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CONSOLIDATION OF DETERIORATED CARBONATE STONES WITH $Ca(OH)_2$ NANOPARTICLES

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Abstract

The consolidation effectiveness and changes in the petrophysical properties of dolostones, typically used in historical buildings, are studied after one year of their consolidation with a $Ca(OH)_2$ nanoparticles based product. Dolostone samples were subjected to different accelerated aging tests to simulate the most common outdoor heritage deterioration due to weathering agents (salt crystallization, freezing-thawing, marine aerosol spray and thermal shock). Then, the product was applied using the most currently used application methods (capillarity, total immersion, spray and brushing). The combination of non-destructive techniques (computerized X-ray tomography, spectrophotometry, propagation of ultrasound velocity and Nuclear Magnetic Resonance (imaging and relaxometry)) together with destructive techniques (ion chromatography and mercury intrusion porosimetry) was conducted on the samples to determine the effectiveness of the consolidating product in a long term, depending on the type of decay and damages location, the application method and the penetration depth of this product.

Keywords: Consolidations, weathering, carbonate stones, calcium hydroxide nanoparticles, application methods

1. Introduction

In the architectural and sculptural heritage of the Community of Madrid (Spain), Redueña dolostone has been one of the most commonly used carbonate stone through history from Roman times until the sixteen century. Moreover, it was not only used as building or ornamental stone, it was also used for aggregate crushing in mortars or in the manufacture of ceramics and paintings. Is an ocher-colored stone and was easy to remove from the quarries, handling and working. However, these favorable conditions for construction have been unfavorable for its preservation. As well as other materials that constitute the historic and built heritage, dolostone is exposed to several deterioration processes, either by the intrinsic characteristics of the stone such as its mineralogical composition and petrophysical properties, or by extrinsic agents related to the environment, causing the deterioration and loss of many of these structures that are eventually needing restoration interventions. In many cases, this is essential to proceed with consolidation procedures to restore cohesion and unity, slow down damage and to increase the durability of the stones. In the search of products for these consolidation interventions, the development of inorganic nano-consolidating materials offers the possibility of having compatible products with the substrate by solving some negative aspects that cause traditional consolidating products developing new and promising products for the consolidation of carbonate stones (Daniele, 2008). However, even though calcium hydroxide ($Ca(OH)_2$) nanoparticles are considered consolidating materials compatible with carbonate stones and that may increase their durability, these products are not frequently used by restorers because there are still unsolved issues related to the real and in-situ application. The best application method, the penetration depth of the consolidant, the interaction between the consolidant and the solubles salts or their effectiveness in a long therm are still unsolved questions. For that reason, traditional consolidating products are chosen, even knowing their incompatibility with the substrate and its long-term instability.

The aim of this research is to study the damage caused to carbonate stones (dolostone) by the most common extrinsic agents related to the environment to determine the effectiveness of calcium hydroxide ($Ca(OH)_2$) nanoparticles in a long term, depending on the type of decay, damages location, the application method and the penetration depth of this consolidating product.

2. Materials and methods

Fourteen cubic dolostone specimens of 5.5cm side were used in this study. The samples come from the ancient quarry where the stone was extracted in the past (Redueña) to be broadly used in historical buildings of Madrid (Spain).

The stone samples were subjected to different accelerated ageing test to simulate the most common outdoor heritage deterioration processes due to weathering agents (Table 1). Two samples were subjected to freezing- thaw cycles (120 cycles, following the standard UNE-EN, 2002); four samples were subjected to marine aerosol spray ageing test with sodium cloride (120 cycles, following the standard 14147:2004 UNE-EN, 2004); four samples were subjected to thermal shock ageing test (42 cycles, following the standard UNE-EN 14066:2003); and the rest four samples were subjected to salt crystallization cycles with sodium sulfate (7 cycles, following the standard UNE-EN 12370:1999).

The $Ca(OH)_2$ dispersion used in this study is a commercial product (Nanorestore®) developed at the University of Florence (CSGI Consortium) (Dei et al, 2006). It is based on a colloidal suspension of nanoparticles of slaked lime ($Ca(OH)_2$) dispersed in isopropyl alcohol (5 g/l). The nanoparticles were exposed to room conditions (35 % ± 5.7 relative humidity (RH) at 23.5 ºC ± 1.7 and 470 ppm ± 50 of CO_2) during one year in the laboratory. The environmental conditions during the application of the consolidating product and the storage of the samples were monitored because of their influence on the results of consolidation with $Ca(OH)_2$ nanoparticles (López-Arce et al, 2011, 2010; Gomez-Villalba et al, 2011a, 2011b).

The consolidating product was applied using the most currently used application methods (Ferreira et al, 2008) depending on the damage location. Capillarity and total immersion application were used in the most deteriorated samples, while spray and brush application were used in the samples where the weathering is located in the surface (Table 1). The amount of applied product depends of the application method. 6gr of product were applied by capillarity and by total immersion. However, in the samples where the product was applied by brushing and spraying only 3gr were applied because the surface is saturated earlier and no more product was accepted by the sample.

Table 1. Ageing test, amount of product and consolidation application method used in the studied samples

Ageing test	*Nomenclature*	*Application method*	*Amount of product*
Freezing- thawing	F-C-1 F-C-2	Capillarity	3gr
Marine aerosol	M-S-1 M-S-2	Spray	3gr
	M-B-1 M-B-2	Brush	3gr
Thermal shock	T-S-1 T-S-2	Spray	3gr
	T-T-1 T-T-2	Total immersion	6gr
Salt crystallization	S-C-1 S-C-2	Capillarity	6gr
	S-T-1 S-T-2	Total immersion	6gr

The stone specimens with the consolidating product were analyzed with several non-destructive techniques (NDT), before and after one year of treatment, to study the changes in their physical properties.

For visualizing, locating and measuring internal non-visible damage and to analyze surface weathering, computed X-ray tomography (CT-Scanning) was used. The CT-scanning conditions were: voltage, 120kV; current, 380-mA; angle, 360º; exposure time 0.943s; 8 frames; binning 1x1; 4mm steal filter; pixel size 92µm; and projections, 900. Three-dimensional reconstruction and modelling were performed with VGStudio Max software and UTHSCSA Image Tool 2.0 was used for slice analysis.

Nuclear Magnetic Resonance (NMR) relaxometry and imaging (NMRr-MRI) analyses were performed to observe and to quantify the location and distribution of water inside the objects been able to analyze pore size and location before and after the consolidating application. Obtaining relaxometry curves are related to the size, shape and surface-to-volume ratio of the pores while MRI allows visualizing sections of the samples fully saturated with water showing the internal structure of the samples. NMR parameters: slice thickness SLTH=5mm, matrix size=128x128 and number of acquisition NEX=1.

Spectrophotometry was used to measure the chromatic parameters on the surface of the stone specimens, by means of a spectrophotometer (MINOLTA CM-700d) using the Lab color space or CIELAB. Standard illuminant was D65 and observer 10º and the measured parameters were L*, which accounts for luminosity, a* and b* coordinates (a* being the red-green parameter and b* the blue-yellow), WI for the white index, YI for yellow index and brightness. The total color difference ΔE* is provided as a result of the formula $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$ and the total chroma difference ΔC* is also provided as a result of the formula $\Delta C^* = (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$. Propagation of ultrasound velocity was measured to evaluate the increase in durability and the distribution of the consolidating product that is related to effective porosity. P-wave propagation time was measured to a precision of 0.1µs with a PUNDIT CNS Electronics instrument. Standard recommendations were followed according to Spanish and European standard UNE-EN 14579 (UNE-EN, 2005). The frequency of the transducers used was 1 MHz. Measurements were taken in direct transmission/reception mode, across opposite parallel sides of the cubic specimens in the three spatial directions.

Destructive analyses were also carried out to obtain a better determination of the modifications caused by the accelerated aging test and the application of the consolidating product. Mercury intrusion porosimetry (MIP) was used to assess sample pore structure before and after the ageing tests and before and after consolidation, studing changes in total porosity (P) and pore size distribution (PSD). MIP readings were taken at pore sizes of 0.005 to 400 µm under measuring conditions ranging from atmospheric pressure to 60 000 psia (228 MPa) on a Micromeritics Autopore IV 9500 MIP. Ion chromatography (IC) was performed to identify soluble salts in the samples where salt crystallization ageing test was carried out to identify the salt content that could remain after the ageing test by the determination of some anions (F^-, Cl^-, NO_2^-, NO_3^-, SO_4^{2-}). The soluble salts (anions) in the extracted sample were quantified on a Metrohm 761 Compact IC ion chromatograph. The method used for extracting soluble salts was based on an alternative to the method described in the NORMAL standard (Iñigo et al, 2001) with some additional modifications.

3. Characterization of stone specimens

3.1 Computed X-ray tomography

The results show the internal structure of the samples, being a powerful non-destructive technique for the study of changes in the pore system modifications. Samples submitted to salt crystallization ageing test (with Na_2SO_4) display the most severe damages, while samples submitted to thermal shock test are the least damaged (Table 2 and Figure 1). The 3D reconstruction of the samples submitted to salt crystallization test show loss of material and surface and internal cracking. Also the porosity, observed with image analyses, is the highest (5.4%) and the central slice shows fissures and material loss in the internal structure (Fig.1d).

Table 2. Porosity measured with image analyses on CT-scanning slices showing pores larger than 92µm diameter in the central slice of the dolostone samples

Specimen	*% porosity (pores >92µm diameter)*
F-C-2 (Freezing- thawing)	1.14
M-S-2 (Marine aerosol)	0.5
T-T-2 (Thermal shock)	0.2
S-T-2 (Salt crystallization)	5.4

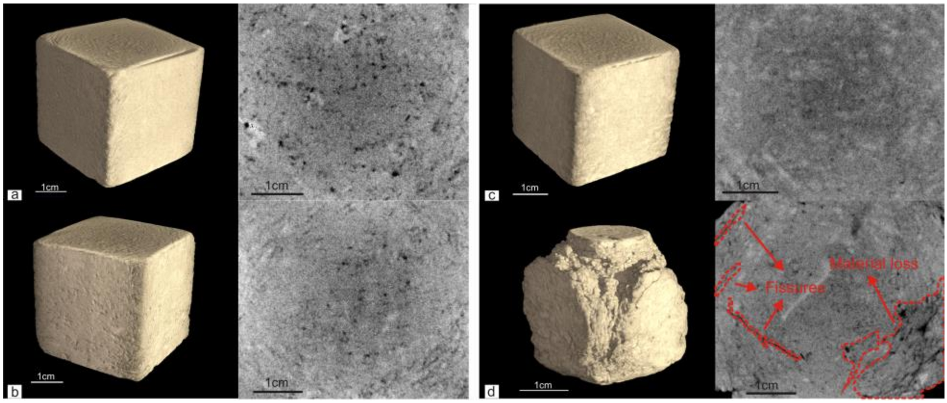

Figure 1. Ct-scanning images of dolostone samples. a) 3D reconstruction of sample submitted to freezing-thaw cycles and central slice. b) 3D reconstruction of sample submitted to marine aerosol ageing test and central slice. c) 3D reconstruction of sample submitted to thermal sock and central slice and d) 3D reconstruction of sample submitted to salt crystallization cycles and central slice

The sample submitted to marine aerosol spray has damage localized in the surface with loss of material and no damage in its internal structure displaying a more internal compact structure and few pores larger than 92µm (0.5%) compared to the other samples.

3.2 Mercury intrusion porosimetry (MIP)

The MIP results are shown in Table 3. Both total porosity and pore size distribution (PSD) change a lot after the ageing tests carried out in the samples. There is an increase of the total connected porosity in all the aged samples (Table 3 and Figure. 2). This increase is in agreement with the results obtained in the CT-scanning analyses, where the highest internal damage is observed in the salt crystallization sample (porosity increases 101%) followed by the samples submitted to freezing-thaw cycles (with an increase of the 42%). The samples with the lowest damages were the samples submitted to marine aerosol (increase of 23%) followed by the sample submitted to thermal shock ageing test. The sample submitted to salt crystallization ageing test displays the highest increase in the specific surface area (SSA). Having a higher SSA means that the area exposed to weathering agents is higher and higher condensation can take place in the pores of the stone. SSA may be used as a durability estimator because high SSA values mean that a greater surface area of the material will be decayed (Benavente, 2004).

Regarding PSD, due to the damage caused after the ageing tests, there is a loss of the smallest pores and an increase of the largest pores. This is observed in the decrease of pore diameters in the range between 0.01 and 1µm and in the significant increase in the range between 1 and 100µm and a slight increase in pores >100µm (Table 3 and Figure 2). There is a modification in the PSD of all the samples with an increase of largest pores, but this modification is especially high in the specimens submitted to salt crystallization test.

Table 3. Specific surface area, total porosity and pore size distribution (diameter) obtained with mercury intrusion porosimetry in non-deteriorated dolostone samples and in samples after accelerated ageing tests

	Stone specimen	*Non-deteriorated*	*Freezing-thaw*	*Marine aerosol*	*Thermal shock*	*Salt crystallization*
	Specific surface area (m^2/g)	0.336	0.312	0.342	0.256	0.382
	Total connected porosity (%)	11.8	16.8	14.5	10.5	23.75
Pore size distribution (%)	*< 0.01 µm*	0.00	0.00	0.00	0.00	0.00
	0.01 - 0.1 µm	2.62	1.34	2.21	1.5	0.93
	0.1 - 1 µm	31.87	20.38	22.82	24.73	15.97
	1-10 µm	61.97	69.03	68.26	67.58	70.84
	10 - 100 µm	1.67	6.09	2.60	1.75	9.89
	>100 µm	1.86	3.16	4.10	4.43	2.37

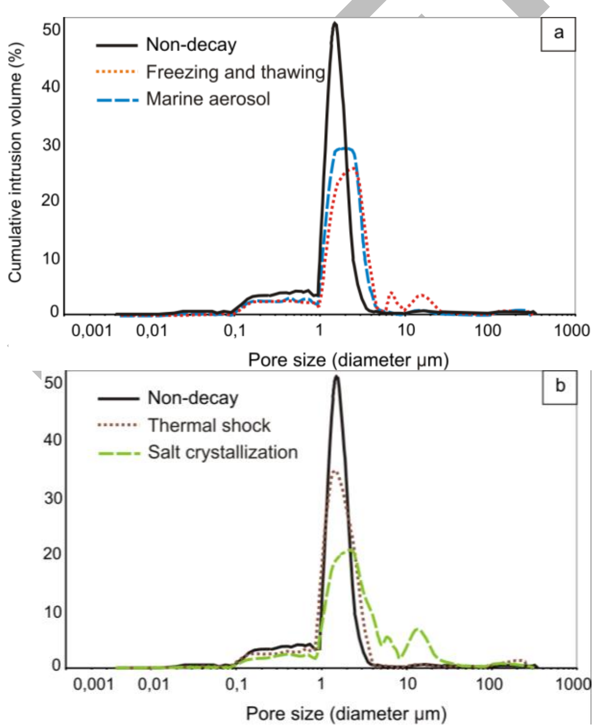

Figure 2. Pore size distribution curves obtained with MIP in the stone specimens. a) samples with no decay and after freezing-thaw and marine aerosol tests; b) samples with no decay and after thermal shock and salt crystallization aging tests.

3.3 Nuclear Magnetic Resonance (imaging and relaxometry)

The results of relaxometry (located NMRr) after submitting the samples to the different ageing tests show higher T2 values (relaxation times) in samples submitted to salt crystallization and freezing- thaw cycles, meaning the presence of larger pores in these specimens (Figure 3) (López-Arce et al. 2010). These values are higher in the central areas of the samples (2.5-3cm deep) than in the surface areas, meaning more internal than superficial damage (in agreement with the 3D CT-scanning reconstruction of the freezing-thaw samples in which no damage is observed in the surface and as well with the slice analysis of the salt crystallization samples which displays internal fissures). These results are in agreement with the results obtained with MIP. Marine spray ageing test submitted sample shifted on larger pores (from 1-3 ms up to 10-20 ms) in the central areas loosing the smallest characteristic pores of the stone. Thermal shock sample shows the lowest T2 values in the surface of the sample; at the central area of the sample the values increase only with a slight decrease of the smallest pores meaning less internal damage.

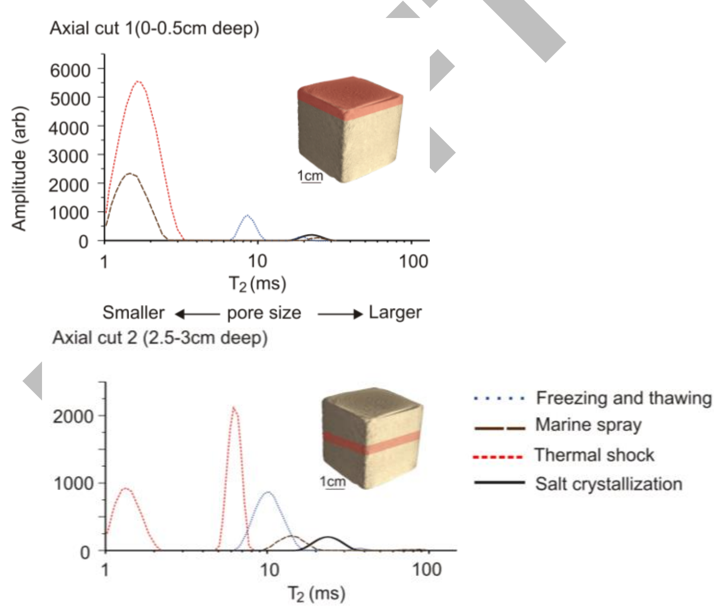

Figure 3. Nuclear magnetic resonance results based on Relaxometry (Located NMRr T_2 distribution) of deteriorated dolostones. Axial cut 1, surface part, between 0 and 0.5cm deep and axial cut 2, central part, between 2.5 and 3 cm deep

After 1 year of the consolidation treatment, the located NMRr T_2 distribution curves show a reduction in the pore size (Fig. 4) in all samples. The samples submitted to salt crystallization cycles and consolidated by total immersion show the highest reduction produced by de filling of the largest pores losing them and showing up smaller pores (Figure 5b). However, this change is slightly higher in the surface part than in the central part because less amount of product arrives to the central part of the sample. However, even though in the central area the reduction of the pore size is smaller, the fissures caused by the cycles of salt crystallization are filled with the consolidating product (Figure 5a). The same process happened in the samples submitted to freezing-thaw cycles. However, the application of the product in this case was by capillarity so, the reduction of pores sizes in the surface is much higher than in the central area because less amount of product penetrates towards the inner of the sample. In the case of the samples submitted to marine spray ageing test, in which the product was applied by spray, the smallest pores disappear from the surface due to their filling and the size of the largest pores is reduced becoming smaller pores. Nevertheless, the central area slightly changes because the consolidating product doesn't penetrate because of the spray application method. Samples submitted to thermal shock ageing test (in which the product was applied by total immersion) the smallest pores are filled and disappear from the surface. Also in the central part, the smallest pores are filled by the product, but there is no change in the case of the largest pores. This may be because the total connected porosity of this sample is the lowest, due to its good conservation state, making more difficult the penetration of the product even though the application method used, total immersion, is the most effective.

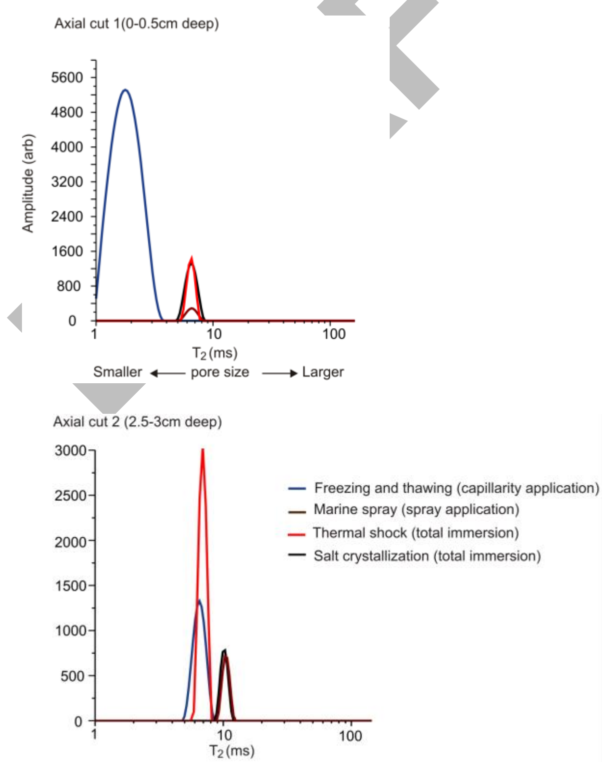

Figure 4. Located NMRr T_2 distribution curves of deteriorated stones after 1 year of consolidation. Axial cut 1, surface part, between 0 and 0.5 cm deep and axial cut 2, central part, between 2.5 and 3 cm deep.

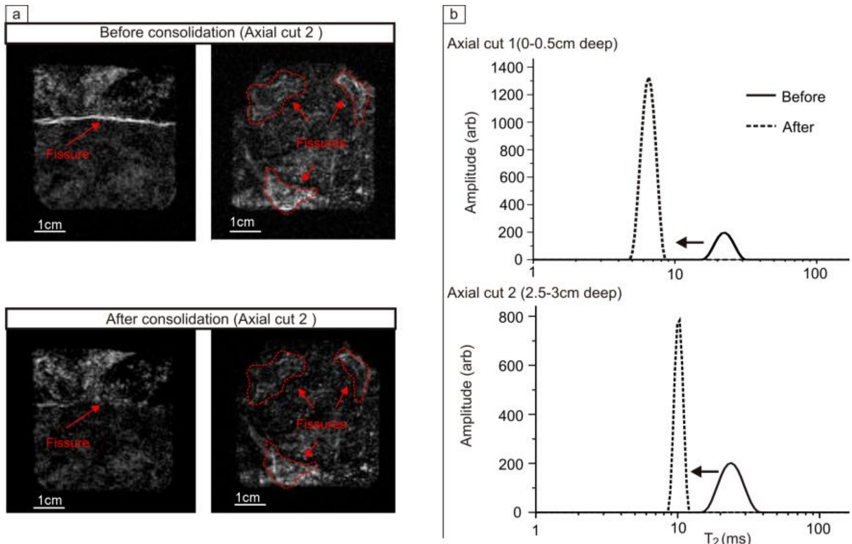

Figure 5. Nuclear magnetic resonance (NMR) of the stone samples submitted to salt crystallization ageing test. a) NMR images of the central part of two samples before and after the application of the consolidating product. The bright areas is the porosity filled with water b) Located NMRr T_2 distribution curves of the superficial and central parts, before and after consolidation by total immersion.

3.4 Ion chromatography (IC)

Even though after the salt crystallization ageing test the samples are kept in water during 24 hours and then these are cleaned with water, some salt could still remain in the pore network (Table 4). The interaction between the consolidating product based in nanoparticles and the soluble salts that still remain in the stone is unclear. Therefore, is important to know the type and quantity of salt content in the samples to identify consequences in the effectiveness of the product in a long term. The highest anion content is displayed by the sulfates because these were used in the salt dissolution to carry out the salt crystallization aging test (sodium sulfate 14%). However, the quantity of chlorides is very low, even though this was also used in the marine aerosol spray ageing test. In this case, during the aging test, the sodium chloride is applied by spray on the surface of the samples, while in the case of salt crystallization test the sodium sulfate is applied by immersion.

Table 4. Anion concentration in bulk material (%) of stone after satl crystallization ageing test

Specimen	F^-	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	*Total ions (%)*
Salt crystallization aging test	0.0007	0.0048	0.0009	0.0029	0.1029	0.1121

3.5 Spectrophotometry

The results of spectrophotometry measurements are shown in Table 5. A slight tendency to darkening of the treated surfaces due to the reduction of the luminosity (ΔL*) can be observed. The chrome (ΔC*) and the yellow index (ΔYI) parameters, in most cases also decrease to a less pure and less yellow color (the untreated stone surface color), due to the mixing of the surface color with the nanoparticles. Nevertheless, the white index (ΔWI) and the brightness parameters in general increase because of the white color of the nanoparticles and due to higher gloss degree of the mineral in comparison to the stone surface. The T-S-1 and T-S-2 specimens show the highest differences, especially in ΔC*, ΔE*, ΔYI and brightness values. On both specimens there is a decrease of the chrome difference (ΔC*) and of the yellow index (ΔYI) and an increase of the white index (ΔWI), the brightness and the total color difference (ΔE*). This may be due to the good conservation state of these samples, resulting in a lower total connected porosity. The thermal shock ageing test was the less aggressive and, due to the spraying application method of the consolidating product, lead to a less penetration of the product, remaining more amount of this in the surface and eventually giving rise to a higher color changes. Therefore, in all specimens the consolidating product does not significantly affect the stone color parameters after 1 year, considering the compatibility criteria indicators available in the literature, since ΔE* is lower than 5 and 3 (Benavente et al, 2003: Delgado et al, 2007: Grossi et al, 2007.)

Table 5. Color variation promoted on dolostone specimens after 1 year of the treatment with $Ca(OH)_2$ nanoparticles.

Specimen	Δ*L**	Δ*a**	Δ*b**	Δ*C**	Δ*E**	Δ*WI*	Δ*YI*	Δ*Brightness*
F-C-1	-0,43	0,40	0,09	0,14	0,59	-0,57	0,26	-0,70
F-C-2	-0,30	0,27	0,00	0,04	0,41	-0,18	0,09	-0,46
M-S-1	-0,51	0,05	0,19	0,20	0,54	-0,94	0,42	-0,92
M-S-2	0,15	-0,09	-0,24	-0,25	0,29	0,89	-0,39	0,41
M-B-1	-0,14	-0,14	-0,63	-0,65	0,66	2,14	-0,91	0,29
M-B-2	-0,27	0,01	0,10	0,10	0,29	-0,43	0,20	-0,46
T-S-1	0,05	0,23	1,37	-1,38	1,38	4,41	-2,04	1,09
T-S-2	-0,12	-0,39	-2,58	-2,61	2,61	8,30	-3,81	1,75
T-T-1	-0,75	0,00	-0,33	-0,32	0,82	0,82	-0,27	-0,81
T-T-2	-0,11	0,01	-0,82	-0,81	0,83	2,69	-1,16	0,46
S-C-1	-0,25	0,05	0,65	0,65	0,70	-2,39	1,02	-0,89
S-C-2	0,51	-1,96	-2,67	-2,11	3,35	8,75	-4,65	2,76
S-T-1	0,29	-0,31	-1,91	-1,93	1,95	6,47	-3,00	1,88
S-T-2	-0,20	0,21	-0,80	-0,76	0,85	2,52	-1,10	0,33

3.6 Propagation of ultrasound velocity (UV)

The propagation of UV of the specimens before and after consolidation is shown in Table 6. Salt crystallization ageing test samples show the lowest UV velocity because of more deteriorated internal structure. Marine spray ageing test samples show the most rapid UV velocities because the weathering concentrates in the suface of the stone, having less internal damage. Except the cases in which the consolidation was applied by capillarity, where the ultrasound velocity (UV) slightly changes, there is an increase in UV in all the specimens. These increases are higher in the specimens submitted to salt crystallization and marine spray ageing tests. In the first case, the stones have higher porosity due to the deteriorated conservation state, making easier the penetration of the consolidating product decreasing so the porosity of the stone by the filling the pores. Is important to take into account that the highest increases in UV occur in the case of the application of the product by total immersion (+15.5%). In the second case, the marine spray ageing test the deterioration is located in the surface and in the first milimeters of the stone. Even though the penetration of the product is lower by using brush or spray application, in the case of samples subjmitted to marine aerosol ageing test, these methods seem to be enough effective to fill the porosity generated in the surface during the wheathering process.

Table 6. Ultrasound velocity (Vp) values before and after 1 year of consolidation

Specimen	*Average Vp for 3 axes (m/s)*		*ΔVp (%)*	*ΔVp (%) average*
	Before consolidation	*After 1 year*		
F-C-1	2936	2958	1	3±2.8
F-C-2	2920	3060	5	
M-S-1	3377	3513	4	4.5±0.7
M-S-2	3134	3294	5	
M-B-1	3260	3316	2	1.5±0.7
M-B-2	3409	3451	1	
T-S-1	2594	2624	1	1±0
T-S-2	2837	2859	1	
T-T-1	2934	3076	5	3.25±2.5
T-T-2	2946	2988	1.5	
S-C-1	1717	1859	8	9±1.5
S-C-2	1632	1794	10	
S-T-1	1977	2451	24	15.5±12
S-T-2	1044	1117	7	

4. Conclusions

According to the obtained results, the highest damage is caused by the salt crystallization ageing test followed by the freezing-thaw cycles test, displaying higher total connected porosities and largest pores in the range between1 and 100 µm diameters. In the case of the samples aged by salt crystallization, the decay is produced both in the internal structure and the surface. However, in the case of samples submitted to freezing-thaw cycles the damage mainly concentrates in the inner part of the samples. Marine aerosol ageing test causes the deterioration mainly in the surface, while thermal ageing test produces minor changes, keeping the best conservation state of all the samples studied.

The changes on the petrophysical properties promoted in the dolostone samples, after one year of the application of the consolidating product based on $Ca(OH)_2$ indicate an increase of the cohesion and unity of the samples, slowing down the damages previously caused in the stone.

Although the soluble salt content in the samples was not enough to generate adverse aspects in the consolidation process, the interaction between this type of consolidating product and soluble salts has to be investigated in further researchs. The identification of the type and amount of salts that could generate undesiderables effects for its the use of $Ca(OH)_2$ nanoparticles in pre-consolidation treatments, especially in the cases where the amount of salt in the porous network is high is very important.

The type of application method has important implications for the effectiveness of the product. The total immersion method seems to be the most effective, entailing greater product penetration, even in the central part of the samples (2.5cm deep), and higher porosity reductions. Spray and brush application methods are the less effective, due to the lesser degree of penetration of the product, causing minor petrophysical changes, in which lesser quantity of product can be applied avoiding the saturation of the surface. Although in these latter cases, where the consolidation is more superficial and more product remains on the surface, no color changes are noticeable.

Therefore, the selection of the type of application method depends on the type of stone and porosity, the displayed decay (internal or superficial) and the type of structure to be treated (masonry, sculptures or decoration artifacts).

Acknowledgments

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