Alkoxy silane-based consolidation treatments: Laboratory and 3-years In-Situ assessment tests on biocalcarenite stone from Roman Theatre (Cádiz)

Giada M.C. Gemelli, Rafael Zarzuela, Francisco Alarcón-Castellano, Maria J. Mosquera, M.L. Almoraima Gil

1. Introduction

Archaeological and historical buildings are subjected to different physical, mechanical and chemical alterations processes under the action of aggressive atmospheric agents, especially those in proximity to the sea, industry or areas with high vehicular traffic [1,2]. Furthermore, the misuse or inappropriate choice of organic or inorganic products to repair and/or mitigate these damages often contributes their decay [3].

In the last decades, the advantages of alkoxysilanes (i.e. versatility of application, suitability for a wide range of porous materials, chemical inertia) respect to other alternatives for stone restoration and conservation have been widely demonstrated [4]. Among their advantageous characteristics for use as stone consolidants, two of special interest are their low viscosity, which facilitates their penetration in the pore structure, and the ability to form Si-O-Si bonds with different substrates to increase stone cohesion and an effective consolidation of the material [5]. This interaction and chemical affinity are remarkably high for stones rich in Si phases (e.g. quartz, silicates, aluminosilicates), such as sandstones. Nevertheless, alkoxysilane-based treatments may experience limitations in some applications due to some general drawbacks: i) the sol-gel process involved in their curing is very sensitive to a wide range of compositional and environmental factors (e.g. pH, type of catalyst, solvent and water content, temperature, ambient moisture, presence of other ions, and type of precursors) which may lead to noteworthy variations in their performance [6-9]; ii) they lack the capacity to form strong covalent bonds with carbonate-based phases, relying on weaker attraction forces or mechanisms such as physical interlocking [4]; iii) the carbonate media may affect the alkoxysilane polymerization due to their pH and composition [10], delaying in some cases the hydrolysis reactions after product application, which leads to undesired (temporary) hydrophobic behaviour [11]; and v) the gel’s tendency to crack during the drying stage due to the capillary pressure, which is inversely proportional to its pore size, exerted by the solvent and/or ethanol and water produced during the sol-gel reaction [12]. Several strategies have been developed mainly to circumvent two drawbacks: (1) prevent gel cracking and (2) enhance the adhesion of alkoxysilanes to carbonate stone. To prevent cracking, the general method is to reduce the capillary pressure gradient, either by decreasing the solvent or byproducts evaporation rate, adding components to decrease the surface tension of the sol (which is proportional to capillary
During the last years, our research group developed a surfactant-assisted route to produce crack-free alkoxysilanes based consolidants. This route prevents gel cracking during the drying stage. During gel drying, the surfactant produces mesoporous (pore size 2–50 nm) xerogels through an inverse micelle mechanism, that reduces capillary pressure during gel drying, and consequently improves the consolidant effectiveness of the alkoxysilane when applied on stone substrates [18]. The consolidants produced by this route have been tested in laboratory and In Sìtu with positive results regarding consolidant effectiveness on carbonate stones [19,20]. Nevertheless, the cited works dealt with the application of the products on decontextualized blocks, collected from the In-Situ archaeological site or near the monument, treated in the laboratory condition and re-placed In-Situ near the corresponding monument. Direct application on the structure and curing/drying under environmental conditions was not addressed.

The majority of the research studies in this field have been concerned with the investigation of specific aspects mainly related to the chemical behavior of consolidants and less with the potential incompatibility and performance of the products when applied in real situations [21,22]. Following this trail, organic consolidant products (e.g. acrylic and epoxy resins) [23–28] have been widely used despite the fact that their short-term negative effects are largely acknowledged [29,30].

The main objective of this research study was the 3-years In-Situ monitoring of the long-lasting performance of a consolidant product reinforced with SiO$_2$ nanoparticles. A preliminary laboratory investigation of two consolidant products, in terms of product/stone substrate compatibility and improvement in the mechanical resistance of the stone selected, was performed. This study was motivated by the following reasons:

i. The remarkable cultural interest of the monument. The Cádiz Roman Theatre is considered the oldest and second largest theatre on the Iberian Peninsula [31]; built in the 1st century BCE [32] using predominantly the local Ostionera stone [31].

ii. The Ostionera stone, a highly porous bioclastic sandstone, largely used as building material in the historic city centre of Cádiz. The high porosity of the stone substrate favours water absorption, the main vehicle of soluble species, which can crystallize inside the pores causing common degradation patterns (i.e. pitting, aggregation, exfoliation) [33]. Furthermore, its proximity to the sea and the predominant East wind promote the exposure to marine aerosol that acts by eroding the surface of the stone material [34] (see Fig. 1a).

iii. Cádiz Theatre is permanently exposed to high levels of humidity in winter and high evaporation in summer, the main influencing factors that determine the content of salts and moisture which are among the most important weathering agents.

iv. Previous maintenance works [32], carried out in the upper part of the selected study area, could have accelerated the stone deterioration. Mainly, the degradation was produced by the outflow of rainwater that would have generated the leaching of the carbonate matrix.

Under these conditions, where water was involved in the main deterioration process, an intuitive solution was to apply a hydrophobic product to avoid water absorption. However, water and solubilized salts entered into the material from zones other than the intervention area that are impractical to treat. Thus, application of a hydrophobic product could have caused a worsening of the stone decay due to retention of water and salts inside the material. Therefore, the application of the hydrophobic product had to be reconsidered in favour of a consolidant treatment, considering as most appropriate type of conservative treatment to restore the condition of the surface and compensate or delay the damage caused by salt crystallization and leaching, increasing the service life of the stone material.

In this work, the products evaluated were prepared by mixing silica oligomer and an aqueous n-octylamine dispersion [35] as a surfactant. In addition, SiO$_2$NPs were integrated into the starting sol to evaluate their effect over consolidant performance, as our previous studies using similar products indicate they can potentially promote an enhancement [36].

The treatment validation study was divided into three phases: (1) the preliminary laboratory characterization of the specimens obtained from the Stone specimens, (2) laboratory validation to verify that the products under study satisfy the compatibility requirements and are effective in terms of improving the stone mechanical properties, and (3) In-Situ application of the best-performance treatment and long-term evaluation.

The Compatibility Indicators (CI) described by Delgado Rodriguez and Grossi [37] have been employed to evaluate the compatibility between the product and the stone substrate. For the test conditions, the

![Fig. 1. Cadiz and Roman Theatre location (a). Sampling area of the decontextualized prismatic block and localization of the intervention area for In-Situ evaluation (b).](image-url)
European Standards has been followed to obtain results that can be comparable with bibliographic data. Different instruments and tests were employed in laboratory to ascertain incompatibility risks and obtain effectiveness data to serve as a reference for comparison with In-Situ studies. After preliminary laboratory evaluation indicating an assumable incompatibility risk between stone/product, the treatment was applied In-Situ for monitoring of the long-term performance along three years.

2. Materials and methods

2.1. Tested stone materials, consolidants and consolidation treatments

A decontextualized prismatic block (hereafter “Stone specimens”) was collected from the upper area of the theatre (Fig. 1 b) and cut according to the dimensions required by each one of the different laboratory tests (Table 1).

The selection of the stone block, for the laboratory experiments, was based on preliminary laboratory tests executed, in order to confirm that the Stone specimens intrinsic characteristics were similar with the characterization data obtained from the In-Situ testing area. Specifically, X-ray diffraction and fluorescence analyses were carried out on both Stone specimens and In-Situ testing area (Fig. 1 b).

The chemical and mineralogical composition was determined by X-ray Fluorescence (XRF) and X-ray Diffraction (XRD) analysis. Specifically, fluorescence analysis was carried out using 10 g of sample powders collected from both In-Situ testing area and Stone specimens samples and analysed with a wavelength dispersion X-ray fluorescence spectrometer (EDXRF), model S4-PIONEER from BRUKER, provided of Rh tube as X-ray source. The XRD pattern of the In-Situ testing area was obtained with a diffractometer (D8 Advance from Bruker) equipped with a secondary monochromator, Cu tube X-ray, using Cu Kα radiation.

Quantitative analysis of the phases was carried out by the Rietveld method on sample powders. The sampling was carried out before the application of the treatment.

Moreover, the water accessible open porosity (AOP) of the untreated Stone specimens were measured according to the procedure published by ICCROM UNESCO WHC Laboratory Handbook [38]. The samples were immersed in deionized water at room temperature and pressure and their weight was monitored over time until saturation was reached (when the difference in weight between 2 successive measurements at 24-hour intervals is <1% of the amount of water absorbed).

The following equation was used in order to obtain the water accessible open porosity (%P).

\[
\%P = 100 \times \left( \frac{V_{oa}}{V_d} \right)
\]

Where (\(V_{oa}\)) is the open pores volume that corresponds to the volume of water absorbed by the sample (i.e. the difference in weight of the sample before and after being saturated) and (\(V_d\)) is the apparent volume expressed as a percentage.

Two consolidant products were synthesized according to procedures described in previous papers [36]. The first product (hereafter UCA_NPs) [36] was prepared, via sol-gel route, by mixing an ethoxysilane (TES40, from Wacker) a n-octylamine (n-8, 98%, from Sigma-Aldrich) aqueous dispersion and 40 nm fumed SiO\(_2\)NPs (AEROSIL OX50, from Evonik) in order to improve the mechanical resistance. The second one, hereafter UCA, was synthesized by using the same route without incorporating SiO\(_2\)NPs particles [35], in order to study the influence of the SiO\(_2\)NPs over the performance. Subsequently to the synthesis, both products were stored for 24 h in airtight vessels.

The synthesis route of the two products consisted of mixing all the components under ultrasonic agitation, at 74% of Amplitude during 10 min, using an ultrasound probe (Bandelin Ultrasonic HD3200).

According to its technical specifications, (1) TES40 is an ethoxysilane with an average degree of polymerization of 5.5Si-O units that provides approximately 41% of silica upon complete hydrolysis. (2) AEROSIL OX50 is a hydrophilic fumed silica with a diameter of 40 nm and a surface area of 50 m\(^2\) g\(^{-1}\).

The addition of the SiO\(_2\) nanoparticles, in the first consolidant product, was chosen for two main reasons: (1) the interaction between the silica precursors of the product (alkoxysilane) is expected to be higher with the silica nanoparticles (SiO\(_2\)NPs) since covalent bonds can be formed and (2) SiO\(_2\) nanoparticles are more transparent than particles with other compositions (e.g. lime, Ba hydroxide, TiO\(_2\)) thus lowering the risk of colour change on highly absorbent stones such as the one studied in this work.

Physical properties of the two sols synthesized were reported in Table 2. Table 3 shows the proportion of the different reagents.

Before applying the products, all the stone samples were oven dried at 60 °C, until constant weight, and subsequently stored in a desiccator (20 ± 2) °C. The application of the products was performed by brushing in 3 application cycles until apparent refusal, allowing its complete absorption between each one. A one-minute waiting interval was

<table>
<thead>
<tr>
<th>Test executed Stone specimens(^a)</th>
<th>Measure</th>
<th>Procedure</th>
<th>Sample</th>
<th>Dimensions (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stone Characterization</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>X-Ray Fluorescence (XRF)</td>
<td>BT</td>
<td>NS</td>
<td>Powder</td>
<td></td>
</tr>
<tr>
<td>Water Accessible Porosity (AOP)(^b)</td>
<td>BT</td>
<td>NS</td>
<td>3x3x3</td>
<td></td>
</tr>
</tbody>
</table>

Table 1

Summary of the size and tests executed on fresh cut Stone specimens and in the samples collected from the In-Situ testing area.

\(\text{NS} = \text{Non-Standardized}; \text{BT} = \text{Before Treatment}; \text{AT} = \text{After Treatment}; 2\) m = 2 months; 1y = 1 year.

\(^a\) A minimum of 5 replicates were used per product for each test.

\(^b\) Determination of the consolidated thickness from DRMS data.

\(^c\) Tests performed after 2 months and repeated after 1, 2 and 3 years.

Physical properties of the two sols synthesized.

<table>
<thead>
<tr>
<th>Viscosity (mPa.s)</th>
<th>Density (g/ml)</th>
<th>Gel Time (h)</th>
<th>SiO(_2) content (%m/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCA</td>
<td>4.64</td>
<td>1.052</td>
<td>&lt; 24</td>
</tr>
<tr>
<td>UCA_NPs</td>
<td>4.91</td>
<td>1.062</td>
<td>&lt; 24</td>
</tr>
</tbody>
</table>
established between each application cycle to allow absorption of the products. Afterwards, the samples were left under laboratory conditions.

### 2.2. Treatments assessment in laboratory

After 2 months in laboratory conditions (20 °C, 40% RH), weight remained stable on all treated samples and the following tests were performed (Table 1). Specifically, the measurements were carried out in each sample before and repeated after 1 year from the treatments application. The measurements of the dry matter (DM) and the water absorption by capillarity (WAC) were carried out after 2 months and repeated after 1 year in order to monitor the drying stage.

#### 2.2.1. Characterization of the treated stone specimens and consolidant effectiveness

The characterization of the treated stone specimens have been carried out by (1) measuring the amount of consolidant absorbed and retained in the samples, (2) recording the FTIR spectra and (3) observing the distribution and morphology of the coatings on the stone surfaces. Moreover, increase in mechanical resistance in depth due to consolidant effectiveness was measured by Drilling Resistance test.

The amount of applied product per unit area was calculated by weight difference before and immediately after the treatments (Up). The amount of consolidant retained (DM) was monitored by weight difference, before and immediately after the treatments (Up) – (DM) and repeated after 1 year (DM1 year) from the treatment. FTIR spectra were obtained from the treated stone specimens in order to monitor the sol-gel transition of the products under study and to confirm their presence in the stone. The spectra of the treated and untreated samples were recorded using a FTIR-8400S from Shimadzu (4 cm⁻¹) in the region from 4000 to 600 cm⁻¹. Measurements were directly performed on powder extracted from the surface of the samples (≤1 cm from the treated surface) in attenuated total reflection mode (ATR).

SEM micrographs were obtained by using a Nova NanoSEM 450 Scanning Electron Microscope (SEM from FEI), working at 15 kV acceleration voltage, coupled with energy dispersive X-ray spectroscopy (EDX). Before observation, the samples were sputtered with a 12 nm acceleration voltage, coupled with energy dispersive X-ray spectroscopy (EDX). Before observation, the samples were sputtered with a 12 nm

#### 2.2.2. Compatibility of the treatments

The incompatibility degree (ID) of the synthesized products applied on the selected stone, was evaluated and compared by calculating an incompatibility degree, which takes into account different indicators related to the consolidated material properties, using formula according to the literature [37].

\[
ID_n = \sqrt{R_1^2 + R_2^2 + \ldots + R_n^2}
\]

Where \(ID_n\) is the incompatibility degree, \(R_1, \ldots, R_n\) are the ratings of the relevant indicators (1 to n), and n is the number of indicators used in the computation of \(ID_n\) [37].

The indicators used are as follow: (1) water vapour permeability (WVP), (2) water absorption coefficient (WAC), (3) drying index (DI), (4) total colour difference (ΔE*), (5) drilling resistance (DRMS) and (6) penetration depth (PD).

Subsequently, according to the scale proposed by Delgado Rodrigues and Grossi [37], each obtained parameter was rated as follow: 0 – no risk; rate = 5 – moderate risk and rate = 10 – high risk of incompatibility.

Evaluation tests were performed after 1 year from the treatment application. However, taking into account the disadvantages shown by alkoxysilanes-based consolidants [6–11] when applied on carbonate substrate, the WAC was also measured after 2 months to monitor the curing process of the treatment and checking if they were hydrophobic due to incomplete hydrolysis of the alkoxysilane-based treatments.

Water vapour permeability (WVP) was determined employing an automatic setup, developed by our research group [39], based on the standard wet cup test in accordance with ASTM E96/E96M-16 [44]. The sample was placed as a cover over a cup, consisting of a methacrylate cube, containing water to maintain a moisture saturated ambient (RH 98%). The cup with the sample was placed into a methacrylate climatic chamber. Specifically, the sample inside the chamber was hung from a modified balance connected to weight recording software. The laboratory temperature was maintained at 20 °C during the experiment. The test chamber was kept at a RH of 30% by means of a desiccating agent. The monitoring of the cup weight allowed the determination of the vapour transport.

Change in water capillary absorption was measured before and after the treatment according to UNI EN 15801:2010 [45], in order to assess the compatibility of the treatments with Ostionera stone. The capillary water absorption coefficient (WAC) was obtained by plotting the mass variation per area versus the square root of time and calculated by linear regression up to \(\sqrt{17}\) s as a time interval. Moreover, the percentage of reduction in the total water uptake (%TWU), was calculated at the end of the experiment (\(\sqrt{294}\) s) in which the samples showed a fully saturated condition. %TWU was calculated as a percentage of increment with respect to the initial condition (t₀).

The following equation was used to obtain the total water uptake (% TWU).

\[
\%TWU = 100 \times \frac{m_{120h} - m_0}{m_0}
\]

Where \(m_{120h}\) is the weight shown by the samples when they reached a fully saturated condition and \(m_0\) is the initial dry weight.

The %TWU parameter has been used as it allows determining if the changes in porosity imply a decrease in the maximum water retention capacity. To compare the obtained results with the CI, the percentage of reduction in the water absorption coefficient (WAC), of each treatment, were also calculated. The experiment was carried out after 2 months and repeated 1 year from the treatment application to monitor the treatment behaviour due to incomplete drying/hydrolysis.

The drying properties of the stone in question were evaluated by following the UNE EN 16322:2016 [46]. The drying properties of the untreated and treated samples were calculated from the weight loss curve of the water absorbed within the sample, as a function of time. The specimens were saturated by capillary absorption for 24 h and total immersion in water, until reaching constant mass (<0.1%). After the immersion the samples surface were dried with a damp cloth, sealed with paraffin all but one and left to drying. The drying behaviour was registered by periodic weighing. During the experiment 24.2 °C and 47% RH were maintained as constant parameters. The drying index (DI) was determined by calculating the integral under the curve of the mass as a function of time, according to the following expression:

### Table 3

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Ethoxysilane (%v/v)</th>
<th>n-8 (v/v)</th>
<th>H₂O (v/v)</th>
<th>SiO₂NPs (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UCA</td>
<td>99.34</td>
<td>0.16</td>
<td>0.50</td>
<td>–</td>
</tr>
<tr>
<td>UCA_NPs</td>
<td>99.34</td>
<td>0.16</td>
<td>0.50</td>
<td>2.00</td>
</tr>
</tbody>
</table>

* Weight percentage respect to the total volume of the sol.
DI = \int^\infty_0 \frac{M_i}{M_{max}} dt

Where $M_i$ is the weight absorbed per area, $M_{max}$ the weight absorbed per area after immersion and $t$ the final time.

Moreover, $M_i$ was calculated as follows:

$$M_i = \frac{m_i - m_f}{A}$$

Where $m_i$ is the sample weight at $t = i$ hours, $m_f$ is sample weight at the end of the test and $A$ is the sample area ($m^2$).

The chromatic variations induced by the treatments were evaluated by the total color difference ($\Delta E^*$) in the CIE L*a*b* color space \( [47-49] \), using a solid reflection spectrophotometer (ColorFlex model from HunterLab) under the following conditions: illuminant D65, observer CIE 10° (CIE 1964 standard).

Penetration depth (PD) reached by the treatments was determined by DRMS measurements. Drilling measurement system was used as a method to analyse the thickness of the consolidated material \( [50] \).

### 2.3. Treatment assessment In-Situ testing area

Previously to the application, the water-soluble salts were extracted from the intervention area in order to promote the penetration of the consolidant and avoid harmful interactions. The desalinization is a process that in real conditions is resolved by reducing the water-soluble salts concentration and not the complete removal from the masonry \( [51] \). Sepiolite-cellulose pulp is an effective choice for salt removal from stone, as both sepiolite and cellulose possess a high absorption capacity. The wet application facilitates the dissolution of salts and the migration of ions outwards, where they recrystallize and are retained \( [52] \). According to procedures reported in the literature \( [52-55] \), the desalinization treatment was performed in 5 consecutive applications using a commercial cellulose pulp poultice (ARBOCEL BC1000 from CTS) mixed with sepiolite (PANSIL 100 from CTS) and distilled water with a pulp-sepiolite-water ratio of about 4:1:23. Table S1, in Supplementary Information, shows the cellulose pulp poultice and sepiolite characteristics as provided by the supplier. Specifically, the cellulose pulp poultice (hereafter CPP) remained in contact with the stone for 1 day in the first four applications and 4 days in the fifth one. The paste was applied to three sides of the In-Situ testing area until a 1–1.5 cm thick coating was obtained, which was then covered with waterproof plastic film. The four applications were made consecutively.

After each application, the electrical conductivity was determined in order to monitor the salt content. For this purpose, 200 g of CPP were dried at 50 ± 5 °C for 24 h to constant weight. A 100 g sample was collected, mixed in 900 ml of deionized water (conductivity <4 μS/cm) and stirred for 30 min at 100 °C, carefully sealing the beaker to prevent water evaporation. Subsequently, the solids were separated by centrifugation at 13,500 rpm for 20 min and filtration. The supernatant was filtered with a 0.45 μm nylon-membrane syringe filter. Finally, the conductivity of the extraction solution was measured with a portable conductimeter CM 35 (from Crison Instruments) equipped with Pt 1000 probe at 20 °C. Semi-quantitative analysis of the Cl, SO$_4$²⁻ and NO$_3$ anions present in the solution was performed using colorimetric test strips (MQuant®, from Millipore Sigma). To estimate the salts concentration in each desalinization cycle a calibration curve was constructed by preparing NaCl standard solutions.

Subsequently, 2 weeks after desalinization, the best performing product was applied, 24 h after its synthesis, by brushing and its validation was carried out. The application of the product involved 3 application cycles, waiting for one-minute between each application and allowing the complete absorption between each application, over an intervention area of 0.20 m². The In-Situ product uptake was estimated by calculating the weight difference of the vessel containing the product before and after application, taking into account the density of the product, and dividing this value by the total area of the intervened zone.

The consolidation treatment was evaluated by using different portable instruments and tests. In addition, the In-Situ behaviour was monitored during 3 years by repeating the tests mentioned below:

i. Portable colorimeter, from PCE instruments, under the following conditions: illuminant D65 and observer CIE 10° was used to establish the potential change in colour due to the application of the treatment \( [47] \).

ii. Drilling was not possible for reasons of monument protection; thus, the adhesive scotch tapes test or “peeling test” was used as a suitable tool for evaluating surface cohesion/degradation and consolidation effect after UCA_NPs consolidant treatment application. Peeling test of the untreated stone was performed after desalinization in order to account for its impact on the peeling test results. Following the procedure described in Dráčák et al. 2015 \( [56] \), 30 transparent double sided tapes (from 3 M Scotch), 40 mm in width, were employed. In order to facilitate the In-Situ handling, the tape samplers were previously (1) glued to a paper sheet; (b) cut with more or less equal dimensions; (3) marked; (4) inserted into a plastic sealed bags and (5) weighed in laboratory to obtain the initial weight. The tape samplers were transferred In-Situ and the peeling test was performed. Specifically, before treatment, the first tape was applied and its edges were marked on the stone. At this point, the following 9 tapes were repeated. In the same way, two other areas were chosen, the first tape was applied, the edges were marked and the 9 measurements were repeated for each area. Before testing, the adhesive layer cover sheet was removed and stored to re-adjust the tape weights. After approximately 90 s of application, the tape was removed at a 90° angle \( [57] \). The process was repeated ten times with different samplers in the same exact position \( [57] \). The above procedure was reproduced in other three areas to take into account the heterogeneity of the material. The measurements before and every year after the treatment were performed in different areas (Fig. S1).

iii. Sponge Contact Tests (WCS from CTS srl, Italy) was assessed in order to evaluate changes in the superficial water absorption capability \( [58-60] \). To perform the sponge In-Situ measurements, 10 polyethylene bags with (i) a polycarbonate plate containing the sponge and (ii) a 10 ml plastic syringe filled with demineralized water were prepared. According to the technical data sheets from the manufacturer (CTS) \( [61] \), the amount of water added has been such that, after a preliminary test, the water did not drip.

### 3. Results and discussion

#### 3.1. Stone materials characterization

Results of the chemical and physical characterization of the samples obtained from the Stone specimens are hereafter reported.

Data on water accessible open porosity (%) and water content (%w/w), obtained under environmental condition of temperature and pressure (Table 4), suggest that Ostonera is a highly porous stone. According to X-ray diffraction and fluorescence analysis (Fig. 2 and Table 4, Physical properties of the untreated Stone specimens used in the measurements).

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water accessible open porosity (%) ( [38] )</td>
<td>27.8 ± 1.3</td>
</tr>
<tr>
<td>Water content under atmospheric pressure (%w/w) ( [45] )</td>
<td>13.5 ± 1.9</td>
</tr>
<tr>
<td>Water vapour permeability (m² s⁻¹ 10⁻⁶) ( [4] )</td>
<td>4.5·10⁻⁶ ± 0.7</td>
</tr>
</tbody>
</table>

$^a$ Following the procedure described in Mosquera et al. 2002 \( [39] \).
Table 5, Ostionera stone is mainly composed of Calcite (80%), Quartz (17%) and, in the minority, terrigenous and fossils remains were also found, in agreement with other analysis reported in the literature [64–66].

Comparative analysis of the In-Situ testing area and Stone specimens showed the same crystalline phases and a predominant carbonate composition, although the presence of quartz is markedly higher for the In-Situ testing area samples. This higher quartz content of the In-Situ testing area sample is likely related to a higher degradation rate of the calcite matrix (i.e. calcite is more susceptible to weathering) under the previously mentioned conditions.

3.2. Treatments assessment in laboratory

3.2.1. Characterization of the treated stone specimens and consolidant effectiveness

Weight increase (Uptake) at the end of the 3rd application cycle is reported in Table 6. As can be seen, uptake values were considerably high for both products, since the stone presents a high porosity and large pores. After 2 months, the weight decreased due to the evaporation of the water and ethanol generated during the hydrolysis and condensation stages of the sol-gel process. However, the dry matter/uptake ratio (DM/Uptake) is higher than the nominal SiO\textsubscript{2} content of the original sols (41%), indicating that the process was not fully completed (i.e. there were remnant ethoxy groups or H\textsubscript{2}O/ethanol still trapped in the pores).

After 1 year, the ratio decreased to 41% for UCA_NPS, confirming that the product was completely cured and dried, whereas the UCA product was still at 71%. This effect of the SiO\textsubscript{2} NPs can be attributed to the role of the SiO\textsubscript{2} NPs that act as nucleation centres for the silica structure, which accelerates the sol-gel reaction [62,63].

The FTIR spectra obtained from the untreated and treated stones (≤1 cm from the treated surface), after 1 year from the application, are shown in Fig. 3. The untreated stone spectrum is characterized by the presence of bands at 1080 cm\textsuperscript{-1} and 1161 cm\textsuperscript{-1} and 795 cm\textsuperscript{-1}, assigned to the presence of SiO\textsubscript{2} in the stone composition. Furthermore, the splitting of the band at 795 cm\textsuperscript{-1} confirms the presence of quartz. In addition, the higher intensity of the characteristic C–O vibrations at 712, 870, 1400 and 1795 cm\textsuperscript{-1} confirm the predominantly carbonated composition (calcite) of the stone material as determined in the X-ray analysis.

Likewise, the treated samples present the same bands, although the Si-O peaks at 1080 cm\textsuperscript{-1} and 1161 cm\textsuperscript{-1} are more intense due to the formation of an amorphous silica gel. Two additional peaks appear at...
G.M.C. Gemelli et al.

Construction and Building Materials 312 (2021) 125398

7

970 cm\(^{-1}\), assigned to Si-OH groups and at 2968-2866 cm\(^{-1}\) attributed to C–H bonds from non-hydrolysed ethoxy groups. These signals are barely noticeable in the UCA_NPs treated sample, whereas their intensity is higher for the one treated with UCA, which provides further evidence of its incomplete drying [64], as corroborated by the DM/Uptake ratio (Table 6). It must be taken into account that the samples were obtained from the surface of the sample (∼1 cm from the treated surface), therefore the observed intensity of the Si-O band, of the consolidant product, is probably higher than the band that can be obtained from the internal part of the stone sample. As observed in prior works, focusing on quantitative analysis (FTIR and XRF) of an alkoxysilane-based treatment on limestone [65], the consolidant can be distributed following a gradient, and the Si-O signals in FTIR are more intense (respect to the CO\(^2-\) ones) near the surface.

The changes in surface morphology and the material compaction/cohesion after the treatments were observed by SEM. As shown in Fig. 4, untreated stone (Fig. 4 a-b) shows a heterogeneous surface, where the mineral grains are clearly visible. After treatment with the UCA product (Fig. 4 c-d), the coating is more compacted and it shows nanoparticles of defined structure, where the gelled product (and the nanoparticles in the case of UCA_NPs) are filling the spaces between the mineral grains, leading to a more cohesive aspect. By observing Fig. 4 c-e, the coating morphology with and without NPs have a different rugosity and a more defined nanoparticles structure can be identified in Fig. 4 e-f. In addition to this structure, there seems to be a proper cohesion between the formed SiO\(_2\) gel and the original material (i.e. no detached grains are observed). As described in prior works [19,66], the amino group of n-octylamine, could interact with the ion CO\(^3-\), promoting the chemical interaction between the carbonate stone and the oligomeric ethoxy-silanes. Xu et al. [67], observed a similar behaviour between calcite and aminosiloxane. Similarly, the stone treated with UCA_NPs (Fig. 4 e-f) presents a more compact and cohesive structure than untreated. As opposed to the poorly defined features of the UCA xerogel, the SiO\(_2\) xerogel shows a more homogeneous nanoparticulate structure, which can be associated to the seeded growth mechanism promoted by the added SiO\(_2\) nanoparticles [62]. Another important feature is the absence of cracks in the coatings confirming the role-played by the n-octylamine preventing cracking. As we previously explained, n-octylamine produces inverse micelles giving rise a mesoporous gel network, reducing capillary pressure during gel drying.

It must be taken into account that the SEM image and the FTIR sampling have been carried out on the surface (∼1 cm from the treated surface) which is where the material is likely more compact due to the presence of a greater quantity of consolidant than in depth.

Increase in mechanical strength was evaluated using the DRMS test which is considered the most suitable methodology to test the consolidation performance in soft stones and is a quasi-non-destructive method [43,68]. Fig. 5 shows the drilling resistance profiles after each treatment and untreated stone for comparison. In light of the general trends observed, it can be considered that the treatments generate an increase of the mechanical strength of the stone, which can be explained by the more compact structure and cohesion with the mineral grains observed by SEM (Fig. 4). Specifically, the increase is evidenced across the full depth of stone tested (30 mm) demonstrating that the products penetrate deeply into the stone structure and produce effective consolidant action. Such a high penetration capacity is directly related to the high porosity of the Ostionera stone and the presence of large (macroscopic) pores.

By comparing the two treatments, it can be seen that the particle-modified product (UCA_NPs), presents a significantly higher mechanical resistance being improved by a factor of around 2 and 5 related to UCA and the untreated samples respectively. This fact can be attributed to two different effects: (i) the nanoparticles in its formulation act as a filler of some larger voids, while also reinforcing the SiO\(_2\) xerogel structure. (ii) As determined by FTIR (Fig. 3) and the dry matter/uptake ratios (Table 6), the presence of the nanoparticles promotes the hydrolysis of the silica precursor, leading to the formation of a more reticulated structure. These results are in line with the effect reported by other authors, who also determined that the addition of nanoparticles can increase the consolidant effect of consolidant products [14,66,69].

3.2.2. Compatibility of the treatments

Considering that the final objective of the tests was the In-Situ application on an archaeological site, the change in the water vapour permeability (WVP) after the treatments is an important parameter for evaluating the compatibility since the loss of the stone breathability may lead to new decay phenomena (e.g. moisture associated damage, delamination). By comparing the WVP value of the untreated stone, (see Table 4), obtained after 1 year from the treatment, the results show that both treatments had a low influence over the permeability (Table 6), with reductions around 13 and 6% for UCA and UCA_NPs respectively. Taking into account the limits defined in the CI [37] % WVP <10% are considered as low risk of incompatibility. However, %WVP values between 10 and 25% are defined as at medium incompatibility risk.

Water absorption by capillary graphs are shown in Fig. 6. Specifically, water absorption capability of the products was monitored after 2 months (Fig. 6a) and 1 year (Fig. 6b) from the treatment application.

One can easily see from Table 7 there is an evident difference between the WAc and TWU results obtained after 2 months and 1 year. Specifically, after 2 months, the noticeable water reduction depends on the presence of non-hydrolysed ethoxy groups on the silica gel structure that inhibits water absorption (i.e. they decrease surface energy). After 1 year, the product drying progressed and capillary absorption got closer to the original material, especially for the samples treated with UCA_NPs (Fig. 6).

This observation agree with the dry matter/uptake ratios and FTIR spectra, which showed an acceleration of ethoxy- groups hydrolysis and gel drying with the addition of SiO\(_2\)NPs.

In order to assess the compatibility of a consolidant, the following criterion can be considered: after treatment, the WAc should not increase nor differ too much from that of the untreated material. Otherwise, degradation may occur in the untreated-treated interface. UCA_NPs product fulfils the first requirement, as it only causes a low reduction of the WAc (19%). On the other hand, UCA product, with a 73% of water reduction, does not adapt to this requirement [37]. Considering the results obtained, UCA_NPs can be considered a product
with a moderate risk of incompatibility compared to UCA, which, due to the high WAc value shown, presents a high risk of incompatibility.

In light of the results obtained from the (i) DM/Uptake ratio, (ii) the presence of C–H bonds in the FTIR spectra and (iii) the apparent hydrophobicity observed in the absorption curves measured, UCA treatment shows an incomplete drying/hydrolysis behaviour after 1 year. Consequently, slow and non-reproducible behaviour was observed between replicates during the drying test and the maximum incompatibility value was assumed for the calculation of the ID. On the other hand, the drying behaviour of the untreated and UCA_NPs treated stones was compared (Fig. 7). As it can be seen, it is impossible to define a clear difference between the first (characterized by a steeper slope) and second drying phases. Therefore, the drying index of the untreated and treated were calculated. The obtained values of 0.26 and 0.44, from the untreated and treated with UCA_NPs respectively, evidenced a reduction of 0.18 units. By analysing these values, it can be concluded that, in the time interval of the experiment, the treated sample has dried slower than the untreated sample, which can be related to a partial filling of the pores by the silica xerogel, which may affect water transport (as indicated by the WAc and permeability measurements).

Therefore, according to the compatibility criteria, the UCA_NPs treatment presents a high risk of incompatibility. Although this factor should be carefully considered during monitoring, the results obtained from the water vapour permeability and the water capillarity absorption indicate that water transport through the treated stone is not severely affected and the slope of the drying curves corresponding to the untreated and treated stone are reasonably similar.
Aside from the hydric behaviour, the visual change induced by the treatment is another key parameter in terms of compatibility. For both products, the total colour difference values ($\Delta E*$), recorded 1 year from the treatment (Table 8), show a low incompatibility risk, according to the rating scale proposed by Delgado Rodriguez and Grossi [37]. Furthermore, values in the measured range are below the perceptibility threshold ($\Delta E^* \sim 1$) of the human eye [47,49].

Considering the DRMS profiles (Fig. 5), the average drilling force calculated for the treated stone increases over 25% respect to the untreated ones. According to the compatibility indicators proposed by Delgado Rodrigues and Grossi [37], this increase can be considered at high risk of incompatibility.

By comparing the penetration depth achieved by the treatments, a uniform penetration up to 30 mm was observed, in line with the recommendations for consolidant in which a penetration depth as high as possible is desired [70]. Furthermore, it should be mentioned that, in most cases, the level of deterioration of the stone is 1–2 cm and therefore, the role of the consolidant is to reach the degraded substrate to be able to cling [70]. Additionally, in the field of conservation it is required

### Table 7
Water absorption coefficient (WAc), total water absorption (TWU) and the corresponding reduction (%) after 2 months and 1 year respectively from the treated and untreated samples.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>After 2 months</th>
<th>After 1 year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TWU (w/w)%</td>
<td>WAc $10^3$ (g/cm² s⁻¹/²)</td>
</tr>
<tr>
<td>UTNTRD</td>
<td>12.68 ± 1.71</td>
<td>24.23 ± 3.12</td>
</tr>
<tr>
<td>UCA</td>
<td>1.21 ± 0.10</td>
<td>0.10 ± 0.05</td>
</tr>
<tr>
<td>UCA_NPs</td>
<td>0.65 ± 0.12</td>
<td>0.12 ± 0.10</td>
</tr>
<tr>
<td></td>
<td>TWU (w/w)%</td>
<td>WAc $10^3$ (g/cm² s⁻¹/²)</td>
</tr>
<tr>
<td>UTNTRD</td>
<td>12.68 ± 1.71</td>
<td>24.23 ± 3.12</td>
</tr>
<tr>
<td>UCA</td>
<td>5.04 ± 0.67</td>
<td>6.59 ± 7.98</td>
</tr>
<tr>
<td>UCA_NPs</td>
<td>11.68 ± 4.35</td>
<td>19.73 ± 4.56</td>
</tr>
</tbody>
</table>

* Value calculated until $\sqrt{17}$ s.

* Total water uptake at the end of the experiment ($\sqrt{294}$ s).

![Fig. 6.](image-url) Comparison of the capillary absorption curves measured after 2 months (a) and 1 year (b) respectively from the treatment applications and untreated counterparts.

![Fig. 7.](image-url) Drying curves of samples treated with UCA_NPs and the untreated counterparts, according to UNE EN 16322:2016 standard. (a) Residual amount of water in the sample over time vs time. (b) Linearized plot representing the residual amount of water in the sample as a function of $t^{1/2}$.

### Table 8
Total color difference ($\Delta E^*$) from the stone specimens 1 year from the treatment application.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$L^*$</th>
<th>$a^*$</th>
<th>$b^*$</th>
<th>$\Delta E^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTNTRD</td>
<td>–</td>
<td>58.6 ± 3.4</td>
<td>11.2 ± 1.7</td>
<td>18.0 ± 2.3</td>
</tr>
<tr>
<td>UCA</td>
<td>1 year</td>
<td>55.0 ± 1.3</td>
<td>9.1 ± 0.6</td>
<td>21.6 ± 1.5</td>
</tr>
<tr>
<td>UCA_NPs</td>
<td>1 year</td>
<td>55.0 ± 1.3</td>
<td>9.1 ± 0.6</td>
<td>21.7 ± 1.5</td>
</tr>
</tbody>
</table>
to achieve a penetration depth of >20 mm in order to be classified the treatment as low incompatibility risk.

Lastly, a summary of the parameters calculated is presented in Table 9 and compared with the Compatibility Indicators proposed by Delgado Rodrigues and Grossi [37] to highlight the degree of compatibility with Ostionera stone. In addition, the ID was presented in order to estimate the overall incompatibility degree of both treatments in relation to the stone under study.

Following the ID values obtained is clearly visible that the synthesized products show a moderate incompatibility degree, 6.7 and 6.1 for UCA and UCA_NPs respectively.

### 3.3. Treatment assessment In-Situ testing area

From the 1-year laboratory test evaluation, UCA product displayed an ID value of 8, therefore, according to Delgado Rodrigues and Grossi [37], the treatment action can be considered highly compatible. On the other hand, UCA_NPs product showed ID value of 6 which indicates that the treatment action is more compatible.

Considering how a high concentration of salts in the masonry can hinder the penetration of the product in depth a pre-conditioning was carried out to reduce the salt content near the surface. In this way, a CPP was used as water-soluble-salts extraction medium. Preliminarily, a UCA and UCA_NPs respectively.

Delgado Rodrigues and Grossi [37] to highlight the degree of compatibility with Ostionera stone. In addition, the ID was presented in order to estimate the overall incompatibility degree of both treatments in relation to the stone under study.

Following the ID values obtained is clearly visible that the synthesized products show a moderate incompatibility degree, 6.7 and 6.1 for UCA and UCA_NPs respectively.

**Table 9**

<table>
<thead>
<tr>
<th>Criteria</th>
<th>Compatibility Indicators</th>
<th>Rating scale</th>
<th>Obtained Values</th>
<th>ID $^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical properties</td>
<td>Drilling Resistance</td>
<td>&lt;10%</td>
<td>UCA $\rightarrow$ UCA $\rightarrow$ UCA 8.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 $^a$</td>
<td>&gt; 25%</td>
<td>10 UCA_NPs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>10% $^a$</td>
<td>25% UCA_NPs</td>
<td>UCA_NPs 6.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25% $^a$</td>
<td>&gt; 25%</td>
<td>UCA_NPs 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 25%</td>
<td>10 UCA_NPs</td>
<td>UCA_NPs 5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 30%</td>
<td>5 UCA_NPs</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 5</td>
<td>10 UCA_NPs</td>
<td>UCA_NPs</td>
</tr>
<tr>
<td>Treating ability</td>
<td>Penetration depth</td>
<td>&gt; 20 mm</td>
<td>UCA $\rightarrow$ UCA $\rightarrow$ 0 $^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>30 mm</td>
<td>0 UCA_NPs</td>
<td>UCA_NPs 30 $^a$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&lt; 5 mm</td>
<td>5 UCA_NPs</td>
<td>10</td>
</tr>
<tr>
<td>Hydrophilic behaviour</td>
<td>Water vapour permeability</td>
<td>&lt;10%</td>
<td>UCA $\rightarrow$ UCA $\rightarrow$ 0 $^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>0 $^a$</td>
<td>13 UCA_NPs</td>
<td>5 UCA_NPs</td>
</tr>
<tr>
<td></td>
<td></td>
<td>25% $^a$</td>
<td>&gt; 25%</td>
<td>73 UCA_NPs 10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>&gt; 25%</td>
<td>10 UCA_NPs</td>
<td>UCA_NPs 5</td>
</tr>
<tr>
<td></td>
<td>Water absorption coefficient</td>
<td>&gt; 25%</td>
<td>UCA $\rightarrow$ UCA $\rightarrow$ n/a UCA_NPs 10</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>10 UCA_NPs</td>
<td>UCA_NPs 19</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Drying index</td>
<td>UCA</td>
<td>UCA_NPs n/a</td>
<td>UCA_NPs 19</td>
</tr>
<tr>
<td>Viscous properties</td>
<td>Total colour difference</td>
<td>&lt;3</td>
<td>UCA $\rightarrow$ UCA $\rightarrow$ 0 $^a$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>3-5 $^a$</td>
<td>UCA_NPs UCA_NPs</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(ΔE*)</td>
<td>&gt; 5</td>
<td>2 UCA_NPs</td>
<td>0</td>
</tr>
</tbody>
</table>

$^a$Ratings of 0, 5 and 10 refer to low, medium and high incompatibility risks.

$^a$Penetration depth estimated as the depth where the treatment displayed consolidating effect (by DRMS).

Incompatibility Degree, ID = 0 $^a$ Perfect compatible action; ID = 10 Fully incompatible action.

As reported in literature [40,57], there are several problems and limitations that must be taken into account to perform the peeling test: the flatness of the tested surface, the material damage or deterioration, the operator ability to perform the test in a consistent manner, the angle and the rate of tape removal and so on. Considering these limitations, peeling test was performed and Fig. 10 shows the results obtained.

As can be seen, in Fig. 10 a diagram from the untreated degraded surface, the adhesive tape is able to remove an appreciable amount of material (Fig. 10d), and a well pronounced asymptote is not appreciable. On the other hand, the amount of material removed from treated surface is significantly lower, practically reaching zero value, after 2–3 cycles (Fig. 10 b–e). For purposes of comparison between the behaviour of the product over time, the regression smoothed values interpolated for the third test repetition were selected as representative for characterizing the surface quality (Fig. 10c and Fig. 5S) [40]. From the data obtained from the peeling test, it is possible to conclude that with the application of the UCA_NPs treatment the surface cohesion was improved with respect to the original degraded stone. According to the results obtained from the DRMs, performed on the *Stone specimens*, it is to be expected that the In-Situ testing area sample may also achieved an increase in surface and depth mechanical resistance. By observing the values of 1–3 years there is an apparent increasing trend, which suggests that degradation may still be occurring in the treated material, although at a slow pace. Nonetheless, the material removed is still low compared to the untreated area (i.e. the reduction is over 95% in all cases) and the differences between each year are ~100 times lower than the variability of the measurements on the untreated area (see Fig. 10 C). Even though the treatment showed a good durability after 3 years, it would be advisable to monitor for longer-time periods if this evolves into a significant degradation of the treated area.

Modifications of the water absorption characteristics promoted by the treated were evaluated by the sponge method from treated-untreated surfaces following previous studies conducted in lab and In-Situ [58,71,72]. Data on Table 12 presents the water absorption values (Wa) measured 2 months, 1, 2 and 3 years after treatment.

After 2 months from the In-Situ treatment application, the decreased water absorption values indicate the incomplete drying of the product (i.e. presence of ethoxy groups on the xerogel), as also seen in the previous
capillarity water absorption test performed in the laboratory (see Fig. 6a). After 1 year and onwards, the values obtained from the capillarity absorption test can be considered very close to the untreated stone (see Fig. 6b). In line with the data obtained in the preliminary laboratory results (water vapour permeability, drying, capillary absorption), it can be confirmed that the UCA_NPs treatment, applied in field conditions, respects the water transport properties of the original material.

Given the results obtained from In-Situ evaluation tests, after 3-years of exposure to an aggressive marine environment, the properties of the superficial consolidant treatment UCA_NPs suffered a low alteration.

4. Conclusions

In this research a 1 year in laboratory and 3-years In-Situ evaluation study of alkoxysilane-based consolidants were assessed on Ostionera stone from Cádiz Roman Theatre. The laboratory tests confirm the consolidant action of the treatments and its enhancement by the incorporation of SiO$_2$ nanoparticles. Moreover, the incorporation of SiO$_2$ nanoparticles improved the mechanical behavior and drying time of the consolidant.

The drilling profiles (DRMS) evidenced a high penetration and consolidating effect of the products, with remarkable resistance in creases down to 30 mm and a regular profile through the stone samples. As evidenced by the SEM micrographs and FTIR, this effect occurs due to the formation of a compact SiO$_2$ xerogel structure after gelification, which is able to fill the spaces between the mineral grains. Addition of SiO$_2$ nanoparticles as a filler increases compactness and further enhances the mechanical properties.

In addition, SiO$_2$ nanoparticles accelerate the product curing and drying, since the treatment without added nanoparticles had not yet reached its complete hydrolysis after 1 year from the treatment application as evidenced by the FTIR analysis and by its hydrophobic behavior.

The results obtained in the laboratory confirmed the need to evaluate the treatment compatibility with the selected stone material as shown by the higher incompatibility risk and drying problems of the treatment.

![Fig. 8](image_url) (a) Calibration curve relating conductivity with NaCl concentrations. (b) Conductivity of the solutions containing the salts extracted from the cellulose poultice used for each desalinization cycle and (c) semi quantitative Cl$^-$ ion analysis by colorimetric test strips.

Table 10

<table>
<thead>
<tr>
<th>Application number</th>
<th>Desalinization Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Application contact time (days)</td>
</tr>
<tr>
<td></td>
<td>Conductivity (mS/cm) at 20 ± 1 °C</td>
</tr>
<tr>
<td></td>
<td>[Cl$^-$] (mg/l)$^a$</td>
</tr>
</tbody>
</table>

$^a$ Estimated according to the calibration curve assuming all salts as NaCl.
without added nanoparticles. In order to take the right decision and avoid harmful interactions, it is not enough to determine only the improvement in mechanical properties, but it is also important to consider the physical and chemical behavior of the treatment/substrate over time.

More specifically, the compatibility analysis proves that both synthesized products show an increase in the mechanical resistance >25% which may suppose a risk of overconsolidation of the stone. Conversely, the uniform penetration up to 30 mm was achieved, indicating that both consolidants are potentially able to reach beyond the weathered area and promote the adhesion between weathered/unweathered zones (generally at 10–20 mm from the surface). Regarding the water transport properties, treatment with the products has a low impact in vapor permeability (13 and 6% decrease) and a medium impact in liquid water movement by capillarity (73 and 19% decrease). However, the impact over hydric properties, may be higher at short curing times (<2 months), where the incomplete hydrolysis of the products leads to hydrophobic character. On the other hand, chromatic variation below the perceptibility threshold (ΔE*~1–2) of the human eye were registered after treatment.

In terms of incompatibility degree, the consolidant without added nanoparticles, with an ID value of about 8 exhibit a high risk of incompatibility. Otherwise, the consolidant with SiO$_2$ nanoparticles showed an ID value of 6 which indicates that the treatment action can be considered as intermediate compatible.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>ΔL$^*$</th>
<th>Δa$^*$</th>
<th>Δb$^*$</th>
<th>ΔE*$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Untreated</td>
<td>58.8 ± 1.3</td>
<td>9.7 ± 0.8</td>
<td>18.6 ± 1.8</td>
<td>–</td>
</tr>
<tr>
<td>UCA NPs</td>
<td>57.5 ± 3.3</td>
<td>8.1 ± 0.7</td>
<td>19.8 ± 1.5</td>
<td>2.4 ± 3.7</td>
</tr>
<tr>
<td>2 months</td>
<td>58.0 ± 4.5</td>
<td>8.2 ± 0.8</td>
<td>20.1 ± 1.5</td>
<td>2.3 ± 4.8</td>
</tr>
<tr>
<td>1 year</td>
<td>60.1 ± 2.0</td>
<td>7.1 ± 0.5</td>
<td>17.8 ± 1.1</td>
<td>3.0 ± 1.3</td>
</tr>
<tr>
<td>3 years</td>
<td>61.4 ± 1.7</td>
<td>7.6 ± 0.4</td>
<td>18.7 ± 0.7</td>
<td>3.3 ± 1.9</td>
</tr>
</tbody>
</table>

Fig. 9. Intervention zone: External view of the vomitory. (a) Close-up views of the vomitory and (b) the stone damages on the intervention area.

Table 11

ΔL$^*$ and ΔE*$^*$ values recorded from the stone surface before and after the treatment application.

Fig. 10. (a) Amounts of removed material by the peeling tests, before and after treatment, from the In-Situ testing area. (b) Close-up of the treated stone results. (c) Regression smoothed value according to Drdacký et Al. 2012 and inset including the value of untreated [40]. Representative photographs of the material removed by the tapes (c) before and (d) after treatment.
According to the preliminary laboratory tests, the consolidant with added SiO$_2$ nanoparticles was applied In-Situ on a selected area and 3-years evaluations were carried out.

The 3 years results highlight that small variations are observed in the treated area, even if they are minor compared to the measurements on the untreated area. However, it would be appropriate to carry out more studies over longer time intervals to verify if they are evidence of degradation and to check if these variations can evolve into a loss of the consolidant effectiveness.

CRediT authorship contribution statement

Giada M.C. Gemelli: Writing – original draft, Investigation, Formal analysis. Rafael Zarzuela: Writing – review & editing, Formal analysis, Visualization. Francisco Alarcón-Castellano. Maria J. Mosquera: Writing – review & editing, Supervision, Funding acquisition. M.L. Almoraíma Gil: Writing – original draft, Investigation, Formal analysis.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This work has been supported by the Spanish Government MAT2017-84228-R (MINECO/AEI/FEDER,UE) and PID2020-115843RB-I00/AEI/10.13039/501100011033. This work has been co-financed by the European Union under the 2014-2020 ERDF Operational Programme and by the Department of Economic Transformation, Industry, Knowledge, and Universities of the Regional Government of Andalusia. Project reference: FEDER-UC18-106613. Giada M.C. Gemelli would also like to thank the Spanish Government for her pre-doctoral grants (PRE2018-085799). We thank the Cadiz Roman Theatre staff and Manuel Luna for their collaboration.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.conbuildmat.2021.125398.

References
