

Article

Basic Protocol for On-Site Testing Consolidant Nanoparticles on Stone Cultural Heritage

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Abstract: Currently the application of consolidants based on nanoparticles is common practice among restorers. Consolidants should not modify the properties of original materials according to international recommendation, which requires previous studies to decide the optimal option. The selection must be based on empirical results, and not only in the expertise of the restorer, because the consolidant's effectiveness is influenced by its own properties and other factors such as the characteristics of the artwork (elemental composition, porosity, texture, etc.) and its context (temperature, relative humidity, etc.). Moreover, new protocols must be sustainable and compatible with on-site restoration. A new protocol to test consolidant nanoparticles has been designed and assessed. This is based on easy trials and low-cost techniques—digital microscope, colorimeter, peeling test and ultrasound—that could be employed by restorers in situ. In this paper, different consolidant nanoparticles were tested on stones from two historical quarries. The first treatment was SiO₂ nanoparticles, and the second, a new nanocomposite of Ca(OH)₂ and ZnO quantum dots that allows us to measure penetration depth easily and discern the treated areas under UV lights. This second treatment was the best option for the studied stones, validating the protocol designed for the choice of consolidants.

Keywords: consolidant; nanolimes; nanosilica; protocol; stone

1. Introduction

Stones have been widely used since ancient times as construction material. The reasons behind the choice of this material are its durability—defined as the capacity to withstand decay, thus maintaining its aesthetical and mechanical properties—and the presence of quarries accessible from human settlements. The quarry defines the stone's characteristics, i.e., composition, texture, resistance, porosity, etc. Nevertheless, even durable stones suffer degradation processes due to both intrinsic and extrinsic factors, worsened by the increment of environmental pollution due to the industrialization process and by changes in climate [1]. Powdering, sanding, scaling or alveolation are some of the most common weathering forms that decrease mechanical and aesthetical properties of our stone-built cultural heritage [2].

The use of consolidants is common in the restoration of stone buildings and other stone artworks. These products help regain cohesion on weathered stones and adhesion between modified and healthy stone areas, without generating any physical–chemical or aesthetical changes [3], following international recommendations. Venice Chapter (1964) [4] set up essential criteria for consolidating processes in cultural heritage, i.e., preserve aesthetic value (art. 9) and proved the efficacy of consolidants (art. 10). These criteria have been revised in the successive Chapters adopted by the General Assembly of ICOMOS (International Council on Monuments and Sites) [5]. In 2004, the Spanish Institute for Historic

Heritage published widely accepted basic criteria for interventions in stone-built cultural heritage [6]. Regarding the consolidating process, this document recommends the use of products that: (1) do not modify aesthetic and chromatic variables of stone and its physical–chemical properties, (2) are applied sustainably on stone surfaces. Furthermore, CEN (European Committee for Standardization) has edited a series of standards, highlighting the UNE-EN 41810 [7] about intervention criteria for stone materials, and others that can be adopted in different phases of the restoration process: characterization of stones [8–11], sampling [12], or the study of surface protection [13].

Currently, there are a high range of consolidants for stone-built cultural heritage based on different chemical compositions, i.e., epoxy resins, acrylics, silica-based consolidants, inorganic consolidants, etc. It is essential to assess the effectiveness and applicability of a consolidant before its widespread application on an artwork or historical building. However, the effectiveness does not only depend on the efficacy of the product, but also on other parameters. Some studies are focused on the influence of weather conditions during treatment applications [14,15] or the physical–chemical properties of the stone substrate [16]. A good restoration practice requires previous assays that confirm the best consolidant product in relation to the specific characteristics of the artwork (chemical composition, physical properties, state of deterioration, etc.) and its context (temperature, relative humidity, etc.) to avoid undesirable consequences. Restoration without previous trials could generate ineffectiveness or incompatibility. In the case of limestones, for example, acrylics and epoxy resins have caused yellowing, strong alterations in its porous system or biodeterioration [17–19]; silica-based consolidants have a low durability and compatibility [20–23]; and traditional inorganic consolidants, such as limewater, have a high durability and compatibility [24], but a low effectiveness and penetration [25,26].

Some institutions have designed useful guidelines for the intervention of stone and earthen walls [3,27]. Nevertheless, they have not designed a basic protocol to support decision making on the best consolidant for on-site restoration with experimental results. Some guidelines or recommendations can be deduced of the methodologies and results of different papers, especially about application methodologies [28], testing methods [29,30] and consolidant evaluations [31] or aging tests to assess the durability of the consolidants [32]. Nevertheless, it was De Rosario et al. [33] who made a substantial difference between laboratory and on-site evaluation. In fact, these authors proposed a simplification of the number of assays for on-site evaluations, avoiding expensive techniques.

The basic protocol designed in this research avoids expensive and complex techniques, so that it can be used by restorers without increasing the budget of their interventions. We propose four easy and low-cost steps to assess the best consolidant for each stone artwork. This protocol is based on common equipment, such as a colorimeter, a handheld digital microscope and a portable ultrasound, and easy trials, like the peeling test.

This protocol was assessed by studying the consolidation effect of two treatments. The treatments selected are based in recent advances from the nanotechnology field. It is the case of silica nanoparticles (SiO_2 NPs) which decreases the time necessary to obtain silica gel and avoid the use of hazardous solvents [16], but they have shown some disadvantages, such as the formation of superficial layers [34]. Calcium hydroxide nanoparticles ($\text{Ca}(\text{OH})_2$ NPs) are the other treatment proposed for the consolidation of stones. This treatment has improved the effectiveness of calcium hydroxide with respect to the use of limewater [26], but only as pre-consolidant [35] due to its low penetration [24,36]. Recent studies try to improve these treatments by studying their application in different solvents and their colloidal stabilities [37,38]. In this research, a new nanocomposite based on $\text{Ca}(\text{OH})_2$ NPs doped with zinc oxide quantum dots (ZnO QDs) has been used. This product has been designed and synthesized by our research group and allows us to measure easily its penetration depth under ultraviolet lights thanks to the fluorescent property of the ZnO QDs [38].

The consolidants were tested on two different stones, with similar chemical composition but different physical properties. The results highlight the efficacy of this protocol for the restorer's decision makings about the best consolidant for a stone artwork.

2. Materials and Methods

2.1. Stones

Carbonate stones have been widely used in the Mediterranean basin since ancient times [39]. Two historical quarries (Espera and Puerto de Santa María, Cádiz, Spain) were chosen. These stones were employed in historic buildings of southern Spain, i.e., the cathedral and the town hall of Seville [40,41] (Figure 1). Espera quarry produced a biosparitic limestone with a composition based on calcite, a low amount of quartz, and a medium pore size of 10–75 μm [42], while Puerto de Santa María quarry produced a biosparitic calcarenite with carbonate and silica grains cemented by calcite, with a pore diameter of 10–100 μm [42].



Figure 1. Town hall of Seville (Spain). The stones used in its construction come from Espera and Puerto de Santa María quarries, among others, according to Guerrero [41].

The open porosity and the water absorption coefficient of both quarry stones were measured according to international standards [9,10]. Espera limestone has an open porosity of 6.4% and a water absorption coefficient of $24.0 \text{ g/m}^2 \cdot \text{s}^{0.5}$, while the values for Puerto Santa María calcarenite are 16.8% and $177.7 \text{ g/m}^2 \cdot \text{s}^{0.5}$, respectively.

Cubic stone samples of 5 cm of edge were used in this research.

2.2. Treatments

The use of inorganic consolidants based on nanoparticles has been increasing in the last few years. Their reduced sizes improve penetration and achieve better stability, while its inorganic composition is more compatible with stone substrates [43]. In fact, consolidants based on silica and lime NPs began to be commonly used by restorers for limestones and calcarenites. Because of that, two consolidants based on inorganic nanoparticles were tested: SiO_2 NPs (Nano Estel[®]) and a new treatment based on $\text{Ca}(\text{OH})_2$ NPs doped ZnO QDs. Nano Estel[®] is an aqueous dispersion of silica nanoparticles with an average size of 10–20 nm. $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs are a nanocomposite with an average size of 100 nm. The ZnO QDs are tiny spherical particles of 8 nm that are posed heterogeneously over the hexagonal portlandite nanoplates. The synthesis was made according to Becerra et al. [44], and the solvent for the application was acetone, due to the good result achieved in previous studies [38] and its low toxicity [45]. In addition, the higher evaporation rate of the acetone (6.6; unit: butyl acetate = 1 [45]), in comparison with alcohols commonly used in these kinds of dispersions (ethanol: 2.0; isopropanol: 2.9 [45]), avoids possible inconveniences due to photochemical reactions caused by a

prolonged presence of the solvents into stone. The initial concentration was the same of commercial $\text{Ca}(\text{OH})_2$ NPs Nanorestor[®] (5 g/L).

The concentration of product used in this assay was calculated according to technical datasheets, following the practice of restorers that might acquire these products on the market. In this sense, each product was diluted (1:1), with a final dry residue content of 15% for SiO_2 NPs and 0.25% for $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs.

The dosage for each stone was calculated according to its open porosity and absorption capacity, using a criterion of saturation [46]. This is 0.04 mL/cm² for Espera limestone and 0.15 mL/cm² for Puerto Santa María calcarenite. Four applications with a micropipette were spread in the upper surface of each stone sample. Each treatment was performed five times. After the last application, the samples were dried at room temperature for 20 days.

2.3. Assessment of the Treatments

An easy and basic protocol to assess the suitability of a consolidant treatment has been designed to be employed by restorers. This protocol is composed of 4 steps. The first step is to detect any aesthetical change. For that, the chromatic change (ΔE^*) was measured by colorimetry (colorimeter PCE-CSM 2; 9 measurements on each treated surface, what means 45 measurements for treatment and lithotype) and calculated according to the equation:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{0.5}, \quad (1)$$

where ΔL^* , Δa^* and Δb^* characterize variations in the color values from the controls in the black-white (brightness), red-green and yellow-blue axes of the CIELAB color-system.

The second step consists on the examination of the sample surfaces with a handheld digital microscope before and after the treatment application. In this study, a Zarbeco MiScope MP2 with 40–140x magnification lens was used.

In the third step, the cohesion on the surface samples is calculated by the use of the peeling test. This was made according to Drdácý et al. [47], using Scotch Cristal tape (3M) with 10 repetitions over the same location. The percentage of consolidation (%C) was calculated according to the equation [38]:

$$\%C = (\text{TRM}_{\text{untreated}} - \text{TRM}_{\text{treated}})/\text{TRM}_{\text{untreated}} * 100, \quad (2)$$

where $\text{TRM}_{\text{untreated}}$ is the total amount of material removed by peeling in the untreated sample and $\text{TRM}_{\text{treated}}$ is the total amount of material removed in the treated sample.

Finally, the in-depth stone consolidation is analyzed in the fourth step. A portable ultrasound equipment (PROETI H0394) was employed according to UNE-EN 14579 [11]. An organic gel was sprinkled on the stone surfaces to facilitate the contact between the stone surface and the high frequency transducers (150 kHz). In this case, the transducers were placed in the treated surface and its opposite face (direct transmission). Restorers may use semidirect transmission or indirect transmission in case of walls. The increment of propagation velocity (ΔV) was calculated as the difference between propagation velocities before and after the application of the treatments.

Additionally, other complementary studies have been proposed to assess the results: scanning electron microscopy (SEM, JEOL JSM-6510) to examine stone surfaces at higher magnification and water absorption capillarity to detect changes caused by the treatments on the stone properties. These studies are useful but not essential for the decision making process.

3. Results

Figure 2 shows the color changes (ΔE^*) caused by treatment on the stones. The standardized criterion establishes that treatments should not generate $\Delta E^* > 5$ [48,49]. In this case, only the $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs modified slightly the color surface with a value of ΔE^* very close to 5. This is

due to smaller modifications of L^* and b^* values. The ΔE^* is lower in the stone with higher pore size, especially with $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs.

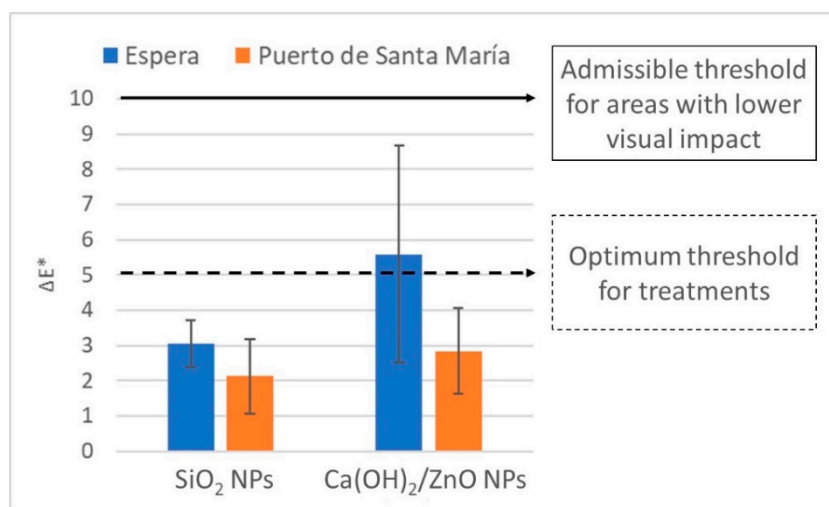


Figure 2. Color change (ΔE^*) on the stone surface after the application of consolidant treatments (SiO_2 NPs and $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs). These color changes and their standard deviations are lower than the threshold for treatments ($\Delta E^* < 5$) [48,49], except for $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs on Espera. Espera stone showed a color change plus its standard deviation lower than 10, threshold admissible in the worst case scenario [50,51], because it implies some change that could be slightly observed by the naked eye.

The analysis of the stone surfaces after treatment application by a handheld digital microscope allows observation of brightness over the stone surfaces treated with SiO_2 NPs (Figure 3b,e). That brightness is produced by a silica layer formed on the surface, just as was confirmed in SEM images (Figure 4a,b). In the case of Espera limestone, its lesser pore size favored the formation of a homogeneous layer over stone surface, which appears cracked as a consequence of the stress produced during the drying process (Figure 4a). In the Puerto de Santa María calcarenite, the layer penetrated through the highest pores (Figure 4b).

In the samples treated with $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs small aggregates of calcium carbonate (CaCO_3) from the stone surfaces could hardly be appreciated. The Figure 3c shows some calcium carbonate aggregates highlighted.

One of the main advantages of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs with respect to commercial $\text{Ca}(\text{OH})_2$ NPs is the possibility of measuring the penetration depth of the treatment easily. For that, it is only necessary to light up the sample with UV light, which could be easily done by restorers. Figure 5 shows the yellow fluorescence of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs in the surface and cross-section of the samples. The treatment achieved a penetration depth of 0.8 cm in Puerto de Santa María calcarenite and 0.18 cm in Espera limestone. The difference in penetration is related to the pore size and porosity of the stone, penetration depth increasing with pore size and open porosity.

Modification of the stone surface may produce changes in the physical properties of the stone. For that reason, water absorption by capillarity was studied after the application of the treatment. The silica layer decreased water absorption capillarity (by 36%) in the Espera limestone, while the treatment based on $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs only reduced it by 6%. The effect of both treatments was similar in the case of Puerto de Santa María calcarenite (around 10%).

The surface cohesion was studied by peeling test. Table 1 shows the maximum and minimum of removed materials in each sequence of the peeling test and their standard deviations. The nonlinear progression of the repeated peeling test (Figure 6) was calculated according to Drdácý et al. [47]. The nonlinear progressions of treated samples are below those of the untreated sample as a consequence

of an increment in the stone's cohesion. This means that the removed material by the Scotch tapes is lesser in treated samples.

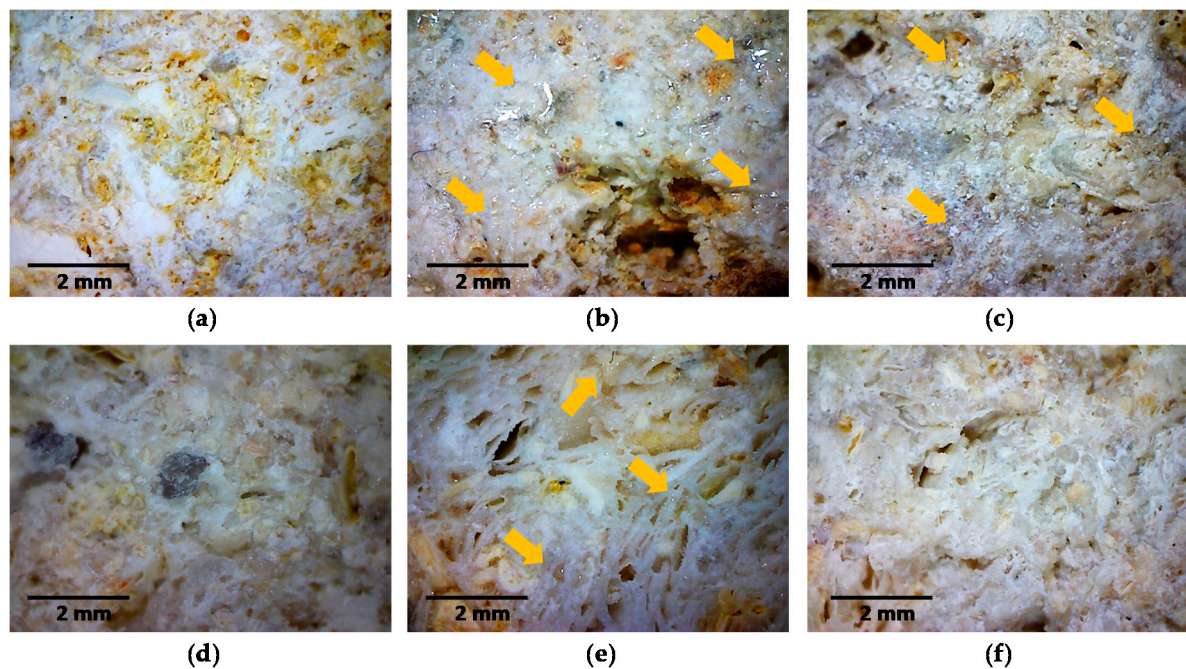


Figure 3. Images of the stone surfaces after treatment applications taken by handheld digital microscope at 40x magnification. Espera limestone: (a) untreated (b) SiO_2 NPs and (c) $\text{Ca(OH)}_2/\text{ZnO}$ NPs. Puerto de Santa María calcarenite: (d) untreated (e) SiO_2 NPs and (f) $\text{Ca(OH)}_2/\text{ZnO}$ NPs. Yellow narrows show little bright crystals in the stones treated with SiO_2 NPs and little white aggregates of calcium carbonate in the stones treated with $\text{Ca(OH)}_2/\text{ZnO}$ NPs.

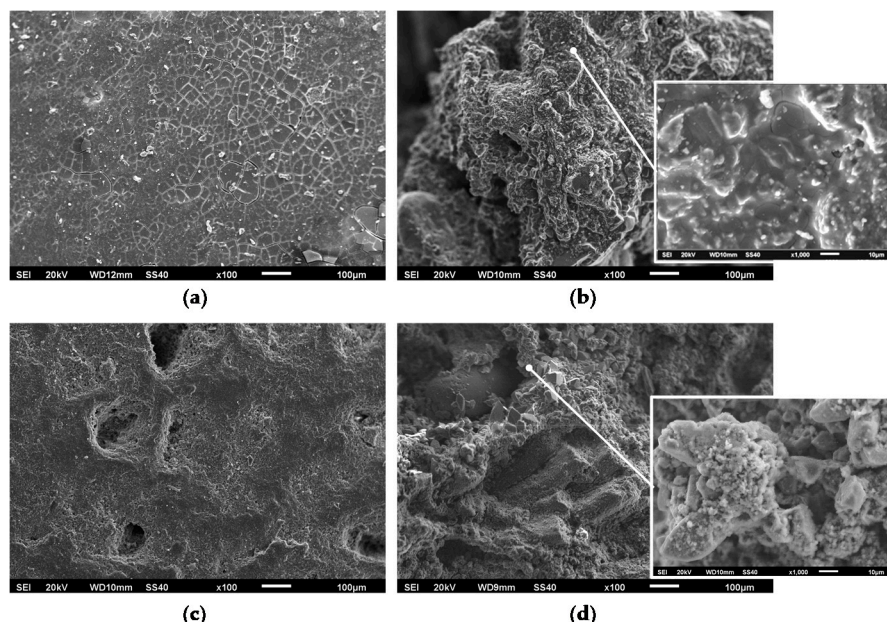


Figure 4. SEM images of samples treated with SiO_2 NPs: (a) Espera limestone and (b) Puerto de Santa María Calcarenite, and with $\text{Ca(OH)}_2/\text{ZnO}$ NPs: (c) Espera limestone and (d) Puerto de Santa María Calcarenite. Samples treated with SiO_2 NPs showed the formation of a silica layer on the stone surfaces (a,b), while on the other case the formation of calcium crystals can be observed at the highest magnification (d).

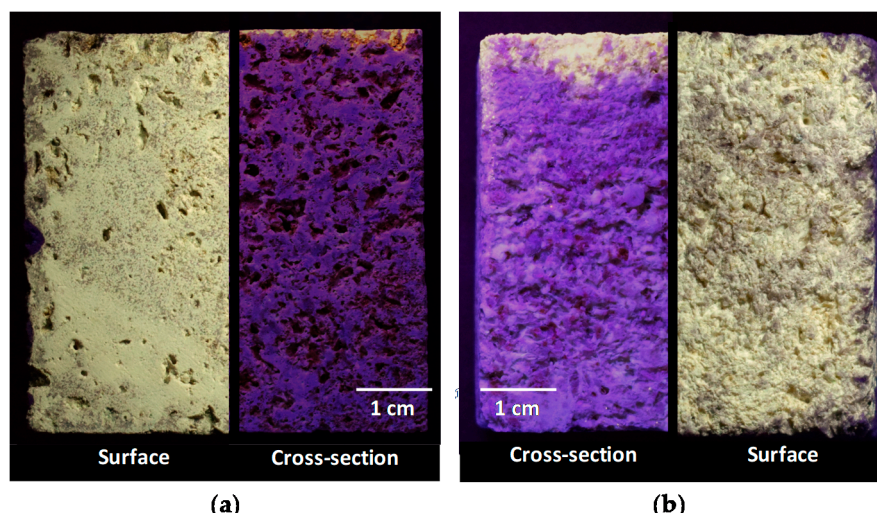


Figure 5. Images of the surface and the cross-section of (a) Espera limestone and (b) Puerto de Santa María calcarenite treated with $\text{Ca(OH)}_2/\text{ZnO}$ NPs under UV light. The presence of NPs on the surface makes discernible the treated areas, while in the cross-section NPs are used to measure the penetration depth of the consolidant.

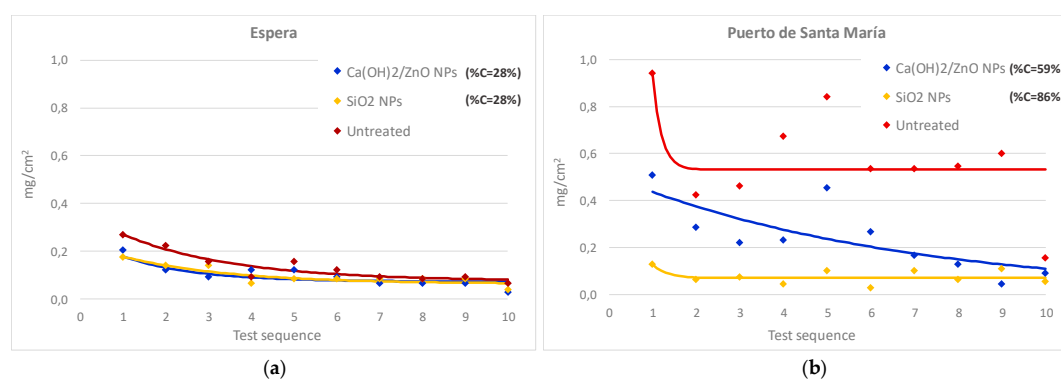


Figure 6. Nonlinear progression (line) and average mass removed (♦) from repeated peeling test carried out on (a) Espera limestone and (b) Puerto de Santa María calcarenite.

Table 1. Maximum and minimum of removed materials (mg/cm^2) in the peeling test sequence and standard deviation.

Stone	Treatment		Sequence									
			1	2	3	4	5	6	7	8	9	10
Espera	Untreated	MAX	0.39	0.30	0.19	0.17	0.28	0.19	0.22	0.14	0.11	0.14
		MIN	0.11	0.14	0.11	0.03	0.08	0.06	0.00	0.03	0.08	0.03
		SD	0.14	0.08	0.04	0.07	0.10	0.07	0.12	0.14	0.02	0.06
	SiO_2 NPs	MAX	0.22	0.19	0.28	0.11	0.22	0.17	0.19	0.17	0.14	0.06
		MIN	0.11	0.11	0.06	0.03	0.00	0.03	0.00	0.00	0.03	0.03
		SD	0.06	0.05	0.12	0.04	0.12	0.07	0.10	0.08	0.06	0.02
	$\text{Ca(OH)}_2/\text{ZnO}$ NPs	MAX	0.25	0.22	0.19	0.33	0.25	0.11	0.11	0.17	0.14	0.08
		MIN	0.14	0.03	0.03	0.00	0.03	0.08	0.00	0.00	0.00	0.00
		SD	0.06	0.12	0.09	0.18	0.12	0.02	0.06	0.09	0.07	0.05
Puerto de Santa María	Untreated	MAX	2.33	0.97	1.11	1.05	2.24	1.41	1.14	1.52	1.61	0.39
		MIN	0.14	0.06	0.11	0.25	0.11	0.08	0.19	0.03	0.17	0.00
		SD	1.20	0.48	0.56	0.40	1.22	0.76	0.52	0.85	0.87	0.20
	SiO_2 NPs	MAX	0.14	0.08	0.14	0.06	0.17	0.06	0.11	0.08	0.19	0.11
		MIN	0.11	0.06	0.03	0.03	0.03	0.00	0.08	0.06	0.03	0.00
		SD	0.02	0.02	0.07	0.02	0.07	0.03	0.02	0.02	0.08	0.06
	$\text{Ca(OH)}_2/\text{ZnO}$ NPs	MAX	0.58	0.39	0.30	0.28	0.61	0.47	0.22	0.22	0.06	0.14
		MIN	0.47	0.17	0.17	0.19	0.25	0.11	0.06	0.08	0.03	0.03
		SD	0.06	0.11	0.07	0.04	0.19	0.18	0.10	0.08	0.02	0.06

The best percentage of consolidation (%C) was achieved on Puerto de Santa María calcarenite treated by SiO₂ NPs (86%), while on Espera limestone, it was 28%. This parameter takes the disaggregation of the untreated stone as a reference and states the improvement in cohesion achieved by each treatment. The %C of the Ca(OH)₂/ZnO NPs was 28% for Espera stone and 59% for Puerto de Santa María.

Finally, the increment of propagation velocity (ΔV) showed a general improvement in consolidation of the treated stones. SiO₂ NPs achieved ΔV of 1.1 ± 0.1 Km/s for Puerto de Santa María calcarenite and 3.6 ± 2.0 km/s for Espera limestone. Nevertheless, the highest increments were obtained in the stone samples treated with Ca(OH)₂/ZnO NPs. The ΔV was 2.1 ± 1 Km/s in Puerto de Santa María calcarenite and 7.7 ± 4 Km/s in Espera limestone.

4. Discussion

Two consolidants based on nanoparticles were tested on two carbonate stones for the assessment of the basic protocol for restorers described in Section 2.3. The samples were dried during 20 days after application, specifically to favor the end of the carbonatation process on the samples treated with Ca(OH)₂ NPs. This time follows the criteria of previous studies about the end of the carbonatation process using Raman spectroscopy [38].

In the samples treated with SiO₂ NPs, any color change was perceptible with ΔE^* lower than 3. This was due to the absence of color in the product, although a rise in the brightness of the treated stone surfaces could be observed. The SEM images confirmed the formation of a continuous layer of silica, in agreement with previous studies [34,52]. In the case of the less porous stone (Espera), the layer was more compact, covering all of the stone surface. This layer appeared cracked, with a behavior similar to consolidants based on alkoxy-silanes [22]. In Puerto de Santa María calcarenite, the silica layer covered the silica grains, although the highest pores remained open, as can be seen in Figure 4b. This treatment modified the hydric properties of the stone, especially in the case of the lithotype with less pore size and porosity (Espera).

The aesthetical changes caused by Ca(OH)₂/ZnO NPs could be admissible in the worst case (Espera) because of the ΔE^* being close to 5 (Figure 2). Some authors [50,51] consider that values less than 10 are also acceptable for cultural heritage although the color changes are slightly detected by the naked eye. The average measurement plus the standard deviation in the worst case did not exceed this threshold ($\Delta E^* < 10$). Nevertheless, our recommendation is to apply this treatment in areas of monuments with lower visual impact.

Only small macroscopic aggregates could be observed on the lowest pore stone surfaces at high magnifications without generating the homogenous white haze discussed by other authors [31,53]. Any remarkable modification of the stone surface was observed in SEM images. The magnification in Figure 4d shows microcrystals of calcium carbonate covering the mineral grains. According to Rodríguez-Navarro et al. [54], the absence of alcohol could favor the conversion of the portlandite (calcium hydroxide) into stable calcite. Further studies must be carried out to confirm this.

The presence of ZnO QDs under UV light allows us to discern easily between treated and untreated areas and measures the penetration depth of Ca(OH)₂/ZnO NPs. The ZnO QDs synthesized have the highest fluorescence under UV light at 256 nm. This QDs have a long-term environmental stability [55] and their exposition under solar radiation [56] is not enough to favor fluorescence as was observed during the experiments. The fluorescence of ZnO QDs is an important advantage, particularly when the consolidants have similar elemental composition than the stone, i.e., Silicon or Calcium, and the use of common techniques, as microanalysis by energy dispersive X-ray (EDX), is not recommended. The phenolphthalein test is a recurrent assay to measure the penetration depth of treatments based on Ca(OH)₂ NPs [57]. The phenolphthalein becomes purple at a pH higher than 9.8, before the conversion of the Ca(OH)₂ into CaCO₃, as when CaCO₃ precipitates the pH lowers under 8.2. Other markers such as those which use colored solvents [58] or nanoparticles with different elemental composition [59] do not measure the real penetration of the consolidant NPs because they do not take into consideration the

retardation factor of the nanoparticles and that nanoparticles with different composition do not have the same behavior, i.e., diameter hydrodynamic or colloidal stability. In our case, a previous study guaranteed the formation of a nanocomposite compound by $\text{Ca}(\text{OH})_2$ NPs and ZnO QDs, and how these quantum dots remain together with the new carbonate crystals without interfering in their formation [17]. The penetration achieved by the treatment is higher in the stone with higher pore size. The implication of the porosity in the penetration depth of the nanolimes has been studied by other authors [14,60], and has been confirmed in the present study. In fact, the penetration depth achieved in Puerto de Santa María calcarenite (0.8 cm) is greater than that achieved by other authors with similar application techniques (brushing) [60]. In the case of the application of the nanolimes by capillarity absorption, Borsoi et al. [35] achieved a penetration depth of 2–4 cm, but this method is not applicable in immovable artworks.

The surface cohesion of the silica-based treatment was higher than that on the calcium-based treatment. In the sequence of the test displayed in Figure 6b, the application of SiO_2 NPs stabilized the released material since the second sequence, but in the case of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs, although the nonlinear progression shows a negative trend, the samples release material until the seventh sequence, when the amount of removed material becomes more stable. This result agrees with Zornoza-Indart et al. [34]. The greater surface cohesion of SiO_2 NPs may be due to the accumulation of the treatment on the surface and the formation of the silica layer. However, taking into account the percentages of consolidation, the efficacy of the $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs was indeed more outstanding because this treatment was applied in a more diluted solution, as the dry residue content of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs (0.25%) was considerably lower than the SiO_2 NPs (15%). This difference is caused by the use of products in the same condition that will be employed by restorers, following manufacture's recommendations. At the same concentration of dry residue, the consolidation effect of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs should increase.

The ultrasound propagation speed increased after the application of consolidants, since the voids have been filled. This increment is greater in the stone with less pore size and porosity (Espera limestone). Regarding the treatment, the best results were achieved in the samples treated with $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs. It may be due to a more homogeneous distribution of the treatment into the stone [14].

Taking into consideration all the results, the treatment based on $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs is the best option for the consolidation of both studied stones because the color changes could be admissible for cultural heritage (ΔE^* close to 5), not modify the physical properties and consolidate the stone in-depth, without generating surface layer. These results agree with the recommendation for consolidant product from COREMANS project [3] and UNE-EN 41810/2017 [7]. The treatment based on SiO_2 NPs should be rejected because it favors the formation of a silica layer on the stone surface that may modify the physical properties of the stone without penetrating through the stone and the consolidation is high on surface stone but may not allow the cohesion in-depth of degraded areas.

5. Conclusions

A new basic protocol for decision making about the best consolidant for a restoration has been designed and tested. This protocol has been designed especially for restorers using techniques that they usually employ, so it is easy, low-cost, more feasible and sustainable. The colorimetry is the most useful technique to detect changes in the aesthetical value of the stones, while the use of a handheld digital microscope makes macroscopic modifications on the stone surface perceptible. The effectiveness must be measured both on the surface level and in-depth. The use of the peeling test and a portable ultrasound is an easy methodology to study the effectiveness of the treatments. The comparison between the results achieved by the treatments allows us to order from the most advantage treatment to the treatments that should be avoided. In this way, the decision making is based on experimental results and not only on the expertise of the restorers or the datasheets of the products.

The protocol has been tested studying the best consolidant, between the two proposed (SiO_2 NPs and $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs), for two carbonate stones. Considering the results achieved, the treatments

based on $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs are more recommended for these types of stone, because it does not change the aesthetical and physical properties of the material. This treatment allows the penetration depth to be measured easily and shows the best results in the ultrasound test. Nevertheless, SiO_2 NPs achieved the best results in the peeling test. This was due to the concentration of product used in this research, employing the same amount of product following the datasheet's recommendations, and not the same dry residue. In the case of $\text{Ca}(\text{OH})_2/\text{ZnO}$ NPs, the quantity of product should be adjusted to achieve the highest surface cohesion.

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