Marine aerosol weathering of Mediterranean Calcarenite stone: Durability of ethyl silicate, nano $Ca(OH)_2$, nano SiO_2, and nanostructured consolidating products

Ainara Zornoza-Indart[1,2], Paula Lopez-Arce[3,4], Karima Zoghlami[5], Nuno Leal[6] and Joaquim Simão[6]

[1]Restoration of Historical Constructions, Urban Evolution and Refurbishment, Doctoral Programme, H.T.S. Architecture, University of the Basque Country (UPV/EHU), Donostia-San Sebastian, Spain; [2]Department of Painting, Faculty of Fine Arts, University of the Basque Country (UPV/EHU), Lejona, Spain; [3]School of Environment, Energy and Resources, Faculty of the Built Environment, Institute for Environmental Design and Engineering (IEDE), The Bartlett, University College London (UCL), London, UK; [4]Property Care Association, Huntingdon, Cambridgeshire, UK; [5]Faculty of Sciences of Tunis, Department of Geology, Laboratoire de resources minerales et environnement, University Tunis el Manar, El Manar, Tunis; [6]GeoBioTec – GeoBioSciences, GeoTechnologies and GeoEngineering, Faculty of Sciences and Technology, NOVA University of Lisbon, Caparica, Portugal

Abstract

Calcarenite stone samples from a historic building (Bizerte, Tunisia) were collected and treated under different environmental conditions with several consolidating products: alkoxysilane (ethyl silicate), a surfactant-templated novel sol-gel, $Ca(OH)_2$, and SiO_2 nanoparticles. These were subjected to marine aerosol accelerated ageing cycles and studied by several non-destructive tests and techniques to assess the stability of the products. Results show that weathering caused by salt crystallization is not inhibited but it is slowed down due to the enhancement of superficial mechanical properties (surface cohesion and micro-hardness) achieved after one month of treatments application. A high or low relative humidity of the consolidation environment significantly affects the final mechanical and aesthetical physical properties and therefore conditions the durability of the treated substrates, even producing higher damage than observed in the blank specimens, depending on the product.

Keywords: Sandstone, Marine aerosol weathering, Durability, Ethyl silicate, Nano $Ca(OH)_2$, Nano SiO_2, Nanostructured consolidating products

Introduction

The elements that influence degradation of materials used in architectural heritage buildings and archaeological stone artifacts can be divided by extrinsic factors, i.e. those related to the surrounding environment such as atmospheric, construction, or anthropic agents, and intrinsic factors, i.e. those that depend upon the material characteristics such as chemical composition, mineralogy, and physical properties. These factors do not act in isolation, but rather interact with each other, enhancing or accelerating weathering patterns and being precursors of further alterations.

Regarding the extrinsic factors, honeycomb weathering can take place under different environments but it is a very common decay pattern of stones exposed to marine aerosol or sea-spray action in coastal areas. The particles of seawater present in the atmosphere mainly originate by the breaking of gas bubbles when the waves collapse (Monahan, 1986). Their principal chemical components are the same as those present in average marine water, being sodium, magnesium, calcium, potassium, and strontium the main cations, and chloride, sulfate, bromide, and bicarbonate the most important anions (Mottershead et al., 2003). Although the term “honeycomb” has been used for a long time (since the nineteenth century), the origin of this type of deterioration pattern is not completely understood, and some controversy still exists about the processes leading to it. Several authors point out the wind erosion, temperature changes, exfoliation, freeze/thaw cycles, salt crystallization, or microorganism action as main causual factors (among others) leading to physico-chemical modifications of the affected stones. However, there is a shortage of laboratory experiments to test many theories proposed for honeycomb development. Relative humidity (RH) and salt crystallization are widely considered as the main factors involved in this weathering progress, concluding that disintegration of mineral grains from the stone surface is the result of physical stress caused by water evaporation and salt crystallization (Mustoe, 1982). Besides RH and soluble salts, some experiments have proved that a heterogeneous wind flux towards the stone surface is a significant agent in this type of pattern development. In fact, Rodriguez-Navarro et al. (1999) refer to wind as one of the key factors in the generation of honeycomb weathering, promoting salt crystallization by evaporation of soluble salts between the mineral grains, causing the formation of small cavities on the stone surface. Reduction of air pressure inside these cavities enhances wind speed, thus accelerating salt water evaporation, promoting a faster and more effective disaggregation in the surrounding regions.

Among the intrinsic factors, both petrographic (mineralogical and textural) and petrophysical characteristics (e.g. effective porosity, surface roughness, permeability) must be taken into account in the process of stone decay. Porosity is the communication path between the stone pore network and the surrounding severe aggressive environment, where degradation agents, such as water, soluble salts, and atmospheric contaminants are able to move through (Fort, 1996a). Depending on the porous characteristics (open porosity, pore size distribution, specific surface, and interconnection pattern), the stone susceptibility can be conditioned by chemical, physical, and/or biological degradation processes. Pore size distribution is one of the more relevant parameters, as it is directly related to the stone capacity of retaining fluids and to the circulation pattern through the porous network. Stones with pores smaller than 1 μm are more susceptible to deterioration than stones with larger ones (Benavente, 2006), as small pores promote water access by capillarity and are more affected by the pressure effect related to salt and ice crystallization (Fort, 1996b; La Russa et al., 2013). Stress caused by salt crystallization must be considered for pore sizes from 0.1 - 10 μm. In a network with smaller pores, a considerable saturation degree is required to produce crystallization and such saturation levels are not frequent in building materials. In the case of pores above 10 μm, these act as sinks consuming high supersaturations caused by the growth of large crystals without producing sufficient stress to damage the stone (Benavente, 2011). Also, the presence of water inside stone materials promotes a reduction of durability, favoring salt and ice dissolution and crystallization processes, pollutant particle adsorption, or biological colonization (Tiano, 1998; Warscheid & Braams, 2000; Benavente, 2006; Miller et al., 2012). In addition, the stone mechanical strength can be reduced by water films generated at the pore surfaces, thus decreasing the material surface free energy (Bell, 2000).

Surface roughness has a strong influence on water retention, particle adhesion, saline spray absorption, salt crystallization, and bio-receptivity patterns. Stone surfaces with low roughness values have lower surface area values, leading to less amount of material exposed to chemical reactions and physical action, lower water retention levels, and lesser amount of organic and pollution particle adhesion. On the contrary, materials with higher roughness values or with large surface cavities display larger exposure areas, allowing higher water and moisture retention levels, as well as greater amounts of particle accumulation, generating suitable micro-environmental conditions for microorganism development. Regarding the influence of surface roughness on the absorption of saline fog and salt crystallization, Urosevic et al. (2010) have studied the weathering of travertine limestones and other carbonate rocks used as building materials. Their results show that the stones with higher roughness values favor saline fog absorption, producing greater alterations and porosity enlargements. Later on, the same authors (Urosevic et al., 2013) studied the influence of limestone surface finishing patterns exposed to marine aerosol weathering, concluding that these strongly control sea spray absorption and salt crystallization on the stone surface. Marine spray tends to go through the pore network of highly rough stone surfaces and salt crystallization occurs inside the substrate, but it promotes greater deterioration processes near the surface. In polished stone surfaces, with lower amount of surface porosity, salt crystallization occurs giving rise to efflorescence, thus reducing salt penetration into the porous system. Silva et al. (2013) carried out experiments on silicate rocks with different surface finishings submitted to salt fog atmospheres. The polished finishing (with lower surface roughness values) acts as a protective finishing in contrast to hammered finishing, which makes fluid infiltration quite easy.

The application of consolidating products modifies the stone porous system and may involve changes on further weathering processes that can be slowed down, or accelerated, after inappropriate interventions. It can also cause differential behaviors inside the same substrate, between areas where the treatments have penetrated and areas not reached by the products.

There are numerous studies on the short term modification of petrophysical characteristics of stone substrates treated with consolidating products based on nanoparticles, just after the application of $Ca(OH)_2$ inorganic nanoparticles (Pittaluga et al., 2012; López-Arce et al., 2013; López-Arce & Zornoza-Indart, 2015), SiO_2 nanoparticles (Calia et al., 2012; Borsoi et al., 2013; Rovella et al., 2014; La Russa et al., 2014; Zornoza-Indart & López-Arce, 2016), or nanostructured consolidating products (Mosquera et al., 2008; Pinho & Mosquera, 2011; Illescas, 2012; Zornoza-Indart et al., 2016). However, there are only a few works considering the durability of these products studied over the long term (Licchelli et al., 2014; Zornoza-Indart et al., 2014).

In previous research (Zornoza-Indart et al., 2016), great differences were obtained on the consolidation effect and changes produced in the physical properties of biocalcarenites just after the application of alkoxysilane products (also nanostructured) and nanoparticles. In the case of the former products (especially exposed to high RH conditions), the internal and surface mechanical properties increased. A coating on the stone substrate occluded the surface pores, maintaining hydrophobic properties after one month and causing drastic changes of hydric behavior with visually detectable aesthetic changes. By contrast, the inorganic nanoparticles produced changes in porosity by the creation of micropores. In the case of SiO_2 nanoparticles, moderate physical changes occurred under dry conditions exposure, resulting in less shrinkage and color changes. $Ca(OH)_2$ nanoparticles was the product that caused the lowest surface and internal consolidation effectiveness since the physical properties of the stone barely changed.

Since the short term effects on the petrophysical properties of stone substrates caused by the application of different traditional and innovative consolidating products were reported in a previous article (Zornoza-Indart et al., 2016), the present research presents innovative advanced work. A main goal of assessing the stability of the novel products under artificial accelerated weathering cycles in a severe marine aerosol environment is presented to determine if the treatments slow down or accelerate damage over the long term, and hence if these increase or decrease the durability of treated stones

Materials and methods

Materials and sample preparation

Stone specimens

The consolidating products were applied on a bioclastic calcarenite that corresponds to a quaternary eolian sandstone widely used in the architectural heritage of Bizerte (Tunisia). These Tyrrhenian to Würm age (Paskoff & Sanlaville, 1983) eolianite deposits outcrop along all the northern coast of Bizerte and belong to the Cap-Blanc geological formation which is 35,000 BP in age according to Paskoff and Sanlaville (1986). Cubic stone specimens (5 x 5 x 5 cm) were used for the laboratory experiments. These were previously extracted from loosened decayed stone ashlars of the sixteenth century Spanish Fort of Bizerta (Tunisia) (Figure 1a-c). Pore size distribution curves obtained by mercury intrusion porosimetry, total connected porosity (%), and pore size distribution (%) of calcarenite blank specimens are displayed in Figure 2. These have high open-porosity values (about 47%); and mostly large pores (53% above 100 µm radius), 29% of pores with radius in the range between 10 and 100 µm, 8% between 1 and 10 µm, and another 8% between 0.1 and 1 µm (Zornoza-Indart et al., 2013). The main mineralogical phases of the stone are calcite (61%) and quartz (29%), with hydromagnesite (10%) as a weathering product, since the stone was collected from a historic building. Further details of collected stones are described in Zornoza-Indart et al. (2016) and Karima et al. (2017).

[Figures 1` and 2 go here]

Consolidating products

As was described in Zornoza-Indart et al. (2016), four types of consolidating products were applied by brush (Table 1) on one side of stone cubes: (i) one of the most used conventional alcoxysilane based consolidants (ethyl silicate: Tegovakon® V100, by Evonik Industries AG) without solvents and with an active content of about 98.5%; (ii) a nanostructured consolidating product not commercially available, composed by a polymeric precursor (silica oligomer: Wacker® Tes 40 WN, by Wacker Chemie AG) with the addition of a surfactant (n-octilamine, by Sigma-Aldrich) to prevent cracking of the formed gel, synthesized by the Chemical Physics Department of the University of Cádiz (Spain) (Illescas, 2012); and (iii) two inorganic products based on colloidal nanoparticle dispersions: calcium hydroxide nanoparticles in isopropyl alcohol (Nanorestore®, C.T.S.) at 5 g/l concentration and silica nanoparticles in water (NanoEstel, C.T.S.) at 150 g/l concentration. Before using these latter consolidants, ultrasonic dispersion was performed introducing both products for 5 minutes in an ultrasonic bath (Selecta model Ultrasounds-H).

[Table 1 goes here]

The amount of product necessary to consolidate each specimen was calculated using as a reference the total amount of water absorbed at atmospheric pressure (37±2 ml) following the standard test UNE-EN 13755 (2002), and finally applying 40 ml of each product by brush. The average quantity of each applied product as weight percent gain (WPG%) per mass of dry stone sample is displayed in Table 1. In spite of the fact that the quantity of product applied is the same in all treated samples, it can be observed that according to the original concentration of the applied product the WPG (%) is greater in the case of samples treated with ethyl silicate (9±1%) and the nanostructured product (11±1%) and smaller in the case of nano SiO_2 (5±1%) and nano $Ca(OH)_2$ (1%).

Experimental conditions

Two atmospheric environments, dry (RH = 40±2% created by means of a closed container with $MgCl_2$ super saturated salt solution), and very humid (RH = 84±2% and 95±2% created by means of a closed container with water in the bottom), were selected to consolidate the stone samples over 30 days (Table 1). Six samples were exposed to the dry environment, two samples for each consolidating product (B2-4 and B2-5 were treated with ethyl silicate, B2-6 and B2-7 were treated with the nanostructured product, and B2-8 and B2-9 were treated with the nano SiO_2). Eight samples were exposed to the very humid environment, six of them treated with the same three products, two samples for each consolidating product (B2-10 and B2-11 were treated with ethyl silicate, B2-12 and B2-13 were treated with the nanostructured product, and B2-16 and B2-17 were treated with the Nano SiO_2). Finally, due to the limited amount of stone samples collected from the monument and, because better previous results were obtained under humid environments (Lopez-Arce et al., 2013), the other two samples (B2-14 and B2-15) were treated with $Ca(OH)_2$ nanoparticles. A yeast fermentation system to maintain a CO_2 concentration above 2500 ppm (Lopez-Arce & Zornoza-Indart, 2015) was connected to the container and was registered by a CO_2 detector (Telaire® 7001, Goleta, CA, USA) linked to a Hobo® Data Logger. Environmental data loggers, ibuttons® Hygrochron model, were introduced in each container and also placed in the laboratory room to measure T and RH during the period of consolidation while recording conditions every 10 minutes, using the software OneWireViewer version 3.04. Further details of environmental conditions are described in Zornoza-Indart et al. (2016).

Marine aerosol ageing test

A marine aerosol ageing test was carried out to evaluate the effect of a sea-spray atmosphere while checking the stability of the applied consolidation treatments. It was assessed if the applied products entailed a durability increase of the stone subjected to this type of weathering. The ageing test was carried out with one of the blank specimens (B2-1) and in one sample treated with each consolidating product and environmental conditions (B2-5, B2-7, and B2-9 under dry environment and B2-11, B2-13, B2-17, and B2-15 under humid environment). The ageing was carried out with one specimen per each type of product because the previously treated specimens were used to perform destructive analyses in order to study the consolidation effectiveness of the products after their application (Zornoza-Indart et al., 2016) (Table 1). To include the wind factor in the process of honeycomb weathering, the standard test UNE-EN 14147 (2004) was followed with adaptations introducing, as a modification, the use of fan ventilation in the drying process of the cycles due to the impossibility of placing an air generator inside the chamber. The ageing test was carried out using a marine aerosol ageing chamber (Ascott S120T) of the Faculty of Sciences and Technology of NOVA University of Lisbon (Portugal) (Figure 3a). Samples were submitted to 28 cycles consisting of 12 hours of saline fog exposition with a 1:9 solution of sodium chloride (NaCl) in distilled water (35ºC), 6 hours of drying without ventilation (25ºC) (Figure 3b), and 6 hours of drying with ventilation (25ºC) (Figure 3c). At the end of the cycles the samples were submerged in deionized water to remove the absorbed salts. The volume of water in the tank was three times the total volume of the specimens. This process is very slow and the water was changed every day until desalination was completed. The salt removal was considered completed following the standard, when the conductivity of the solution in contact with the specimens does not exceed twice the characteristic initial value of the water. The conductivity was measured with a HI98311 tester (Hanna Instruments).

[Figure 3 goes here]

Analytical techniques and experimental procedure

The stone specimens were analyzed with several non-destructive techniques (NDT) before and after 30 days of the consolidating products application (exposed to dry and very humid environments) and after the marine aerosol ageing test. Surface detail images of the treated stone specimens after one month from the consolidating product application, after marine aerosol ageing test and after being cleaned with water, were taken with an Olympus binocular loupe (SZ51) and a Olympus camera (C5060WZ, 5.1 megapixels, 5.7-22.9 mm).

The retained salt quantity and the weight loss of each stone specimen were calculated after the ageing test following the standard test UNE-EN 14147 (2004).

A -eeling test was carried out over the consolidating absorption face of the stone samples to study the decrease of released material with transparent double-side adhesion tape (Tesa®), 1.5 cm wide × 5 cm long, 2 zones per sample (10 sequence in each one) and 90 seconds per each sequence (Drdácký et al., 2012).

Surface micro-hardness was measured by means of a metal hardness tester Equotip 3 (Proceq), standardized according to the standard test ASTM A956-12 (2006). An impact device “D” was used to obtain HLD values with a range of measurements between 1-999 HLD, accuracy ± 4 HL (0.5% at 800 HL), with impact energy of 11.5 $N.mm^{-2}$, and automatic correction for impact direction. Ten measurements were performed on each specimen, over the consolidant absorption face.

The ultrasonic velocity (Vp or P-wave velocity) was measured to evaluate the decrease in effective porosity due to the filling of the pores by the consolidating products and to study the increase of porosity due to salt crystallization after the marine aerosol ageing test. P-wave propagation time was measured to a precision of 0.1 μs with a PUNDIT CNS Electronics instrument. Standard recommendations were followed according to the Spanish and European standard UNE-EN 14579 (2005). The frequency of the transducers with diameter of the flat contact area of 50 mm was 54 MHz. Four measurements were taken in direct transmission/reception mode, across opposite parallel sides of the cubic specimens in the three spatial directions.

Optical surface roughness (OSR) analyses were performed on the treated face of the stone sample specimens to evaluate the change in surface roughness after the application of the treatments and after the ageing test. Three measurements were performed on each specimen, over the consolidating absorption face. The equipment used was a contact-free surface profilometer (white light), TRACEiT, Innowep GmbH. The OSR analyses included 3D-topography maps (25 mm^2) using Gyddion 2.44 software displaying the average roughness parameters according to the DIN EN ISO 4287 standard (1998): Ra (arithmetic mean of the absolute values of profile deviations from the mean line) and Rz (sum of the vertical distances between the five highest peaks and the five deepest valleys within the sampling length). The cutoff (λc) used for calculations is 0.80 mm.

Spectrophotometry was performed with a spectrophotometer MINOLTA CM-700d using the CieLab color space; standard illuminant was D65 and observer angle, 10º. The measured parameters were L*, which accounts for luminosity, a*, and b* coordinates (a* being the red-green parameter and b* the blue-yellow). Total chrome difference ΔC* was provided as a result of the formula $\Delta C^* = (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$, and total color difference ΔE* provided as a result of the formula $\Delta E^* = ((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$. White (WI) and yellow (YI) indexes were measured according to ASTM E313-73 (1993), and brightness measured according to ISO 2470-2 (2008). Six measurements were performed on each specimen over the consolidating absorption face.

Results and discussion

Weight loss and salt retention

Table 2 shows the quantity of salt retained by the specimens after the marine aerosol aging test. The blank specimen shows a greater material loss when compared with the specimens treated with ethyl silicate, $Ca(OH)_2$ nanoparticles, and SiO_2 in humid environment. In the case of the specimen treated with SiO_2 nanoparticles in dry environment, the loss of material is greater than in the blank specimen and the same as in the case of the specimens treated with the nanostructured product in very humid environment. The nanostructured sample measurements in dry environment were discarded, since the specimen was broken, losing material and altering the measurements. Therefore, while with some products the weathering is lower (a smaller quantity of specimen is lost), with others this is greater than with the blank specimen.

[Table 2 goes here]

When studying the quantity of retained salt (NaCl), the blank specimen retains 10% of salt compared to its original mass, while the specimens treated in humid environment show a salt retaining percentage way lower (1% in the case of ethyl silicate and 0.5% in the case of the nanostructured product). However, while the specimens treated with $Ca(OH)_2$ and SiO_2 nanoparticles show lower salt retaining percentages than the blanks, they are greater than for the other products.

The saline efflorescence visually observed in the blank specimen is greater, especially in the central parts (Figures 4 and 5). The specimens treated with ethyl silicate almost do not show any efflorescence on the surface, since only thin whitish vails are observed. The reduction of the observed efflorescence's retained salt and weight can be given by the generation of a superficial microporous coat (Mosquera et al., 2008) with the occlusion of the pores, modifying the hydric behavior and reducing the penetration of marine aerosol, avoiding salt crystallization due to the smaller size of the pores in the hydrophobic coating layer. Therefore, the crystallization is only possible in the originally coarse surfaces and sections with larger pores where the gel has penetrated but which have not been filled by it.

[Figures 4 and 5 go here]

The specimens treated with the nanostructured product display more efflorescence and greater mass loss than the ones treated with ethyl silicate (even larger than the blank specimen). The efflorescence is concentrated in the superficial coat of the product. This difference may be due to the pore size of the gel generated on the surface, since in this case it is mesoporous (with a pore diameter between 4 and 6 nm (Illescas, 2012), inferring greater pore sizes where soluble salt can crystallize.

There are notable differences between the specimens treated with nano $Ca(OH)_2$, where efflorescence is concentrated at the edges, and those treated with nano SiO_2, where efflorescence is present over the whole consolidated surface. Consequently, marine aerosol can still penetrate and crystallize through the pores. In the case of nano $Ca(OH)_2$, the product precipitates in the center of the treated face favoring the formation of efflorescence in the edges where less consolidating product is present, as already shown in previous research with detrital limestones (biocalcarenites) (Lopez-Arce & Zornoza-Indart, 2015). For nanosilica, it seems that the product is homogenously distributed over the surface, avoiding concentration of efflorescence.

Nevertheless, a greater salt retention does not mean a greater mass loss in all cases. For the nanostructured product, even if a notoriously smaller salt retention is observed the mass loss is greater when compared to the blank specimen or to those treated with nanoparticles.

Peeling test

The results of the peeling test after the marine aerosol ageing test are shown in Table 3. The damage caused by the 28 cycles is limited in the blank specimen. This limited superficial damage could be related to the pore size distribution of the substrate, since the stone contains 82% of pores with diameters greater than 10 µm (Zornoza-Indart et al., 2013). These pores could act as sinks consuming great supersaturations caused by the growth of large size crystals without producing enough stress to damage the surface (Benavente, 2011).

[Table 3 goes here]

In the specimen treated with ethyl silicate in dry environment, the surface damage is greater than in the blank specimen, increasing the released material by 70%. However, if it is treated in a very humid environment, the released material is 25% reduced, increasing its durability after the ageing test. In the specimens treated with the nanostructured consolidating product, a reduction of released material is produced. This reduction is greater in the case of the dry environment, with a reduction of 62%, while a reduction of 2% takes place if this is exposed under a very humid environment. In the case of SiO_2 nanoparticles a greater reduction of released material is also observed in a dry environment, with 25% released material. However, a 7% increase is observed in humid conditions. The $Ca(OH)_2$ nanoparticles are the least effective as surface consolidating product, since the released material increases 62%.

Measurements of ultrasonic velocity

The results of Vp before consolidation, one month after the application of the different consolidating products, and then again after the marine aerosol ageing test are presented in Table 4. In all cases, with the exception of SiO_2 nanoparticles in dry environment, the values of the treated specimens are lower than the blanks, where Vp is reduced a 12%. This might be due to the increased porosity of the substrate after the damage produced by salt crystallization. This Vp decrease also suggests internal damage apart from the surface damage observed after the peeling test.

[Table 4 goes here]

In the case of the consolidated specimens with the ethyl silicate product, a very similar speed reduction is produced in both environments that is near four times lower than the blanks. The Vp value almost does not show any variation in the specimens treated with the nanostructured product and exposed to the humid environment. In contrast, a 4% Vp reduction is observed after dry conditions, inferring that internal porosity did not suffer important modifications.

Regarding the specimens treated with SiO_2 nanoparticles and exposed to dry conditions, greater damage is produced (18%reduction of Vp values). However, in the humid environment, the damage is lower compared to the blanks, with 5% Vp reduction.

The specimens consolidated with $Ca(OH)_2$ nanoparticles show greater a Vp reduction than the other treated specimens (9%), with values very close to the blanks. Therefore, it is the least effective treatment to achieve the reduction of internal damage.

Regarding the stability of the applied products under the marine aerosol ageing test, comparison of the values obtained just after consolidation and after ageing shows that ethyl silicate and nanostructured products are more stable in a dry environment. A reduction of 7% and 2%, respectively, are observed. In the case of SiO_2 nanoparticles, they show a greater stability in humid environment, with a 14% reduction opposed to a 22% reduction observed in the dry environment. Therefore, this is the less stable product, since it suffers greater variation. Finally, even if the variations produced by the $Ca(OH)_2$ are the less intense, the product is kept stable, suffering smaller modifications than the rest of the products applied to the specimens.

Surface micro-hardness

The results presented in Table 5 show the values of surface micro-hardness measurements. The treatments slow down the surface damage and increase the durability of the stone in terms of surface micro-hardness, since the obtained values are greater in all the consolidated specimens compared to the blanks after the accelerated ageing test. The specimen treated with the nanostructured product and exposed to humid conditions presents the greatest hardness values, with a 90% increase after one month of consolidation and before the ageing test. In the case of ethyl silicate and SiO_2 nanoparticles in dry environment, an increase of 71% and 31% respectively is produced. In contrast, only an increase of 15% and 6% is obtained in the humid environment. An increment of 10% of this property is observed in the specimen treated with $Ca(OH)_2$ nanoparticles. Therefore, this product is the one that generates the lowest increase in surface micro-hardness values before being subjected to marine aerosol ageing.

[Table 5 goes here]

In terms of the consolidation stability, with exception of ethyl silicate treatment in very humid environment, a reduction of the surface micro-hardness, acquired after one month after treatment application, is produced. This is due to the salt crystallization weathering generated during the marine aerosol ageing test. In the cases of ethyl silicate, the nanostructured product, and the $Ca(OH)_2$ nanoparticles, similar slight reductions take place. In the case of SiO_2

nanoparticles, greater reductions are observed, 21% in the dry environment and 12% in humid conditions. This means that this latter consolidating product has a lower stability under marine aerosol damage than the rest of the applied treatments, especially when this is exposed under dry relative humidity conditions.

Optical Surface Roughness (OSR)

The optical surface roughness parameters, one month after the consolidating product application and then after the marine aerosol ageing test, are shown in Table 6. Figure 6 compiles the surface roughness 3D height maps of the specimens. In the blank specimen, both Ra and Rz values increase due to the surface damage produced by salt crystallization. However, the increase of Ra value is slightly higher than Rz, creating a coarser surface instead of producing deeper cavities. In all the treated specimens, surface roughness values are lower except for the ethyl silicate in very humid environment. This could be due to the fragmentation observed in the superficial coat produced by the consolidating product after its application (Zornoza-Indart et al., 2016). Consequently, greater damage of the treated surface takes place.

[Table 6 goes here]

[Figure 6 goes here]

In the specimens treated with the nanostructured product, OSR values before and after the marine aerosol ageing test barely change. Figure 7 shows the OSR micro-detail images obtained on the blank and treated stone specimens. A white opaque layer can be observed on the samples treated with the ethyl silicate and nanostructured products (Figures 7c and 7d).

[Figure 7 goes here]

The greatest roughness reductions are obtained in the specimens treated with SiO_2 in dry environment. Micro-detail images of these specimens after the ageing test show a reduction of surface porosity where a surface layer coating the substrate grains is observed (Figure. 7e). In the very humid environment, the values are very similar to those obtained before the treatment.

The reduction of OSR values of specimens treated with nano $Ca(OH)_2$ is lower than the ones treated with ethyl silicate and the nanostructured products and similar to those consolidated with SiO_2 nanoparticles. The formation of a superficial layer is observed in the samples treated with $Ca(OH)_2$ nanoparticles (Figure 7f). The transformation of metastable $CaCO_3$ polymorphs (e.g. vaterite) into the most stable polymorph (i.e. calcite) give rise to the increase of the product density during this process, which is favored under highly humid environments, over 75% RH (Lopez-Arce, 2013).

The nanostructured product is the least stable, since after the ageing test it loses all the previously gained effectivity, especially in the dry environment (Figure 6). The ethyl silicate product provides a low stability, since a great increase of surface roughness values is also produced, when compared to the values just after consolidation, especially under humid conditions. However, these values decrease on the samples treated with $Ca(OH)_2$ and SiO_2 nanoparticles in dry environment, while these are almost the same in very humid environment.

Spectrophotometry

The results of chromatic parameters determination on the stone treated surfaces are shown in Table 7 and Figure 8. In the case of blank specimens, although a slight increase in luminosity and brightness values is observed after the ageing tests, no visually perceptible color changes occur because total color difference (ΔE^*) is lower than 5 (CNR-ICR, 1996) or lower than 3 according to other authors (Benavente et al., 2003; Delgado & Grossi, 2007). The specimens treated with the ethyl silicate and nanostructured products display reduced ΔE^* and luminosity values, showing a lower stability compared to the other products. In the specimens treated with nanoparticles, ΔE^* keeps constant or slightly increases after the ageing test (Figures 8a and 8b).

[Table 7 goes here]

[Figure 8 goes here]

The chromatic parameters of the specimens treated with ethyl silicate suffer similar modifications, being greater in the humid environment. These would not be noticeable but are greater than the blanks. A decrease in the yellow index and an increase of the white index are produced in both dry and humid environments. In the specimens treated with the nanostructured product in dry environment (with worse mechanical behavior), the chromatic variations reach the same level as the specimens before treatment. This might be caused by the loss of the gel coat. In the case of humid environment, the specimens show a more stable behavior since a more homogeneous coat was generated, no fragmentation was produced, the mechanical behavior is better, and lower chromatic variations take place after the ageing test. Nevertheless, the color change is still perceptible and greater than the blanks (ΔE^* 6.25) (CNR-ICR, 1996; Benavente et al., 2003; Delgado & Grossi, 2007).

The specimens treated with SiO_2 nanoparticles show lower chromatic variations and greater stability. Lower variations are observed in the case of dry environment, with values closer to the blanks, like the results obtained just after consolidation. Luminosity and ΔE^* values increase slightly after the ageing test, in contrast to the other products, although being visually unnoticeable (Figures 8a and 8b).

The specimen treated with $Ca(OH)_2$ nanoparticles, which just after consolidation showed low chromatic variations, display a ΔE^* of 4.62 after the ageing test. The increase of the white index and brightness values of the treated surfaces, typical feature produced with this type of consolidating product, is also lost after the ageing test. This can be due to the damage caused by salt crystallization, generating a loss of the surface coat.

Durability of consolidated stone

A compilation of the most remarkable results obtained from the characterization of the stone specimens consolidated with each product and subjected to the marine aerosol ageing test to assess their durability is summarized in Table 8. The evaluation of internal damage is based on retained salt quantity, weight loss, ultrasonic velocity, and micro-hardness measurements while the evaluation of superficial damage is based on peeling test and optical surface roughness.

Due to the limited number of samples that was possible to collect from the loosened ashlars of the monument, only greater variations could be attributed to product consolidation behavior whereas small variations might be caused by the internal variability of the stone specimens. It is important to take this into account unless the results obtained after the ageing test were always compared individually with the previous results of that same specific sample under study. To overcome this issue the results obtained from the characterization of the same stone specimen before treatment, one month after treatment, and after ageing, are always compared individually considering the previous results obtained from each of those stages on that same specific sample.

[Table 8 goes here]

Blank specimens

The internal damage of blank specimens is inferred by the reduction of Vp due to salt crystallization produced during the ageing test, which increases the effective porosity of the substrate. Greater internal damage may have been favored by the fan device. The material loss is limited, even though the salt retention by the substrate is high and efflorescence appears. Regarding surface damage, a slight increase in decohesion and surface roughness is observed while the micro-hardness values decrease without producing any visually perceptible chromatic variations. Therefore, salt crystallization and surface efflorescence almost did not transform the substrate’s surface, which shows low damage. This may be caused by the high porosity of the substrate (45±2%), and the pore size distribution. It contains only 16% of pores between 0.1 and 10 µm (the pore size where the stress caused by salt crystallization is concentrated) and 82% of pores higher than 10 µm, that could act as drain without producing enough stress to cause damage (Benavente, 2011).

Ethyl silicate

The internal damage suffered by salt crystallization is lower i.e. less material loss than the blanks. Surface roughness values increase in both environments due to salt crystallization in the pores of the coat generated on the stone surface. In the case of humid conditions, the consolidating effectiveness is maintained, reducing the quantity of material released, while it increases in dry conditions. In both environments, there are no visually detectable chromatic variations.

Nanostructured product

The internal damage suffered by the treated specimens is lower than the blanks. Even though the mass loss is greater, the durability or effectiveness of the product remains in both environments. The surface roughness increases in the same manner as the ethyl silicate. This is possibly caused by the salt crystallization in the coat layer produced by the consolidating product. The chromatic parameters are on the same level as the blanks in dry environment, with no visually detectable variations. However, in the humid environment higher visually detectable esthetical changes are produced.

SiO_2 nanoparticles

The internal damage is reduced by half under the humid environment compared to the blank specimen. However, the generated internal damage is higher in the sample treated in the dry environment and a higher mass loss is produced. This difference may be due to a greater reduction of substrate porosity with micropore generation under the dry conditions. This pore size reduction could be the cause of the greater salt crystallization damage, with higher amount of material loss compared to the blank specimens. However, surface damage diminishes in the dry environment while it increases when the treated specimens are exposed to humid conditions. This damage may be favored by the adsorption and desorption capacity of the formed surface gel in humid environment (Zornoza-Indart & Lopez-Arce, 2016). In terms of produced color changes, the specimens treated with SiO_2 nanoparticles show closer values to those produced in the blank specimens especially in the case of the dry environment, but being in both cases visually unnoticeable. Despite both alkoxysilane products and SiO_2 nanoparticles generating silica gel, the final results are different, since the “curing” type is different. In the case of ethyl silicate and nanostructured products, the “cure” is produced by hydrolysis while, in the case of SiO_2 nanoparticles, it is produced by the evaporation of the solvent (water)

$Ca(OH)_2$ nanoparticles

The internal damage suffered by the stone specimens consolidated with this product is slightly lower than the damage produced in the blanks; the surface hardness is greater, and the roughness values are lower. However, surface hardness values are reduced after the ageing test. Also, an increase of surface decohesion is produced, with greater amount of released product compared to the blanks. A decrease of surface hardness and increase of released material after ageing is produced. This is the product with the lowest concentration, due to the reduction of pore sizes just after consolidation (Zornoza-Indart et al., 2016) where salt crystallization produces greater damage due to the smaller pore sizes and higher stress (Benavente, 2011).

Conclusions

The application of different consolidating products does not inhibit the damage produced to calcarenite stones by salt crystallization during a marine aerosol ageing test. However, in some cases the stone decay is slowed down by the increase of mechanical properties reached just after consolidation, whereas no improvement with respect to the non-treated samples is achieved. These results show that the consolidation environment RH (in this case dry or humid environments) affects the final stone physical properties and therefore the durability of the treated substrates. All treatments provide both advantages and drawbacks under the two environments.

The nanostructured product is able to reduce stone internal damage, especially under a humid environment, and reduces surface damage under both environments. However, it generates visually perceptible chromatic changes in humid conditions, making it unsuitable according to conservation criteria. Ethyl silicate reduces internal damage by four when exposed to both environments but results are inadequate to reduce surface damage in dry conditions. In terms of the stability of both products, they are both stable, especially under dry environments, although a consolidating coat layer damaged by salt crystallization is generated on the stone surfaces. SiO_2 nanoparticles reduce internal damage by half under a humid environment but this internal damage is higher under dry conditions, only working to decrease surface damage in a dry environment. This product is also the most unstable one. Stone treated with $Ca(OH)_2$

nanoparticles under humid conditions show similar internal damage as blank specimens, producing a negligible durability increase. However, the product is unsuitable for surface consolidation due to the higher amount of material released. Despite this, even with low consolidation effectiveness, it is still stable after the marine aerosol ageing test.

The optimal consolidating product has to be chosen taking into account: (i) composition of the substrate (which can determine the conservation state); (ii) chemical and physical compatibility between applied product and substrate; (iii) superficial or internal damage, which determine the conservation needs; (iv) environmental conditions of exposure and the possibility of creating artificial environmental conditions onsite (through tarpaulins, humidifiers, or desiccators in the scaffold shelfs) and choosing the suitable time of the year to perform the consolidation treatments; (v) need of further treatments, especially those based on water; (vi) the budget of the restoration project; (vii) the consolidation effect and the increase of durability achieved with each product to determine whether it is worthwhile or not to carry out the consolidation treatment; and (viii) future of the treated object, such as exposition, storage, or conservation on site.

In spite of the advantages in analytical precision provided by sophisticated tools for materials characterization, and better understanding of stone consolidation or weathering processes, sometimes simple non-destructive tests like ultrasonic velocity or surface micro-hardness, and procedures such as the peeling test or accelerated ageing tests that can be performed on-site and in-lab by conservators, make it possible to assess a global efficacy of consolidating products and the durability of stone building materials.

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Tables with captions

Table 1. Stone specimens, applied consolidating products, environmental conditions, and ageing test

Specimen	Applied consolidating product		Environmental conditions	Weight percent gain (WPG%)	Ageing test
	Consolidant	Commercial product			
B2-1	Untreated	Blank specimen	Laboratory 20±5 ºC 50±10% RH	-	Marine aerosol
B2-2					-
B2-4	Ethyl silicate	Tegovakon® V100	Dry environment 23±4 ºC 40±2% RH	9	-
B2-5				10	Marine aerosol
B2-6	Nanostructured	Not commercially available		12	-
B2-7				12	Marine aerosol
B2-8	Nano SiO_2	NanoEstel		4	-
B2-9				5	Marine aerosol
B2-10	Ethyl silicate	Tegovakon® V100	Very humid environment 23±4 ºC 95±2% RH	8	-
B2-11				8	Marine aerosol
B2-12	Nanostructured	Not commercially available		10	-
B2-13				10	Marine aerosol
B2-16	Nano SiO_2	NanoEstel		5	-
B2-17				4	Marine aerosol
B2-14	Nano $Ca(OH)_2$	Nanorestore®	Very humid environment 23±4 ºC 84±2% RH ≥2500 ppm	1	-
B2-15				1	Marine aerosol

Table 2. Weight loss and salt retention percentages of blank and treated specimens after marine aerosol ageing test

Consolidating product		Specimen	Initial weight (g)	Weight with salt (g)	Weight without salt (g)	Weight loss (g)	Weight loss (%)	Salt retention (g)	Salt retention (%)
Blank specimen		B2-1	166.28	182.85	165.44	0.84	0.51	16.57	9.97
Dry 40% RH	Ethyl silicate	B2-5	185.22	186.46	184.99	0.23	0.12	1.24	0.67
	Nanostructured	B2-7	183.20	181.98*	176.94	6.26	3.42	-1.22	-0.67
	Nano SiO_2	B2-9	170.61	180.67	169.54	1.07	0.63	10.06	5.90
Very humid 84-95% RH	Ethyl silicate	B2-11	199.62	201.59	199.25	0.37	0.19	1.97	0.99
	Nanostructured	B2-13	194.61	195.61	190.84	3.77	1.94	1.00	0.51
	Nano $Ca(OH)_2$	B2-15	189.26	195.04	188.84	0.42	0.22	5.78	3.05
	Nano SiO_2	B2-17	184.62	196.03	184.40	0.22	0.12	11.41	6.18

(*) discarded measurement because the specimen was broken during the ageing test

Table 3. Released material (mg) by peeling tests on blank and treated specimens after marine aerosol ageing tests

		Released material (mg)							
		Blank specimen	Dry 40% RH			Very humid 84-95% RH			
			Ethyl silicate	Nanostructured	Nano SiO_2	Ethyl silicate	Nanostructured	Nano $Ca(OH)_2$	Nano SiO_2
Test sequence	1	1.00	0.75	0.35	0.70	0.90	0.60	2.40	1.45
	2	0.30	0.90	0.10	0.50	0.25	0.45	0.20	0.30
	3	0.40	0.65	0.30	0.20	0.20	0.30	0.00	0.30
	4	0.30	0.35	0.00	0.10	0.10	0.00	0.50	0.10
	5	0.00	0.30	0.00	0.00	0.05	0.45	0.10	0.00
	6	0.00	0.30	0.00	0.00	0.00	0.15	0.05	0.00
	7	0.00	0.15	0.00	0.00	0.00	0.00	0.00	0.00
	8	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	9	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
	10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Released material (mg)		2.00	3.40	0.75	1.50	1.50	1.95	3.25	2.15
Decrease of released material (%)			+70	-62	-25	-25	-2	+62	+7

Table 4. Ultrasonic velocity (Vp) values in three spatial directions (X, Y, and Z) and variation of Vp before and after one month from the treatments application and then, after marine aerosol ageing test

Consolidating product		Specimen	Average Vp for 3 axes (m/s)				Vp (Δ%)		
			Before	After treatment	After ageing test	ΔVp (%)	After treatment	After ageing test	Δ (%)
Blank specimen		B2-1	2404±26	/	2127±9	-12	/	/	/
Dry 40% RH	Ethyl silicate	B2-5	2423±85	2527±10	2359±16	-3	4	-3	-7
	Nanostructured	B2-7	2460±71	2416±62	2367±21	-4	-2	-4	-2
	Nano SiO_2	B2-9	2615±92	2730±33	2135±33	-18	4	-18	-22
Very humid 84-95% RH	Ethyl silicate	B2-11	2550±59	2875±19	2498±14	-2	13	-2	-15
	Nanostructured	B2-13	2526±90	2820±20	2512±24	-1	12	-1	-13
	Nano $Ca(OH)_2$	B2-15	2981±32	2899±26	2724±34	-9	-3	-9	-7
	Nano SiO_2	B2-17	2512±44	2727±29	2386±16	-5	9	-5	-14

Table 5. Surface micro-hardness (HLD) values and variation (Δ) of stone specimens before and after one month from the application of the consolidating products and then, after marine aerosol ageing test

Consolidating product		Specimen	Surface hardness (HLD) average				Surface hardness (HLD) (Δ%)		
			Before	After treatment	After ageing test	Δ (%)	After treatment	After ageing test	Δ (%)
Blank specimen		B2-2	154±56	/	148±81	-4	/	/	/
Dry 40% RH	Ethyl silicate	B2-5	153±81	270±32	261±36	71	76	71	-5
	Nanostructured	B2-7	158±109	215±11	210±15	33	36	33	-3
	Nano SiO_2	B2-9	123±89	187±18	161±95	31	52	31	-21
Very humid 84-95% RH	Ethyl silicate	B2-11	162±74	176±45	186±90	15	9	15	6
	Nanostructured	B2-13	83±56	159±14	158	90	92	90	-2
	Nano $Ca(OH)_2$	B2-15	193±132	219±4	212±63	10	17	10	-7
	Nano SiO_2	B2-17	186±122	219±4	198±53	6	18	6	-12

Table 6. Optical surface roughness (OSR) parameters (Ra and Rz) variation promoted on calcarenite specimens before and after one month from the treatments application and then, after marine aerosol ageing test

Consolidating product		Specimen	Ra (µm)				Ra (Δ %)		
			Before	After treatment	After ageing test	Δ (%)	After treatment	After ageing test	Δ (%)
Blank specimen		B2-1	14.32±0.91	/	14.42±0.53	0.70	/	/	/
Dry 40% RH	Ethyl silicate	B2-5	15.25±0.75	13.23±0.4	14.68±0.73	-4	-13	-4	9
	Nanostructured	B2-7	13.84±0.33	11.30±0.68	13.78±0.18	-0.4	-18	-0.4	17.6
	Nano SiO_2	B2-9	14.25±0.26	14.00±0.01	13.31±0.34	-7	-2	-7	-5
Very humid 84-95% RH	Ethyl silicate	B2-11	14.57±0.04	14.15±0.97	15.04±0.75	3	-3	3	6
	Nanostructured	B2-13	15.17±0.93	13.39±0.48	15.09±0.7	-0.5	-12	-0.5	11.5
	Nano $Ca(OH)_2$	B2-15	15.79±0.37	15.42±0.33	15.16±1.03	-4	-2	-4	-2
	Nano SiO_2	B2-17	15.86±1.26	15.67±0.71	15.92±0.04	0.4	-1	0.4	0.6

Consolidating product		Specimen	Rz (µm)				Rz (Δ %)		
			Before	After treatment	After ageing test	Δ (%)	After treatment	After ageing test	Δ (%)
	Blank specimen	B2-1	52.77±3.1	/	52.91±1.84	0.30	/	/	/
Dry 40% RH	Ethyl silicate	B2-5	57.68±3.21	50.86±0.75	54.95±2.12	-5	-12	-5	7
	Nanostructured	B2-7	50.82±0.75	42.15±3.11	50.64±0.18	-0.3	-17	-0.3	16.7
	Nano SiO_2	B2-9	51.31±0.21	50.80±0.84	50.45±0.85	-2	-1	-2	-1
Very humid 84-95% RH	Ethyl silicate	B2-11	52.18±1.14	49.10±2.56	54.80±2.73	5	-6	5	11
	Nanostructured	B2-13	55.28±2.7	47.84±2	54.87±2.31	-1	-13	-1	12
	Nano $Ca(OH)_2$	B2-15	58.81±1.06	57.88±1.41	56.11±2.72	-5	-2	-5	-3
	Nano SiO_2	B2-17	57.36±4	55.72±1.93	56.09±0.2	-2	-3	-2	1

Table 7. Average variations (Δ) promoted on chromatic parameters (L*, lightness; a* position between red and green; b* position between yellow and blue; C*, Chroma; E*, total color; YI, yellow index; WI, white index and brightness) on the stone specimens before treatment and after marine aerosol ageing tests

Consolidating product		Specimen	ΔL*	Δa*	Δb*	ΔC*	ΔE*	YI (E313-73)	WI (E313-73)	Brightness (ISO)
Blank specimen		B2-1	0.98	-0.44	0.18	0.02	1.09	-0.32	-0.66	0.71
Dry 40% RH	Ethyl silicate	B2-5	-1.02	-0.58	-1.75	-1.83	2.11	-2.41	4.02	0.08
	Nanostructured	B2-7	-0.68	-0.27	-1.16	-1.18	1.37	-1.50	2.75	0.15
	Nano SiO_2	B2-9	1.10	-0.51	-0.35	-0.50	1.26	-1.07	0.37	1.11
Very humid 84-95% RH	Ethyl silicate	B2-11	-0.37	-0.23	-2.56	-2.48	2.60	-3.79	5.08	1.00
	Nanostructured	B2-13	-6.23	0.13	-0.47	-0.39	6.25	1.99	1.82	-4.99
	Nano $Ca(OH)_2$	B2-15	-4.33	-0.84	1.38	1.03	4.62	3.85	-1.29	-4.27
	Nano SiO_2	B2-17	2.62	-0.28	-0.51	-0.57	2.69	-2.03	0.53	2.38

Table 8. Compilation of the most remarkable results obtained from the characterization of the blank specimens and the specimens consolidated with each product subjected to the marine aerosol ageing test

Dry environment (40% H.R.)				
Technique or method	Blank specimen	Ethyl silicate	Nanostructured	Nano SiO_2
Salt retention and weight loss	Retention: 9.97% Weight loss: 0.51% Efflorescence	Retention: 0.67% Weight loss: 0.12% No efflores.	-	Retention: 5.90% Weight loss:: 0.63% Efflorescence
Peeling test	Superficial decohesion	Decrease cohesion (+70%)	Increase cohesion (-62%)	Increase cohesion (-25%)
Ultrasonic velocity	Decrease 12%	Decrease 3%	Decrease 4%	Decrease 18%
Surface micro-hardness	Decrease 4%	Increase 71%	Increase 33%	Increase 31%
Optical surface roughness (average Ra-Rz)	Increase 0.5%	Decrease 4.5%	Decrease 0.35%	Decrease 4.5%
Spectrophotometry	ΔE*= 1.09	ΔE*= 2.11	ΔE*= 1.37	ΔE*= 1.26

Very humid 84-95% RH					
Technique or method	Blank specimen	Ethyl silicate	Nanostructured	Nano SiO_2	Nano $Ca(OH)_2$
Weight loss and salt retention	Retention: 9.97% Weight loss: 0.51% Efflorescence	Retention: 0.99% Weight loss: 0.19% No efflores.	Retention: 0.51% Weight loss: 1.94% Efflorescence	Retention: 6.18% Weight loss: 0.12% Efflorescence	Retention: 3.05% Weight loss: 0.22% Efflorescence
Peeling test	Superficial decohesion	Increase cohesion (-25%)	Increase cohesion (-2%)	Decrease cohesion (+7%)	Decrease cohesion (+62%)
Ultrasonic velocity	Decrease 12%	Decrease 2%	Decrease 1%	Decrease 5%	Decrease 9%
Surface micro-hardness	Decrease 4%	Increase 15%	Increase 90%	Increase 6%	Increase 10%
Optical surface roughness (average Ra-Rz)	Increase 0.5%	Increase 4%	Increase 0.25%	Decrease 0.8%	Decrease 4.5%
Spectrophotometry	ΔE*= 1.09	ΔE*= 2.60	ΔE*= 6.25	ΔE*= 2.69	ΔE*= 4.62

Figures

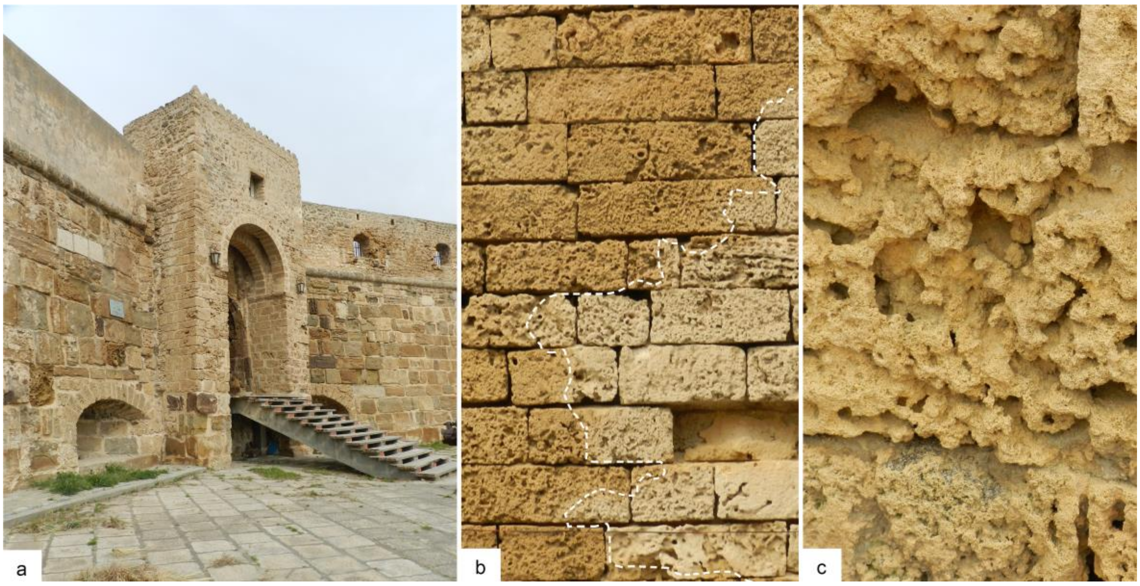
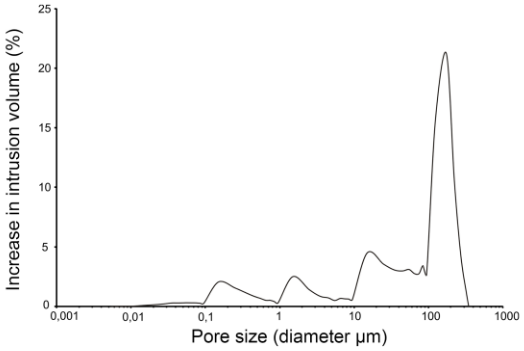


Figure 1. a) Spanish Fort of Bizerta (view from the port); b) Wall of the Fort with honeycomb weathering and moisture problems; c) Honeycomb weathering and loss of material on decayed stone ashlar



Blank specimen		
Total connected porosity (%)		46.87
Pore size distribution (%)	< 0.01 µm	0.00
	0.01 - 0.1 µm	2.21
	0.1 - 1 µm	7.92
	1-10 µm	8.38
	10 - 100 µm	28.67
	>100 µm	52.82

Figure 2. Pore size distribution curve obtained by mercury intrusion porosimetry and total connected porosity (%) and pore size distribution (%) of non-treated and non-aged calcarenite samples

Figure 3. Marine aerosol accelerated ageing test. a) Marine aerosol ageing chamber; b) Drying process without ventilation (6h); c) Drying process with ventilation (6h)

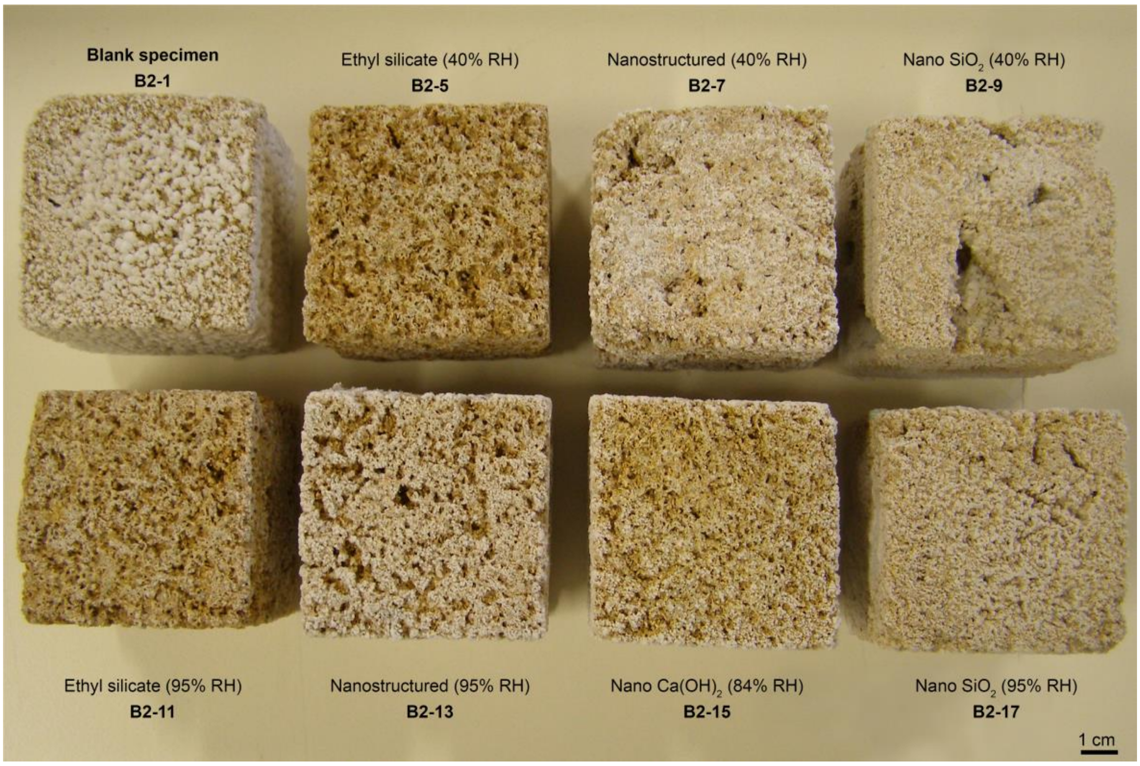


Figure 4. Calcarenite stone cubic specimens after treatment with different consolidation products exposed to different relative humidities (RH) (dry (40% RH) and very humid (84-95% RH) environments) after marine aerosol ageing test and before cleaning with water.

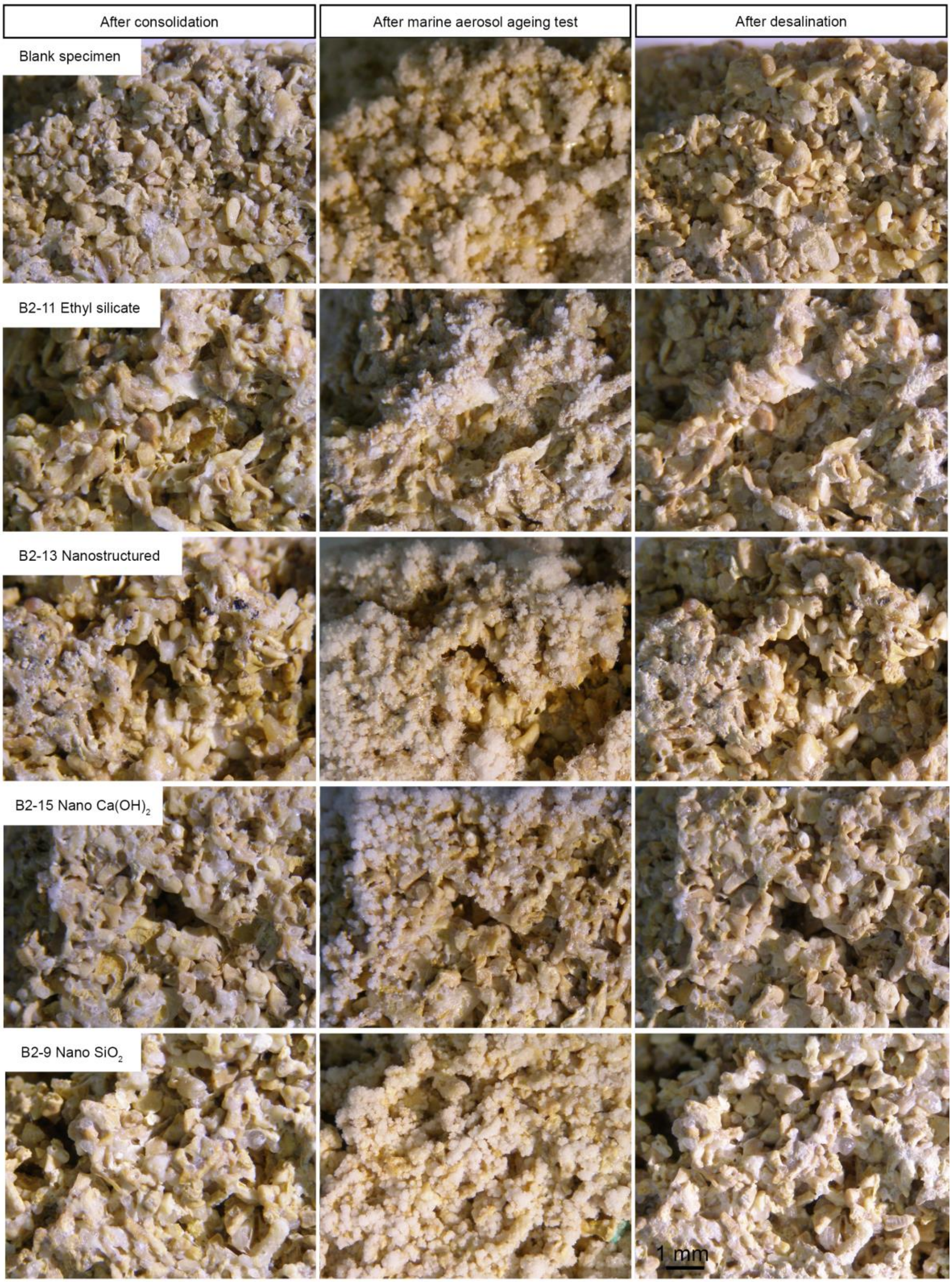


Figure 5. Surface detail images of the treated stones specimens (upper left corner) one month after the consolidating product application, after marine aerosol ageing test, and after cleaning with water. The pictures were taken with an Olympus binocular loupe (SZ51) and an Olympus camera (C5060WZ, 5.1 megapixels, 5.7-22.9 mm)

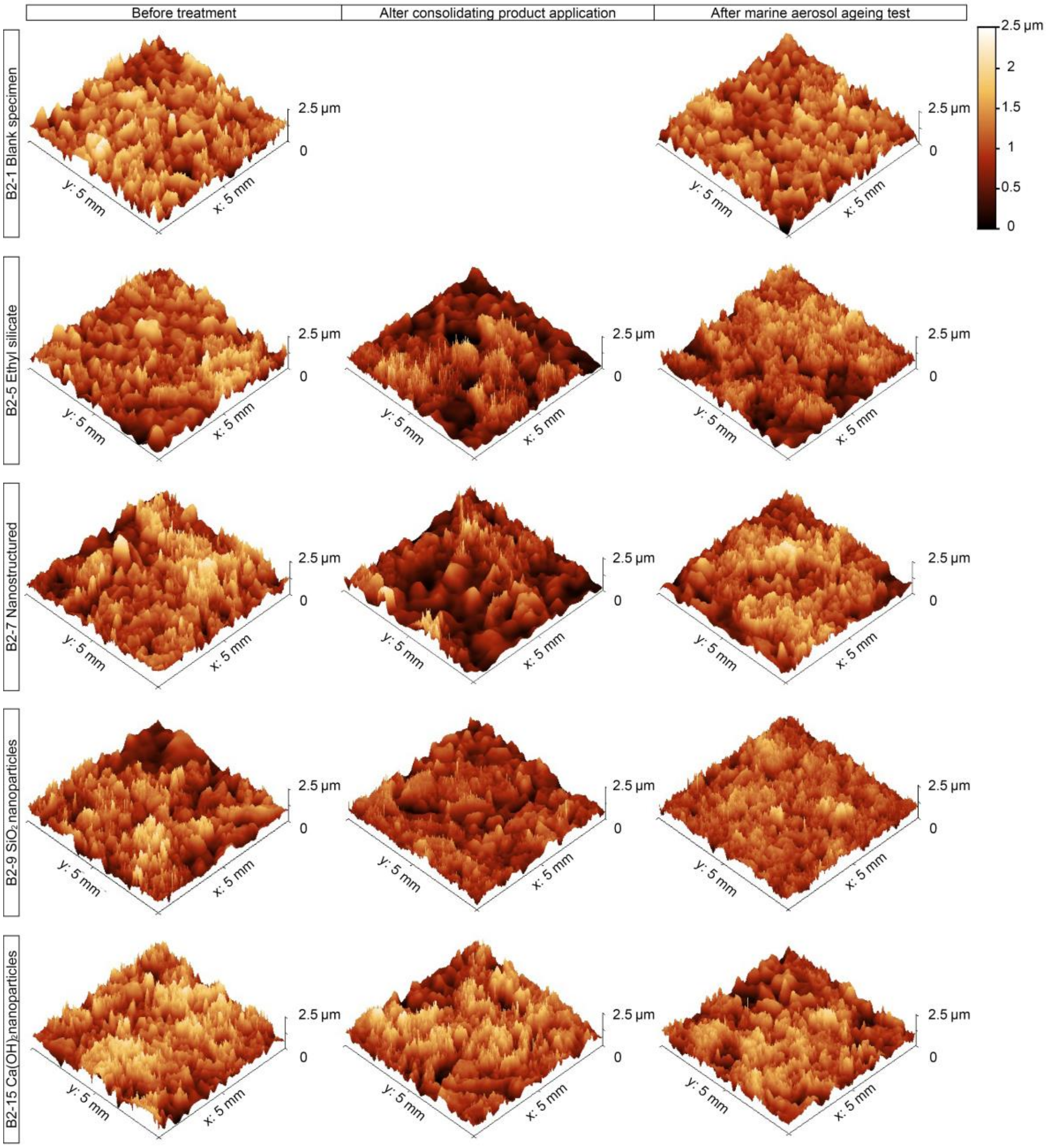


Figure 6. Surface roughness 3D height maps obtained under optical surface roughness (OSR) on the top surface of specimens before, after consolidating product application, and after marine aerosol ageing test.

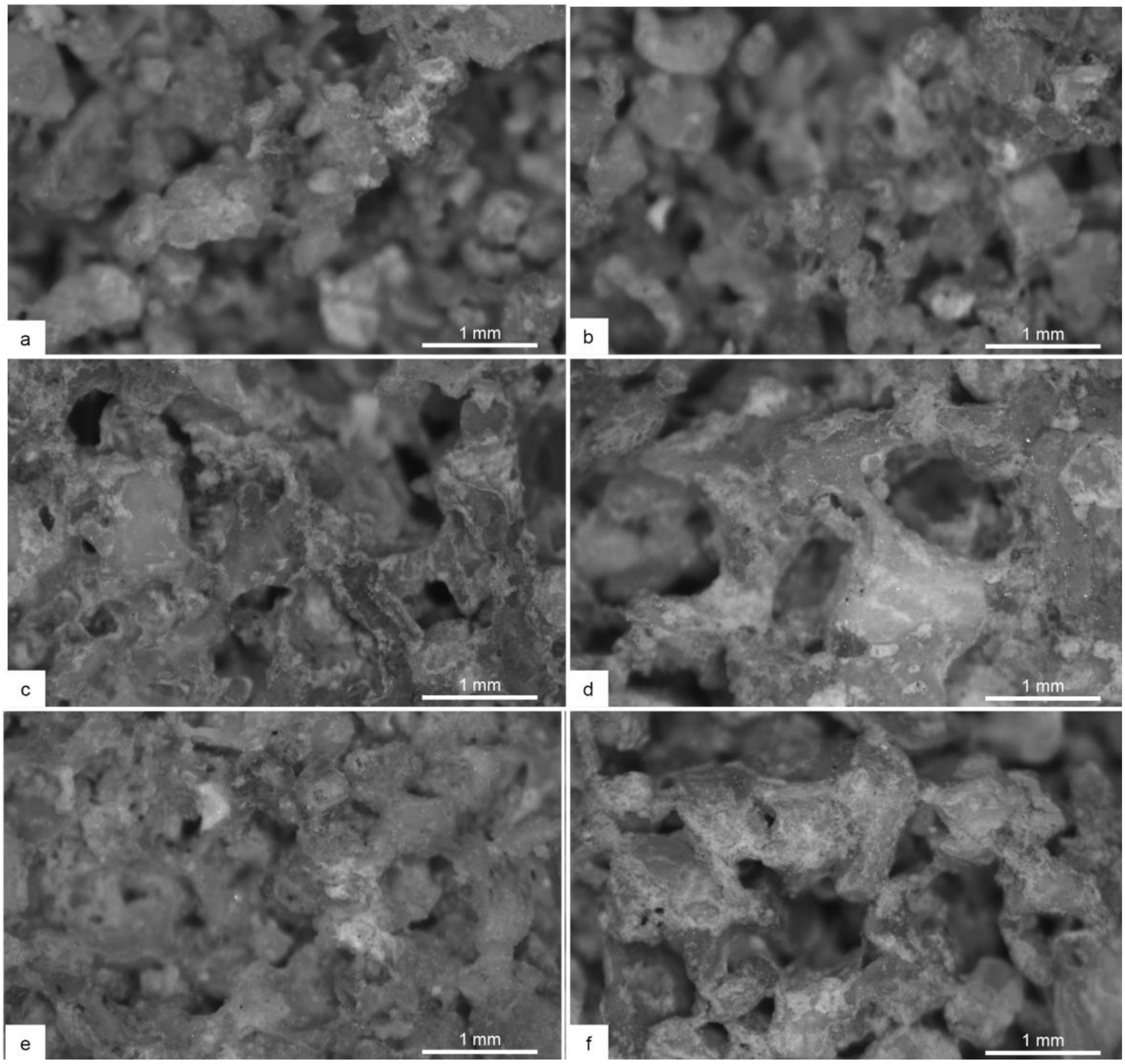


Figure 7. OSR micro-detail images of the treated stone specimens after the marine aerosol ageing test. a) and b) Surface of blank specimen; c) Surface of sample treated with ethyl silicate; d) Surface of sample treated with the nanostructured product; e) Surface of sample treated with nano SiO_2; f) Surface of sample treated with nano $Ca(OH)_2$

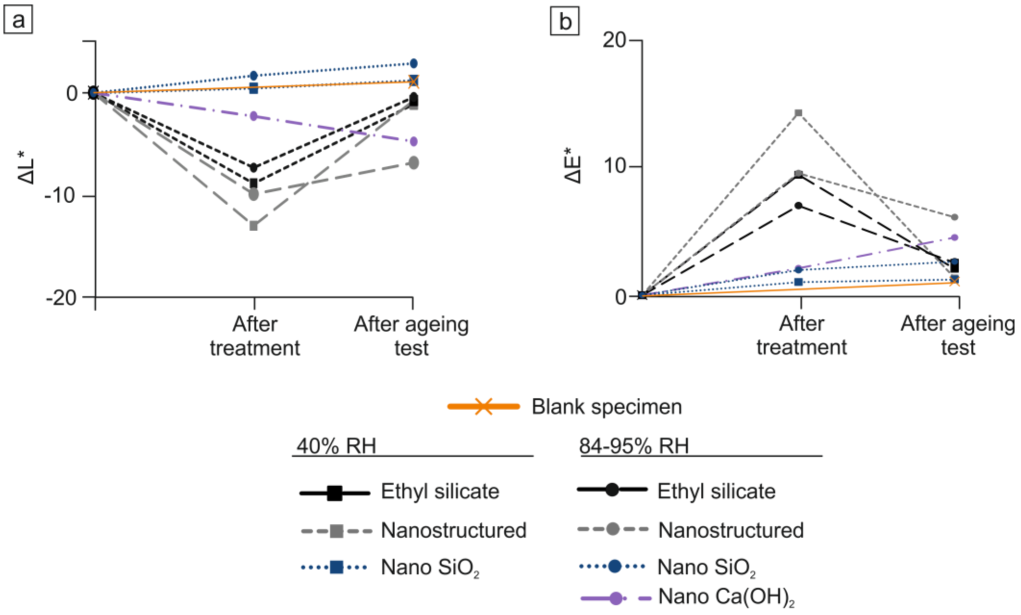


Figure 8. Comparison of luminosity (ΔL*) and total color (ΔE*) variations promoted on the stone specimens one month after the application of different consolidating products and then after the marine aerosol ageing test

Figure captions (list)

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