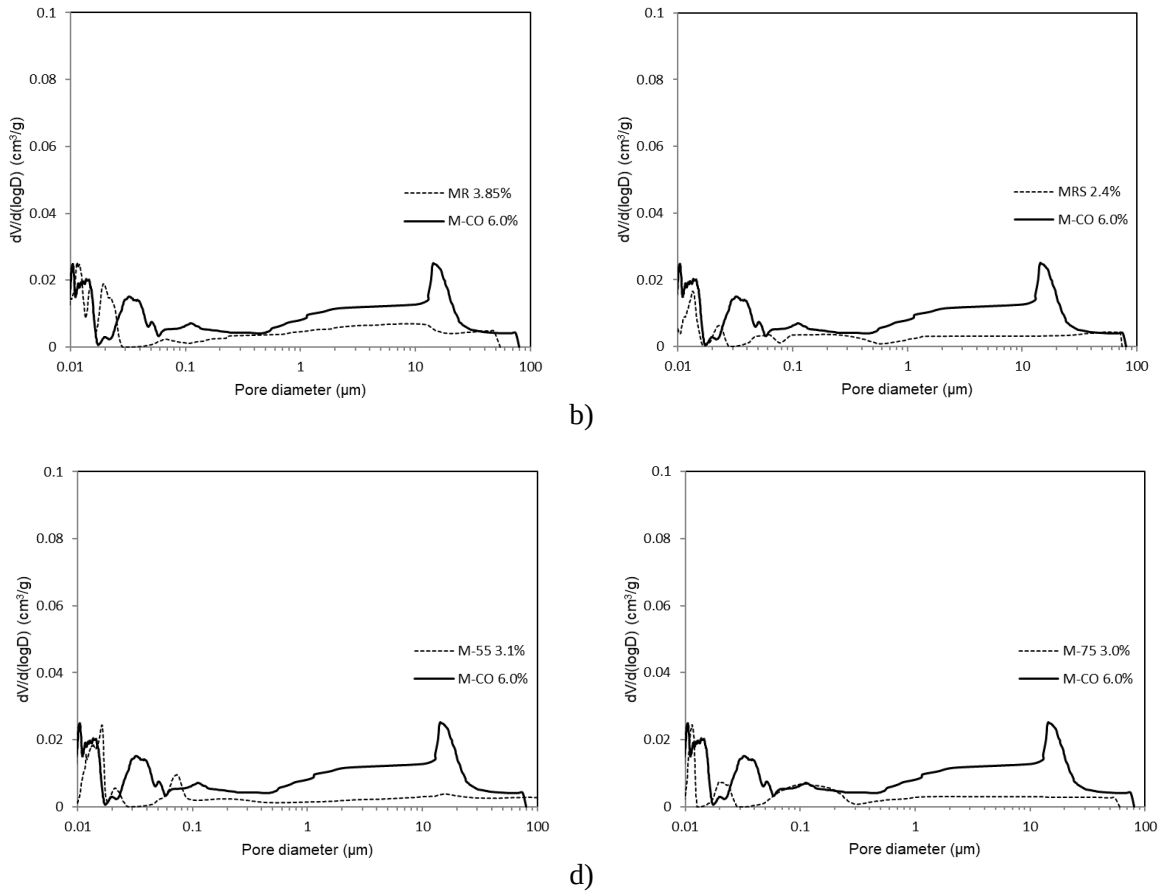


Figure. 3. Differential volume of intruded mercury versus pore diameter of treated and untreated marble samples: a) MR; b) MRS; c) M55; d) M75.

The results of the Scotch Tape Test (STT) for both Indiana limestone and weathered marble are shown in Table 4. All treatments yielded decreased values for the material removed ($\Delta W \approx 54$ - 83%). These results confirm that all

surfaces are more compact after nanolime treatments in all tested environmental conditions. The samples sprayed with carbonated water (IRS and MRS) yielded the highest increase in superficial cohesion (ΔW ≈ 77.2 and 82.8%, respectively). Marble samples stored at 75%RH (M75) yielded higher superficial cohesion than marble samples stored at 55%RH (M55), confirming that keeping samples in high relative humidity environments (~75%RH) increases the consolidation effectiveness [45].

Table 4. Scotch Tape Test (STT): experimental results

	Released material (mg/cm^2)	ΔW (%)	SD
ICO	5.59	-	0.86
IR	2.55	54.3	0.93
IRS	1.28	77.2	0.19
M-CO	9.01	-	2.17
MR	3.56	60.5	1.66
MRS	1.56	82.8	1.47
M55	4.52	49.9	1.78
M75	2.9	67.9	1.54

Scotch area: 3 x 1.5 cm; SD (standard deviation of released material)

Drilling resistance results for the Indiana limestone samples are shown in Figure 4a and Table 5. The Indiana limestone shows a constant drilling resistance throughout the 20 mm drilling depth (F ~ 15N (±1.34)). The samples treated with ET25 stored in room conditions showed no increase in the drilling resistance. In contrast, the samples treated with ET25 and sprayed with carbonated water (IRS), showed an increase in the drilling resistance (F ~ 16.5 N (±1.43)) within the outer 2-3 mm of the sample. These results are also in line with STT results that show that IRS samples present higher superficial cohesion after treatment. However, the increase in the drilling resistance in IRS sample is close to the experimental error.

Drilling resistance results for the marble samples are shown in Figure 4b and Table 5. The drilling resistance of the weathered layer (up to 10-12 mm deep) is lower than in the core of the sample. The drilling resistance average in the outer 10 mm of the stone is F ~ 37.4N (±11.35), while for the inner 10 mm is F ~ 53.5 N (±1.36). This result confirms that the formation of gypsum ($CaSO_4$) (see section 2.1) decreased the compactness of the stone on the surface. The treated marble samples which were sprayed with carbonated water (MRS) yielded a significant increase in the drilling resistance of the external weathered layer (ΔF ~ 51.82%) up to 10 mm. In contrast, samples

kept in the same room conditions (<50%RH) but not sprayed (MR) did not present any increase in the drilling resistance. This result clearly shows that a regular input of moisture enhances the carbonation of nanolime when in low relative humidity environments. Additionally, results also suggest that the inner values, due to the lower weathering of samples, are not affected by the treatment. MR and MR55 treated samples obtained lower drilling resistance compared to the control samples, probably due to the presence of a thicker layer of gypsum on their surface compared to the control samples. Marble samples which were treated and kept at 75%RH (M75) developed the highest increase in drilling resistance on the external weathered layer (ΔF ~ 72.12 %). This confirms that a high relative humidity environment increases the nanolime effectiveness by providing a constant supply of moisture which enhances nanolime carbonation more than an intermittent input of moisture

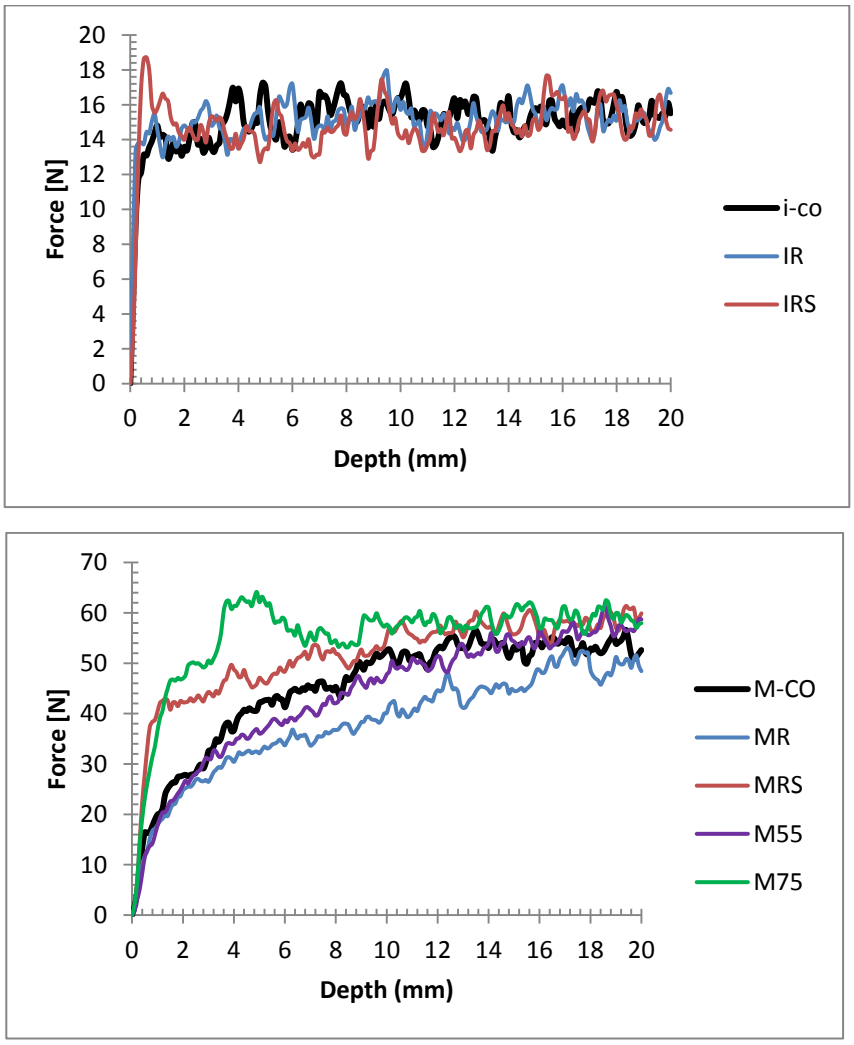


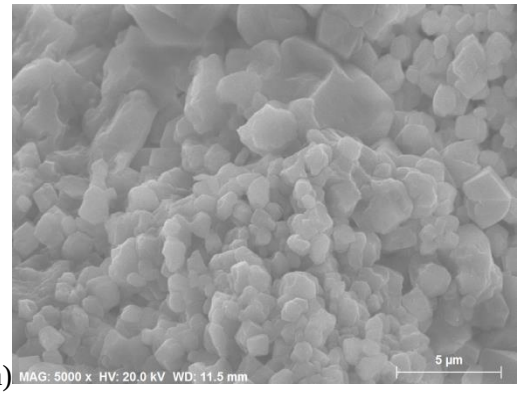
Figure 4. DRMS measurements of untreated (black line) and treated (colours) samples: a) Indiana limestone; b) marble

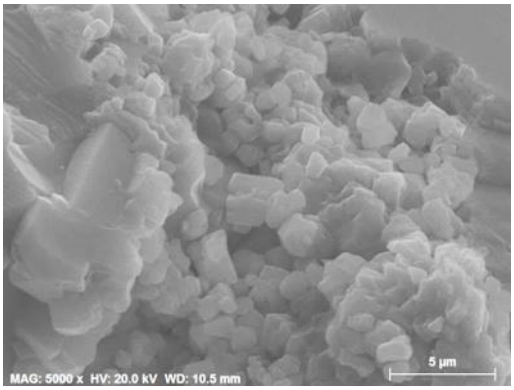
Table 5. DRMS: experimental results

	Force [N]	
	Outer section (10mm)	Inner section (10 mm)

ICO	**14.09 (±0.89)**	**15.49 (±0.62)**
IR	14.4 (±0.61)	15.41 (±0.76)
IRS	16.06 (±1.43)	15.51 (±0.97)
M-CO	**37.42 (±11.35)**	**53.03 (±1.62)**
MR	30.20 (±7.89)	49.15 (±3.66)
MRS	45.84 (±9.79)	57.38 (±1.72)
M55	34.05 (±9.40)	53.56 (±1.83)
M75	51.98 (±10.94)	58.76 (±1.62)

Cross-sections of treated surfaces were examined by SEM. In the case of the Indiana limestone, treated and untreated samples presented no significant differences in terms of morphology, as it is difficult to distinguish between the newly formed calcite crystals from nanolime and the calcite from the limestone. However, SEM images suggest that some newly formed calcite crystals from nanolime are present in the IRS samples, which seem to present smaller size compared to the calcite from the limestone (Figure 5c). This would be in line with DRMS and STT results, which show that these samples present higher drilling resistance in the surface which is attributed to the higher presence of carbonated nanolime particles.

a) 

b) 

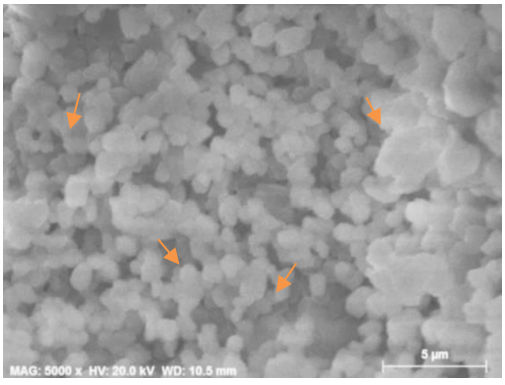
c) 

Figure 5. SEM images of Indiana Limestone samples all at 5,000X: a) I-CO; b) IR; c) IRS, where the orange arrows point to probable calcite crystals from the nanolime.

SEM images of marble samples show some hexagonal plates of portlandite crystals in the core of the samples which were kept at room conditions (MR) and at 55%RH (M55) (Fig. 6a and 6b). SEM images also suggest the possible presence of some gypsum crystals (Fig.6a and 6b). In contrast, no portlandite crystals were observed in samples which were sprayed with carbonated water (MRS) or kept at 75%RH (M75). Furthermore, both MRS and M75 seem to have higher amount of calcite crystals in the pores, which present smaller crystal size than the marble grains (Fig 6b and 6d). These results suggest that the increase in strength and the reduction in porosity of both samples (MRS and M75) could be attributed to a higher carbonation degree of the lime nano-particles. Recent research studies showed that the carbonation of nanoparticles synthetized by this method (anion exchange resins) dispersed in alcohol solvents can take more than a month to occur in low RH environments (<50%RH) and at high concentrations (i.e. 25 g/L) [45, 46].

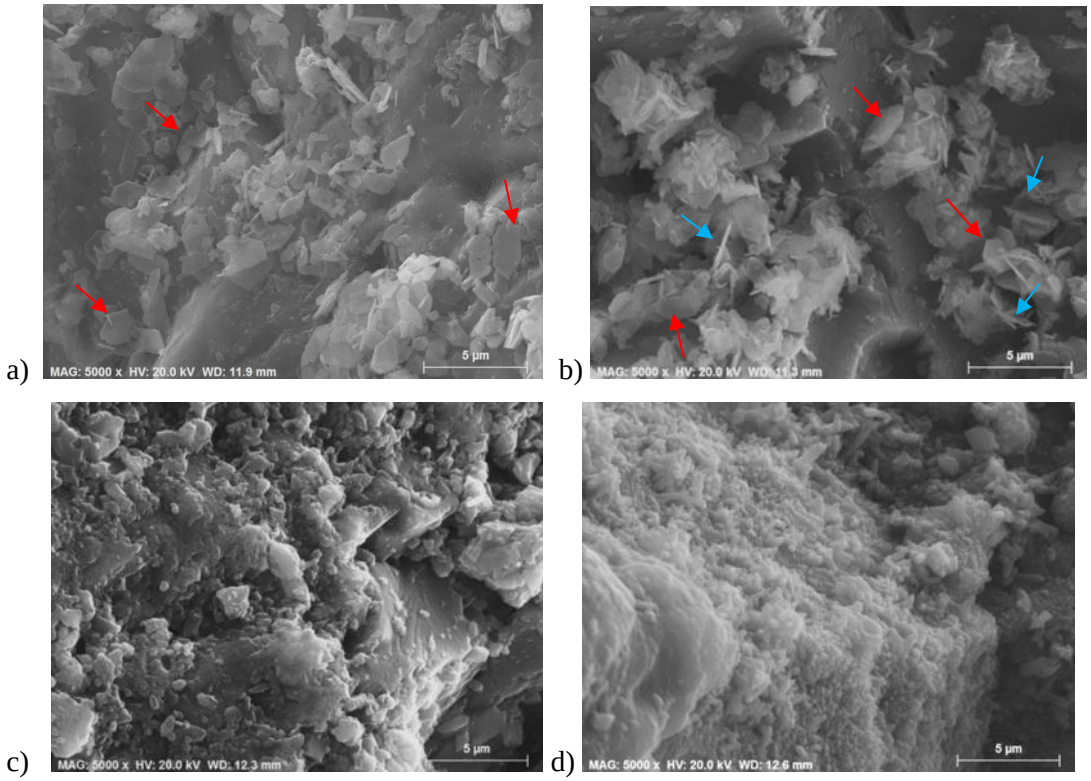


Figure 6. SEM images of treated marble samples all at 5,000X where the red arrows point to Portlandite, and the blue ones to gypsum crystals: a) M-CO: b) MR , c) M55, d) MRS, e) M7.

The colorimetric analyses were carried out to evaluate the changes in L* (white-black parameter) and ΔE* (total colour variations) following treatment. Results (Table 6) show that all the treatments caused minor whitening of the stone surface with both ΔE* and ΔL* values above 5, apart from IR sample which resulted in both ΔE* and ΔL*

values <5. The whitening effect was slightly lower than that observed in the previous studies [14, 47]. This could be attributed to the fact that the application time in the previous tests was longer , resulting in an increased amount of nanolime deposition on the surface [14,47]. These values are slightly higher than the threshold recommended for consolidation treatments [48]. However, despite the increase in both ΔE* and ΔL* values, a recent study found that the whitening effect induced by consolidations with nanolime slightly decrease to values which are not perceivable by naked eye after moisture and UV light exposure without compromising its mechanical properties [24].

Table 6. Chromatic alterations for treated samples with regards to the control one.

	ΔL*	**Δa***	**Δb***	**ΔE***
IR	6.61 (±1.79)	-0.74 (±0.04)	-0.19 (±0.96)	6.65
IRS	4.43 (±0.68)	-0.59 (±0.13)	-0.63 (±0.24)	4.51
MR	2.26 (±0.43)	-0.05 (±0.0.19)	-1.37 (±3.46)	2.64
MRS	2.95 (±3.31)	-0.46 (±0.20)	1.81(±0.42)	3.49
M55	1.18 (±1.93)	-0.10 (±0.34)	1.32 (±0.66)	1.77
M75	2.34 (±0.75)	-0.55 (±0.12)	0.04 (±2.19)	2.4

Mean Values determined on 30 measurements

5 Conclusions

This preliminary study has shown that nanolime can be used effectively for the consolidation of weathered marble stones with a gypsum surface layer. A solution of IP25 of nanolime synthetized by anion exchange processes is considered suitable for an in-situ application on the weathered marble sills of the west facade of the Reynolds Center, which houses both the Smithsonian's National Portrait Gallery and the American Art Museum (Washington, D.C., USA). Nanolime may be applied during the wet season to increase the consolidation effectiveness, or, if applied during the dry season, marble surfaces should be sprayed regularly with carbonated water. In the case of the Indiana Limestone, which was not weathered, only a slight superficial consolidation was observed, although further research needs to be carried out on weathered samples.

In both stones the treatments that involved exposure to high relative humidity or spraying (IRS, MRS and M75) yielded a slightly higher consolidation effectiveness. Both treatments successfully recovered the surface cohesion of the stones as measured by Scotch Tape Test (STT). The treated samples which were sprayed with carbonated

water (IRS and MRS) obtained a higher increase in the surface cohesion compared to samples kept in the same room conditions but without the addition of water by spraying. Marble samples kept at 75%RH obtained higher consolidating results than those kept at 55%RH which confirms that higher moisture conditions enhance the consolidation effectiveness. Drilling resistance results are in line with the STT results. Samples which were sprayed with carbonated water (IRS and MRS) obtained a higher increase in the drilling resistance in both types of stone than samples kept in the same environment without the input of moisture. IRS obtained a slight increase only in the outer 2 mm of the sample, whereas the consolidation in MRS stones occurred throughout the sample but especially in the outer 8 mm, where the weathered layer was consolidated. However, samples kept at 75%RH (M75) obtained the highest increase in drilling resistance of the external weathered layer. This suggests that a high relative humidity environment seems to increase the nanolime effectiveness by providing a constant supply of moisture which enhances nanolime carbonation more effectively than an intermittent input of moisture such as that provided by spraying. Conversely, samples stored at room conditions (50% RH) and samples kept at 55%RH obtained the lowest drilling resistance due to a poorer carbonation rate. This could be associated with the reactivity of the nanoparticles. Recent research showed that the carbonation of nanoparticles synthetized by anion exchange resins, which are dispersed at high concentration (i.e. 25g/L) in pure alcohol solvents, can take more than a month to carbonate in low RH environments [46].

Finally, these results suggest that for an on-site consolidation treatment with nanolime in dry environments, treated surfaces should be regularly sprayed with carbonated water to increase its consolidation effectiveness.

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Conflict of interests

The authors declare that there is no conflict of interest and take a neutral position to offer an objective evaluation of the consolidation process.

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