1 **Carbonation acceleration of calcium hydroxide nanoparticles**
2 **Induced by yeast fermentation**
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16 **Abstract**
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18 Carbonation of Ca(OH)₂ nanoparticles and consolidation of limestone are accelerated
19 by high humidity and a yeast fermentation system that supplies a saturated
20 atmosphere on CO₂, H₂O vapor and ethanol during 28 days. Nanoparticles were
21 analyzed by X-ray diffraction and differential thermal analyses with thermogravimetry.
22 Spectrophotometry, scanning electron microscopy analyses, hydric and mechanical
23 tests were also performed in stones specimens. Samples exposed to the yeast
24 environment achieve 100% relative CaCO₃ yield, whereas at high humidity but without
25 the yeast and under laboratory environment, relative yields of 95% CaCO₃ and 15%
26 CaCO₃ are respectively reached, with white crusts and glazing left on the stone
27 surfaces when the nanoparticles are applied at a concentration of 25g/l.
28
29 The largest increase in the drilling resistance and surface hardness values with slight
30 increase in the capillarity absorption and desorption coefficients and with lesser stone
31 color changes are produced at a concentration of 5g/l, in the yeast system
32 environment, in stone specimens initially with bimodal pore size distributions, more
33 amounts of pores with diameters between 0.1 and 1µm, higher open porosity values
34 and faster capillary coefficients.
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36 An inexpensive and reliable method based on water and yeast-sugar solution is
37 presented to speed up carbonation of nanoparticles used as a consolidating product to
38 improve the mechanical properties of decayed limestone from archaeological and
39 architectural heritage.
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41 **Keywords:** *carbonation; yeast fermentation; Ca(OH)₂ nanoparticles; environmental*
42 *conditions; humidity; CO₂; limestone; consolidation*
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1 Introduction

When calcium hydroxide (Ca(OH)_2) is exposed to atmospheric carbon dioxide (CO_2) under moist conditions, it reacts and converts into calcium carbonate (CaCO_3) releasing water as a result of carbonation. This reaction takes place in biomineralization, medical and pharmacological processes [1,2], in concrete and mortars [3-5] or as a product binder to improve the cohesion of highly porous materials [6,7]. Achieving its stability is very important in architecture and decorative arts [8,9].

An approach to improve conservative treatments based on the use of inorganic compounds was to enhance and stimulate the growth of new calcite crystals inside the porous system using biomineralization mechanisms [10]. Bacteria have been used to create microbial deposited carbonate layers on ornamental stones. After the first patent using microbial induced carbonate precipitation for the protection of ornamental stone in the 90s, called Calcite Bioconcept technique, different approaches, bacterial strains and methods, have been studied to solve the limitations of the technique. Even though bacteria induced carbonate mineralization is considered a promising consolidation treatment, compatible with carbonate stones and lime-based mortars and cements, is not frequently used on-site by restorers. This is because it is a more complex application process than traditional products, the incompatibility with previous or subsequent treatments, their expensive price, need of knowledge on the bacteria carbonation process and the interaction with the substrate with possible appearance of secondary effects together with the lack of awareness on the long-term behavior [11-13].

Nanoscience deals with a large diversity of research fields and applications considering that most of the properties are modified or improved by effect of the reduction in size of nanomaterials. The use of nanoparticles is funded by the fact that the specific surface area of a solid increases exponentially with the decrease of its volume, having a much superior surface area available to react [14]. Colloidal nanoparticles are used for cleaning, consolidation, and deacidification of materials from cultural heritage [15]. Calcium hydroxide (Ca(OH)_2) nanoparticles have been applied to improve the petrophysical properties of lime mortars and carbonate stones, acting as a cementing product to avoid decohesion of construction and building materials [16,17] or to consolidate archaeological wall paintings [18].

There are known factors and conditions that control the precipitation of CaCO_3 polymorphs, such as pH, temperature, saturation, conductivity or impurities and additives that determine the mineral precipitation and phase transformations together

with morphological and structural variations. The variables that play a role in the carbonation of $\text{Ca}(\text{OH})_2$ nanoparticles, and the resulting mineral phases, are essential for the final physical properties in a short- and longer- term [16]. It has been found that these colloidal nano-dispersions are highly conditioned by the relative humidity (RH) and exposure times [7,19] in the environment. These conditions directly influence the speed of carbonation and the precipitation of CaCO_3 polymorphs, as vaterite and aragonite, which are less stable than calcite [20,21]. The alcohol present in the environment also influences the stabilization of metastable CaCO_3 polymorphic phases, especially at high RH, where the rate of alcohol evaporation is slower, giving rise to higher content of metastable phases, such as vaterite and aragonite [20]. Moisture content and relative humidity during carbonation is a major factor in determining the final mineral phases and pore structure of the resulting matrix in stone, mortars or cement materials [16, 17], where the formation of nano-droplets of water is necessary for the gaseous CO_2 to react with $\text{Ca}(\text{OH})_2$ [22]. Due to the adsorption of multilayers of water onto the solid $\text{Ca}(\text{OH})_2$ [23], high RH values (>75%) speed up the carbonation process and the consolidation of lime mortars and carbonate stones [7,16, 17, 20, 21].

Besides, even though CO_2 is another key factor involved in the carbonation reaction, its concentration and registration is not often considered in the studies of carbonation of $\text{Ca}(\text{OH})_2$ nanoparticles. The influence of CO_2 concentration on the acceleration of carbonation process of $\text{Ca}(\text{OH})_2$ has been extensively debated. Even though, Van Balen and Van Gemert [24] concluded that lime mortar carbonation depends on the presence of water and occurs very quickly especially in a saturated CO_2 atmosphere, Van Balen [25] later shows that the reaction speed is not dependent upon the CO_2 concentration, within the limits he tested. Dheilly et al. [26] demonstrate the importance of CO_2 concentration and RH during carbonation process. These authors observed how a lime paste displays a rapid and complete reaction in a carbonic atmosphere, while in a low CO_2 environment carbonation takes twice as long. Cultrone et al. [5], also demonstrate that high CO_2 concentrations favor a faster and more complete carbonation process, with 8 days being enough to convert portlandite ($\text{Ca}(\text{OH})_2$) into 90wt.% calcite (CaCO_3) of lime-based mortars. They showed that under natural conditions, carbonation is much slower and similar levels were not reached for 6 months, suggesting that the carbonation process is influenced by the amount of CO_2 . Recently, Visser [27] showed that a change in CO_2 concentration does not change the carbonation process and that the amount of material that can carbonate can be determined on the basis of the amount of calcium in the unreacted material.

Nevertheless, Cizer et al. [28] show that carbonation process is kinetically favored under high RH and high $p\text{CO}_2$ where supersaturation plays a critical role on the nucleation density and size of CaCO_3 crystals.

The control the CO_2 concentration during carbonation process of lime based products, for structures and building materials in the construction field, on-site under natural conditions is a difficult task. It is hard to obtain CO_2 sources that are reliable, durable, cheap and easy to manage [29]. Saitoh et al. [30] developed an easy and cheap method to produce CO_2 for diseases purposes by using a yeast-sugar solution in plastic bottles. Under anaerobic conditions, yeast (synonym for strains of *Saccharomyces cerevisiae* or baker's yeast) converts sugar into CO_2 and ethanol [31-33].

The aim of this research is to demonstrate the acceleration of carbonation of $\text{Ca}(\text{OH})_2$ nanoparticles by a yeast fermentation system that supplies a saturated atmosphere on CO_2 , H_2O vapor and ethanol, presenting an inexpensive and reliable method based on water and yeast-sugar solution to improve the consolidation of decayed limestone.

2 Materials and methods

2.1 $\text{Ca}(\text{OH})_2$ nanoparticles

Two nanometric $\text{Ca}(\text{OH})_2$ colloidal dispersions employed as commercial consolidating products were used in this study. Nanorestore®, developed at the University of Florence (CSGI Consortium [34]), are hexagonal plate-like $\text{Ca}(\text{OH})_2$ nanocrystals (<100 nm in size [20]) with a concentration of 5g/l in isopropyl alcohol. CaLoSil® (Ziegenbald [35]), was previously characterized [36] and consists of disaggregated hexagonal nanoparticles with particle size from 60 to 130 nm. In this research we have used a concentration of 25 g/l. Ultrasonic dispersion was performed introducing the products during 5 min in an ultrasonic bath (Selecta model Ultrasounds-H). Both colloidal dispersions were deposited on laboratory plastic dishes to leave them being absorbed by capillarity by each stone specimen while these were exposed to three different environmental conditions. Part of the concentration at 5 g/l that was not absorbed by the specimens and remained on the dishes, was used to carry out X-ray diffraction analyses and differential thermal analyses and thermogravimetry.

2.2 Stone specimens

Fresh stone detrital limestone samples, commercially called Leccese Stone (from Southern Italy), and Bateig Stone (from Alicante, Eastern Spain), typically used in

historical and present-day buildings, were chosen for the application of Ca(OH)_2 nanoparticles.

The Lecce Stone, also called Lecce Stone, selected for this study is a fine-grained bio calcarenite, with a characteristic pale-yellow color, mainly composed of micritic fraction (CaCO_3 crystals $<5 \mu\text{m}$), mixed with fine clay minerals and poor cryptocrystalline calcite cement; it contains fine microfossil fragments, grains of glauconite, sporadic quartz grains and phosphate nodules. The total open porosity is around 30-40% (with pore radius mainly below $5 \mu\text{m}$). The rock has around 80% of CaCO_3 and the insoluble residue is essentially made of clay minerals and glauconite [37,38]. The Bateig stone selected for this study, also called Novelda Stone, is the commercial variety named Diamante (Diamond), a fine-grained bio calcarenite, with a white-pale-yellow color, 75-80% of calcite (CaCO_3), 5-10% dolomite $\text{CaMg}(\text{CO}_3)_2$, 5-10% quartz and 5-10% phyllosilicates [39]. It contains fossils, such as foraminifers and bryozoan, mollusk and echinoderm traces, as well as fragmentary quartz in different amounts. There is hardly any cementing material (under 10%) and cement is constituted by sparite (CaCO_3 crystals $>5 \mu\text{m}$) and to smaller extent silica (SiO_2). The total open porosity is circa 22% [40] with pore radius mainly below $5 \mu\text{m}$.

Two specimens for each stone type (Lecce (L) and Bateig (B), with the two selected product's concentration (5g/l and 25 g/l), were exposed to three different environmental conditions, ventilate laboratory, closed container with high humidity and yeast fermentation container with high humidity. A total of 24 cubic specimens $5 \times 5 \times 5 \text{ cm}$ were placed in individual laboratory plastic dishes with 32 ml and 20 ml of both colloidal dispersions (quantity related to the capillary absorption of Lecce and Bateig stone, respectively) to leave them being absorbed by capillarity through the porosity of each stone specimen. Control specimens were used as a blank (with no nanoparticles application) for each stone type, to evaluate the differences of mechanical properties of the stones with and without nanoparticles exposed to the three environments during 28 days.

2.3 Environmental conditions

An air conditioning system inside the laboratory room stabilized the temperature (T) at $18 \pm 1^\circ\text{C}$. The CO_2 concentration inside the room and inside the container connected to the yeast system was registered by a CO_2 detector (Telaire® 7001, Goleta, CA, USA) connected to a Hobo® Data Logger to register CO_2 ($0 - 10,000 \pm 1 \text{ ppm}$ on display and $0 - 2,500 \text{ ppm}$ on data logger, with accuracy of $\pm 50 \text{ ppm}$ or $\pm 5\%$ of reading up to 5,000 ppm), T range $0 - 50 \pm 1^\circ\text{C}$, and relative humidity (RH) range 0-95%. Environmental

control devices, ibuttons® model DS1923-F5 were introduced in each chamber and placed in the laboratory room to measure T and RH during the 28 days experiment, using the software OneWireViewer version 3.04.

The first group of samples were exposed to ventilate laboratory room conditions, 449 ± 34 ppm CO₂, 18 ± 1 °C and 59 ± 11 % RH. Water was placed underneath the samples to increase a little bit the regular humidity of the room environment (45 ± 20 % RH). The second group of samples was introduced into a closed desiccator, used as a container. The equilibrium relative humidity (RHeq) of supersaturated MgSO₄·7H₂O salt solution, placed at the bottom underneath the samples, was used to keep the humidity constant, 90% RH at 20°C. The final average conditions registered by the environmental sensors were 449 ± 34 ppm CO₂ (initial room air concentration), 18 ± 1 °C and 87 ± 1 % RH. Finally, a third group of samples were exposed to a yeast fermentation system connected to a closed container with a supersaturated salt solution of MgSO₄·7H₂O at the bottom. The final average environmental conditions registered were above 2500 ppm CO₂, T 20 ± 1 °C and 87 ± 7 % RH. To avoid the contact of the samples with the water or magnesium sulfate salt solutions, the plastic dishes and stone specimens were set on a grille placed several centimeters above the bottom (Fig.1).

The yeast fermentation system was prepared using as a reference the data published by Smallegange et al [29]. These authors calculated different carbon dioxide flow rates (ml/min) produced by different yeast-sugar solutions. One of the mixtures used by them to produce CO₂ was 7g of yeast (Y) + 100 g of sugar (S) + 1L of water (W) with a rate CO₂ production of 3.5 ± 2.7 ml/min. In the present experimental work we use the proportion 21g (Y) + 150g (S) + 1L (W), reaching 2,485ppm CO₂ in 2 hours. This CO₂ value is the maximum value registered by the data logger of the probe; however, on display the value was much higher, showing values above 5,000 ppm. The value recorded by the data logger of 2,500 ppm, was taken as a reference of the minimum amount of CO₂ produced by the yeast fermentation in a closed environment. A flask filled with the prepared mixture was connected to a closed desiccator, used as a container, through a lateral tube to supply the CO₂ produced during the fermentation of the yeast. The mixture was renewed 9 times, changing it every 3 days until the end of the 28 days experiment, to ensure that the amount of CO₂ inside the chamber were always above 2,500 ppm.

2.4 Analyses of Ca(OH)₂ nanoparticles

The samples of $\text{Ca}(\text{OH})_2$ nanoparticles at 5 g/l concentration were analyzed every 7 days during 28 days, using X-ray diffraction (XRD) to determine the mineralogy of the different CaCO_3 polymorphs precipitated during the carbonation reactions. Differential thermal analyses and thermogravimetry (DTA-TG), was also carried out after the first week (7days) and at the end of the last week (28 days) of the experiment, in order to quantify the $\text{Ca}(\text{OH})_2$ and CaCO_3 relative proportions in the samples for each environment.

X-ray diffraction (XRD) was performed with a PHILIPS PW 1752 powder diffractometer with $\text{CuK}\alpha$ radiation. The samples were deposited in zero-background Si sample holders. XRD patterns were obtained by step scanning from 2° to $68^\circ 2\theta$ with a scan step size of 0.02° and $2^\circ/\text{min}$ in a continuous mode. The working conditions were 40 kV and 30 mA. The identification of the mineral phases was performed using the Bruker AXS DiffracPlus EVA software.

Differential thermal analyses and thermogravimetry (DTA-TG), was performed using a SDT Q600, TA Instruments analyzer, at a heating rate of $10^\circ\text{C}/\text{min}$ over a range of 20 - 1000°C . Approximately, samples of 10 ± 1 mg were placed in alumina sample holders and analyzed in N_2 atmosphere. The total mass loss (%) during the thermal decomposition of the samples was registered by the thermogravimetric analyses (TG). The first derivative of the TG data (dTG curve) indicates the starting and ending temperatures of mass loss during the TG analysis. So, the carbonation degree (yield) has been calculated by means of the relative total proportion of $\text{Ca}(\text{OH})_2$ vs. CaCO_3 present in the samples. These were recalculated for each temperature interval and corresponding mass loss occurred during the dehydroxylation (loss of OH groups) and decarboxylation (loss of CO_2) processes. DTA curves indicate the range of temperatures and maximum rates where these endothermic reactions take place.

2.5 Analyses and testing of stone samples

Spectrophotometry was used to measure the chromatic parameters before and after the consolidation. Scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS) analyses were performed to observe the surface morphology of the stone samples. The elemental composition of some selected components was qualitatively determined by means of EDS microanalyses. Mercury intrusion porosimetry (MIP) was used to assess sample pore structure, i.e., total porosity (P) and pore size distribution (PSD) of the blank stone specimens. Hydric properties (water absorption by capillarity and water desorption) and mechanical properties (surface hardness and drilling resistance) were measured in control specimens for each type of

stone used as blanks, and in all the specimens with the Ca(OH)_2 nanoparticles after the exposure during 28 days to the three different environmental conditions. Water absorption under vacuum was performed in the blank and treated specimens to determine changes on apparent density, real density, open porosity, and water saturation.

Spectrophotometry was performed with a spectrophotometer MINOLTA CM-700d using the CieLab color space; Standard illuminant was D65 and observer angle, 10° . 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^* provided as a result of the formula $\Delta C^* = (\Delta a^*)^2 + (\Delta b^*)^2)^{1/2}$, 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 [41], brightness measured according to ISO 2470-2 [42] and reflectance.

The surface of stone blanks, with no nanoparticles, and the surface of the stone specimens with nanoparticles at the end of the experiment, were analyzed with an scanning electron microscope JEOL JSM 6400 and the analyses conditions were 0.2–40 kV accelerating voltage, 6×10^{-1} A current, 10^{-5} Torr vacuum, 35°A resolution, 8 mm and 35 kV working distance and 20 kV accelerating voltage for image acquisition. The spectrometer (EDS) was a microanalyzer Oxford instruments analytical Inca with a 133 eV–5.39 kV nominal resolution. Gold-sputtered samples were studied in secondary electrons mode to observe the surface morphology and in retro-dispersed electrons mode to analyze the chemical elementary composition.

Mercury intrusion porosimetry (MIP) readings were taken on three samples of each stone type, at pore diameters of 0.005–400 μm under measuring conditions ranging from atmospheric pressure to 60,000 psia (228 MPa) on a Micromeritics Autopore IV 9500 MIP. Water absorption under vacuum was performed in the blank and treated specimens to determine changes on apparent density, real density, open porosity and to quantify the amount of water absorbed by the specimens once they reach saturation as described in standard test UNE-EN 1936:2007 [43]. Water absorption by capillarity and water desorption was carried out to calculate the capillary coefficients through the stone according to the standard test UNE-EN 15801:2010 using $\text{g}/(\text{m}^2 \cdot \text{s}^{1/2})$ instead of $\text{kg}/(\text{m}^2 \cdot \text{s}^{1/2})$ [44].

Surface hardness was measured by means of a metal hardness tester Equotip 3 (Proceq), standardized according to the standard test ASTM A956-12 [45]. An impact device “D” (tungsten carbide ball, 3mm diameter and 5.45 g weight) 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/mm² and with automatic correction for impact direction. Fifty measurements were performed on each blank specimen, and ten measurements were performed on each specimen after treatment, over the nanoparticles absorption face. Drilling resistance analyses were carried out with a drilling Resistance Measurement System, DRMS Cordless by Sint Technology (Italy). The drilling conditions were 15mm/min penetration speed for both types of stones and 400 rpm rotation speed for Bateig Stone and 200 rpm rotation speed for Lecce Stone. Ten measurements with different drilling conditions, up to 25 mm penetration depth, were performed on the blank specimens, to select the most appropriate and homogeneous drilling conditions with less standard deviation. Then, three measurements were done through the face surface that was directly in touch with the colloidal dispersion.

3 Results and discussion

3.1 Characterization of nanoparticles

3.1.1 Samples exposed to ventilate laboratory room conditions

The XRD results show that after 7 and 14 days, portlandite (Ca(OH)₂) is the main mineral phase. Diffractograms display scarce peaks of calcite (C), only visible after 7 days (Fig.2a). After 21 days, the diffractogram pattern shows signs of amorphization with the broadening of portlandite (P) peaks that are not well defined. After 28 days, the crystallinity of portlandite seems to improve. However, there are only a few peaks of calcite. These samples barely carbonated, displaying almost the total amount of initial portlandite nanoparticles after 28 days under this environmental condition.

The TG analysis from 20°C up to 1000°C indicates a total mass loss of 27.46 % after 7 days (Fig.2b). DTA analysis shows three main endothermic peaks, which correspond with the loss of adsorbed H₂O with a maximum reaction rate at 140°C, the loss of OH groups from portlandite dehydroxylation at 436°C and loss of CO₂ from calcite decomposition at 682°C. The TG and dTG curves indicate that the mass loss during dehydroxylation of portlandite (76%) occurs between 350° and 455°C, whereas decarboxylation of calcite (24%) takes place between 516° and 722°C. After 28 days (Fig.2c), there is a total mass loss of 29.94 % and two endothermic peaks with maximum rates at 429°C and 648°C, which correspond to portlandite and calcite, respectively. From 307°C up to 450°C there is a mass loss of 85% from

dehydroxylation of portlandite vs. 15% of mass loss from decarboxylation of calcite, that takes place between 525° and 720°C.

3.1.2 Samples exposed into closed containers with high humidity

The XRD results show that after 7 days, calcite (C) and portlandite (P) are the main mineral phases present in the sample (Fig.3a). Some small peaks could correspond to ikaite phase ($\text{CaCO}_3 \cdot 6\text{H}_2\text{O}$) that disappears in the diffractogram obtained after 14 days. After 2 weeks, there are some aragonite (A) peaks, together with portlandite and calcite. After 21 days, the peaks of the diffractogram are broadened and not so well defined, showing signs of amorphization. Besides aragonite, portlandite and calcite, there are some vaterite (V) peaks that disappear after 28 days. After one month, the samples almost reached the total carbonation since there are lesser peaks of portlandite and many more of aragonite and calcite showing higher intensities than before.

The DTA analysis shows three main endothermic peaks, which correspond with the loss of adsorbed H_2O with a maximum reaction rate at 133°C, the loss of OH groups from portlandite at 429°C and loss of CO_2 from calcite at 709°C, after 7 days. The TG curve indicates a total mass loss of 36.24 % (Fig.3b). The TG and dTG curves indicate that the mass loss during dehydroxylation of portlandite occurs between 359° and 466°C, which correspond to 31%, vs. 69% of mass loss due to decarboxylation of calcite, between 513° and 732°C. After 28 days (Fig.3c), there is a total mass loss of 42.84 % and three endothermic peaks with maximum rates at 130°C, 399°C and 730°C, which correspond to adsorbed water, portlandite, and calcium carbonates, respectively. From 350°C up to 420°C there is a mass loss of 5% from dehydroxylation of portlandite, vs. 95% of mass loss from decarboxylation of calcium carbonates that takes place between 530° and 756°C. In both dTG curves, 7 and 28 days, there is a small bump between 150° and 300°C (Fig.3b) and between 180° and 347°C (Fig.3c) that corresponds to 3% of the total amount of 95% considered as calcium carbonates polymorphs.

3.1.3 Samples exposed to a yeast fermentation system with high humidity

The XRD results show that after 7 days of experiment, there is presence of portlandite (P) and three calcium carbonate polymorphs, vaterite (V), aragonite (A) and calcite (C) (Fig. 4a). Portlandite remains until the end of the second week of the experiment (14 days), while the number of peaks of vaterite, aragonite and calcite increase. After 21 days, there is no presence of portlandite, and the peaks of vaterite and calcite

decrease, whereas the peaks of aragonite increase. After 28 days, there is no portlandite or vaterite, and the number and intensity of aragonite and calcite peaks seems to decrease.

The DTA analysis shows three main endothermic peaks, which correspond with the loss of adsorbed H₂O with a maximum reaction rate at 140°C, the loss of OH groups from portlandite at 440°C and loss of CO₂ from calcium carbonates at 733°C, after 7 days of exposure. The TG curve indicates a total mass loss of 40.06 % (Fig.4b). The TG and dTG curves indicate that the mass loss during dehydroxylation of portlandite occurs between 374° and 519°C, which correspond to 13%, vs. 87% of mass loss due to decarboxylation of calcium carbonates, between 519° and 755°C. After 28 days (Fig.4c), there is a total mass loss of 45.84 % and just two endothermic peaks with maximum rates at 140°C, and 733°C, which correspond to adsorbed water and calcium carbonates, respectively. From 371°C up to 429°C there is a 2% mass loss that may correspond to aragonite-calcite phase transition, since there is no endothermic peak by dehydroxylation of portlandite. Between 516° and 754°C there is a mass loss of 98% from decarboxylation of calcium carbonates.

3.2 Interpretation of characterization of nanoparticles

From the XRD and DTA-TG results it can be clearly note that the yeast fermentation system is the environment where the carbonation of Ca(OH)₂ is faster compared to the other environments, reaching 100% CaCO₃ yield after 14 days. By the contrary, the environment with the slowest carbonation rate is the one with ventilate laboratory room conditions. In this latter case after 14 days, only portlandite Ca(OH)₂ is present (which corresponds with the original composition of the nanoparticles) in spite of few small calcite peaks detected after 7 days exposure (Fig.2a). After 21 days, some calcite peaks show up and portlandite peaks are broadened, like showing signs of amorphization. This was previously observed when similar experiments were done under a closed system with low RH conditions (33%RH), where the poor crystallinity and the beginning of an amorphization process or loss of crystallinity of portlandite nanoparticles, together with the presence of amorphous calcium carbonate (ACC) was studied [21,36]. Under these conditions, there is a reduction in the size of the unit cells, where the fast evaporation of the solvent (2-propanol) gives rise to smaller particles with low crystallinity. The XRD data after 28 days reveals a better definition of the maximum intensity peaks associated to portlandite and calcite, with no precipitation of other CaCO₃ polymorphs. However, by DTA-TG analyses the proportion of portlandite seems to increase while the amount of calcite decreases, which is a rare behavior. The

pseudomorphic replacement of Ca(OH)_2 particles by calcium alkoxides, which seem to be poorly crystalline [46] together with ACC formation observed by SEM, could explain this behavior and the signs of amorphization observed at 21 days.

At very high humidity (90% RH), calcite nucleation occurs at a very fast rate, because high RH favors great concentration of structural defects. The presence of water around the surface favors the introduction of point defects, enlarging the dislocation network and generating other defects [47]. This allows speed up the carbonation reaction. The high disorder degree contributes to the fast phase transformation from metastable vaterite and aragonite to stable calcite [21]. However, the alcohol present in the environment influences the stabilization of metastable CaCO_3 polymorphic phases, especially at high RH, where the rate of alcohol evaporation is slower, giving rise to higher content of metastable phases, such as vaterite and aragonite [20]. Chen et al. [48], obtained vaterite with traces of aragonite in a solution predominantly constituted by ethanol, and pure aragonite when water predominated. In our closed system with high RH (Fig.3a), vaterite only shows up after 21 days, and aragonite from 14 up to 28 days. Higher amount of vaterite, from 7 up to 21 days, and aragonite from 7 up to 28 days, is obtained when nanoparticles are exposed to the yeast system environment (Fig.4a). In this latter case, there is a larger amount of alcohol that comes from the nanoparticle's product dispersion (2-propanol) plus the ethanol released from the yeast fermentation.

Ethanol, isopropanol and diethylene glycol additives influence the morphology of the formed vaterite crystals and stabilize this mineral phase by preventing the transformation to calcite [49]. This could explain the worst definition of the maximum intensity peaks associated to calcite at 21 days in the closed environment (Fig.3a), and at 21 and 28 days in the yeast system (Fig.4a). Furthermore, the formation of ACC on the faces of portlandite crystals hinders their further dissolution and the eventual precipitation of crystalline calcite [50]. Once carbonation is completed, further exposure to air or CO_2 atmosphere will lead to the dissolution of newly formed CaCO_3 in order to neutralize the pore solution [28]. It is interesting to note that in this yeast system environment there is an increase of 2°C (up to $20 \pm 1^\circ\text{C}$), due to the yeast fermentation process, since the outdoor laboratory temperature condition was set up at $18 \pm 1^\circ\text{C}$, which remains constant in the closed and open environments. Even though calcite precipitation rates and total mineral precipitation increase with temperature, these fall very quickly as calcite precipitates, being the proportion of calcite markedly greater in a longer term in environments with lower temperatures [4].

The abundance of metastable polymorphs (vaterite and aragonite) in both humid systems can be related to an excess of alcohol in the environment (even higher in the case of the yeast environment). Mono ethylene glycol also prolongs the transformation time of metastable polymorphs by delaying the growth rate of more stable polymorphs (calcite) [51]. Local fluctuations in the water/alcohol ratio also significantly affect the precipitation/dissolution of anhydrous and hydrated polymorphs. Changes in lattice parameters and particle size with exposure times, are related to surface tension fluctuations, release of residual water and changes in the crystallinity of the particles during carbonation, leading to differences in the nucleation and stability of each polymorph [21].

Rodriguez Navarro et al. [46] by combining FTIR and micro-Raman analyses found the formation of calcium alkoxides ((Ca(OR)₂) due to the reaction of ethanol and 2-propanol with Ca(OH)₂ particles. The hydrolysis of alkoxides in a humid environment speeds up the carbonation process, increases the CaCO₃ yield and favors the formation of vaterite. It seems that these alkoxides are poorly crystalline or amorphous, since these were undetectable under XRD. The yield depends on the reactivity of Ca(OH)₂ particles (surface area and lattice defects) and exposure time to the alcohol. According to these authors, the contact of particles with alcohol (e.g. during storage of dispersions) results in the replacement of Ca(OH)₂ by calcium alkoxides. So, in freshly made 2-propanol dispersions, the amount of newly formed calcium alkoxides should be minimal, and after deposition of the particles carbonation takes place at a slower rate compared to long contact periods (e.g. storage >> 2 months) where a fast and high yield carbonation is produced. In our case, we used the same product of nanoparticles dispersed in 2-propanol with more than 2 months storage, and hence we can compare the differences produced in the three exposure environments. The high humidity together with the extra alcohol (ethanol) and CO₂ supplied by the yeast fermentation to reach saturation could explain the most rapid carbonation yield in the yeast system. The appearance of vaterite at 21 days in the closed environment and from 7 days in the yeast system (with more amount of alcohol), and the signs of amorphization (by the presence of ACC and alkoxides) observed in the XRD patterns of the three environments indicate when the maximum reactions rates take place.

Calcium alkoxides have been used for consolidation of carbonate rocks and their reactions with atmosphere produce CaCO₃ where vaterite/calcite ratios generated from isopropyl alcohol (2-propanol) solution were found to considerably vary with alkoxide precursors [52]. Some alkoxides compounds after atmospheric exposure, give different crystallographic results, ranging from amorphous deposits to crystalline systems with

vaterite only, vaterite-calcite mixtures, vaterite-portlandite mixtures, without great reproducibility. This, together with alkoxides reactions are time-dependent, partially explain why studies carried out by different authors using similar environmental conditions, do not obtain the same mineralogical phases when the nanoparticles are exposed to the atmospheric environment, since besides the type of alkoxide precursor and storage time, there are several environmental variables that influence the final precipitated product.

From the DTA-TG-dTG graphs (Fig. 2, Fig.3 and Fig.4) can be inferred that carbonation degree from $\text{Ca}(\text{OH})_2$ nanoparticles (CaCO_3 yield, from the relative amount of $\text{Ca}(\text{OH})_2$ versus CaCO_3) increases with the rise of RH and CO_2 concentration of the environment. After 28 days exposure, a rate of 85% $\text{Ca}(\text{OH})_2$ and 15% CaCO_3 is reached at laboratory conditions. Whereas, almost total carbonation is achieved under the closed environment, with a rate of 5% $\text{Ca}(\text{OH})_2$ and 95 % CaCO_3 , and a total carbonation, 100% CaCO_3 yield is reached under the yeast fermentation system.

In the three environments, the thermal dehydroxylation reaction of portlandite at 28 days takes place at lower temperature ranges (between 307° and 450°C) compared to the decomposition at 7 days of exposure (between 350° and 519°C). The decarboxylation temperatures of calcite (with maximum endothermic peaks between 648°C and 733°C) are also lower than those usually reported (between 800 and 900°C). This can be related with the size of the nanocrystals, which thermal decomposition is produced earlier compared to larger crystal sizes.

The DTA endothermic peak around 100°C is due to hygroscopic water (i.e. physically adsorbed water), whereas the dTG peak appearing at about 250°C can be attributed to bound water or to hydrated interlayer cations [53], since at around 241°C the transformation of ACC into CaCO_3 takes place [28]. The thermal decomposition associated to dehydroxylation of portlandite might be influenced by polymorphic CaCO_3 phase transitions. The phase transformation of vaterite into calcite can takes place at a maximum reaction rate ca. 457°C, whereas transformation of aragonite into calcite can occurs ca. 430°C [54]. After 28 days in the closed system, portlandite was identified under XRD and an endothermic peak with a mass loss of 5% was also detected under DTA-TG. In the yeast system, no portlandite was identified under XRD and none endothermic effect by dehydroxylation was found under DTA. The slight 2% mass loss detected by TG, might corresponds to the loss of occluded water contained in mineral aragonite due to the aragonite-calcite phase transition [54]. Therefore, the decarboxylation in this case corresponds to 100% CaCO_3 decomposition and 100%

CaCO₃ yield in the samples exposed to the yeast fermentation system after 28 days, due to the combination of CO₂, high humidity and more amount of alcohol in the environment, that speed up the carbonation reactions.

3.3 Characterization of stone specimens

3.3.1 Stone blank specimens

The physical properties of blanks specimens from both types of stones were firstly characterized in order to compare the results between stone specimens with no nanoparticles (Table 1) and specimens consolidated with the nanoparticles at a concentration of 5g/l and 25 g/l and exposed to the three environmental conditions.

The surface of Lecce stone and Bateig stone blank specimens was observed under SEM. The SEM images show a rough surface with pores of micrometric size. The mercury intrusion porosimetry curves display the pore size distribution (PSD) of both types of stones (Fig. 5). The mercury intrusion porosimetry results give a total open porosity accessible to mercury of 31±5% in Lecce stone and 19±0.5% in Bateig stone. The PSD of Lecce stone is mainly a bimodal distribution (Fig.5a). Circa half of the amount of total porosity is bellow 1µm (Table 1), and corresponds to pores in the range between 0.1µm and 1µm (41±5%), between 0.01µm - 0.1µm (7±2%) and < 0.01 µm (1%). The other half of amount of pores is above 1µm, and is composed of pores in the range between 1µm and 10 µm (49±2%) and pores >100 µm (1%). Whereas, PSD of Bateig stone displays a polymodal distribution (Fig.5b) with most of the pores above 1 µm, with pores in the range between 1µm and 10 µm (58±3%), between 10 - 100 µm (4±1%) and >100 µm (4±2%). Bellow 1µm it displays pores in the range between 0.1µm and 1µm (22%), between 0.01µm - 0.1µm (12%) and < 0.01 µm (1%).

Spectrophotometry results and water absorption values obtained under vacuum are also compiled in Table 1. The water absorption by capillarity and desorption of Lecce stone show a capillarity coefficient of 98±4 g/(m²s^{0.5}) and water desorption rate of 24±2 g/(m²s^{0.5}). Whereas Bateig stone display a capillarity coefficient of 41±0 g/(m²s^{0.5}) and water desorption rate of 15±0 g/(m²s^{0.5}). Lecce stone shows a higher open porosity values and a larger amount of absorption water by capillarity, which absorption and desorption rates are produced at a faster rate compared to Bateig stone.

The results of surface hardness measurements indicate values of 234±21 HLD for Lecce stone blank specimens and much higher values of 342±30 HLD for Bateig stone.

Microdrilling resistance (DRMS) measurements indicate values of 3.96 ± 0.43 N for Lecce stone and three times higher force values for Bateig stone (9.50 ± 1.11 N).

3.3.2 Treated stone specimens exposed to ventilate laboratory room conditions

The main results from the spectrophotometry measurements show clear differences between the two product's concentration in both types of stones (Table 2). Figure 6 shows the macroscopic view of the stone surfaces after the application of Ca(OH)_2 nanoparticles at 5g/l and 25 g/l, together with the SEM images obtained at 1000x and 6000x magnification. The macroscopic images of the stone surfaces after the application of Ca(OH)_2 nanoparticles show a white porous crust on the face where the product was absorbed by capillarity, when the nanoparticles were applied at a concentration of 25g/l in both types of stone (Fig. 6d and 6j). On the surface of Lecce (Fig. 6e) stone a network of nano and micropores left by agglomerated flat nanocrystals with signs of amorphization can be observed, together with some totally amorphous particles that would correspond to amorphous calcium carbonate (Fig.6f). On the surface of Bateig stone (Fig.6k), a similar crust shows smooth areas and cracks in a network of agglomerated granular nanocrystals (Fig.6l) that also give rise to a network of micropores. In the case of nanoparticles applied at a concentration of 5g/l, small spots of white deposits can be observed in the Lecce stone (Fig. 6a) and the microscopic SEM images show the nanoparticles covering the surface of the original minerals of the stone (Fig. 6b and Fig. 6c). In the case of Bateig stone, the macroscopic view apparently does not show white deposits (Fig. 6g). However, the nanoparticles have covered the surface of the minerals with a smooth film (Fig. 6h) of amorphous flat layers (Fig. 6i). The EDS analyses show that the chemical composition of the nanoparticles is mostly made up by calcium, as was previously studied in other research works [7, 20].

There are almost no changes on the average density, open porosity, and water saturation values. Regarding to the capillarity results, there is just a slight change on the water absorption and desorption capillarity coefficients. These variations are a bit higher in the Bateig stone specimens (Table 3). All the stone specimens display changes in the surface hardness, with an increase of 5% and 8% for Lecce stone consolidated at 5g/l and 25g/l, respectively. For Bateig stone, the values slightly increase 1% and 4% when the nanoparticles were applied at a concentration of 5g/l and 25g/l, respectively. The DRMS results show some changes in the drilling resistance in all the stone specimens, with an increase of 19% and 11% in Lecce stone and 1% and 5% in Bateig stone (Table 4).

3.3.3 Treated stone specimens exposed into closed containers with high humidity

The main results from the spectrophotometry measurements show slight differences between the two product's concentration in both types of stones (Table 2). Figure 7 shows the macroscopic view of the stone surfaces after the application of $\text{Ca}(\text{OH})_2$ nanoparticles, together with their SEM images. When the nanoparticles were applied at a concentration of 5g/l, Lecce stone shows small spots of white deposits (Fig. 7a) that cover the surface of the original minerals as an amorphous film (Fig. 7b) where flat particles can barely be distinguished (Fig. 7c). In the case of Bateig stone, the macroscopic view apparently does not show white deposits (Fig. 7g), but the nanoparticles have covered the surface of some original minerals also with a smooth film (Fig. 7h) of amorphous flat layers (Fig.7i). When the nanoparticles were applied at a concentration of 25g/l, the stone specimens show white crust deposits on the edges and corners of the faces where the product was absorbed by capillarity (Fig.7d and 7j). In Lecce stone, the white deposits are formed by agglomerated granular nanocrystals (Fig.7e) that give rise to a network of pores with nanometric sizes (Fig.7f). In Bateig stone the nanoparticles are less agglomerated and these are covering the surface of the stone (Fig. 7k and Fig. 7l). The EDS analyses show that the chemical composition of the nanoparticles is mainly formed by calcium.

There are almost no changes on the average density, open porosity, and water saturation values. There is just a slight change on the water absorption and desorption coefficients, and these variations are a bit higher in the Bateig stone specimens (Table 3). All the stone specimens display a change in the surface hardness, with 8% and 7% increase in Lecce stone consolidated at 5g/l and 25g/l respectively. In Bateig stone the values barely change (3% and 5%, respectively). Both types of stone specimens show a slight increase in the drilling resistance results, with 9% and 17% increase in Lecce stone and 2% and 8% in Bateig stone (Table 4).

3.3.4 Treated stone specimens exposed to a yeast system with high humidity

The main results from the spectrophotometry measurements show very slight differences between the two product's concentration in both types of stones (Table 2). Figure 8 shows the macroscopic view of the stone surfaces after the application of $\text{Ca}(\text{OH})_2$ nanoparticles, together with their SEM images. At 5g/l Lecce stone shows very few small white spots (Fig. 8a) and the SEM images display large amounts of ACC together with nano and microcrystals of calcium carbonate (Fig. 8b and Fig.8c). In Bateig stone, the macroscopic view apparently does not show white deposits (Fig. 8g), but under SEM the surface of the stone appears covered by an amorphous film

(Fig.8h) where agglomerated flat particles can be distinguished (Fig. 8i). In general, no white deposits are observed on the surface of the stones, except on Bateig specimens that show a white glazing on the center of the face where the product was applied at 25 g/l (Fig. 8j). In this case, elongated calcium carbonate and some rhombohedra calcite microcrystals give rise to a network of micropores, together with some small areas filled with ACC (Fig. 8k and 8l). At this concentration, very small white spots can be observed on the surface of Lecce stone (Fig. 8d). At 25g/l the nanoparticles have covered the surface (Fig. 8e) and calcium carbonate nano and microcrystals (some calcite rhombohedra) can be observed together with small areas filled with ACC (Fig. 8f). The chemical composition of these nano and microcrystals shows EDS spectra composed by calcium.

There are almost no changes on the average density, open porosity, and water saturation values. The water absorption and desorption coefficients of Lecce stone specimens slightly increase, whereas these variations are a bit higher in Bateig stone (Table 3). In this case, all the stone specimens display changes in the surface hardness, with 10% and 11% increase in Lecce stone consolidated at 5g/l and 25g/l respectively. In Bateig stone, these values slightly change (6% and 8% respectively). Both types of stones show an increase in the drilling resistance results, 8% and 16% in Lecce stone and 5% and 10% in Bateig stone (Table 4).

3.4 Interpretation of characterization of stone specimens

The results of color variations obtained by spectrophotometry on the surface of the treated stone specimens show clear differences in the chromatic parameters depending on the substrate, environment and concentration of the product (Table 2). In Lecce stone specimens consolidated at 5 g/l, the chromatic differences decrease with the rise of RH and CO₂ in the environment. Lightness (ΔL^*), white index (ΔWI^*) and brightness are the parameters with the highest increase due to the white color left by the nanoparticles. It should be highlighted that the magnitude of the standard deviations produced in the chromatic variations decrease with the increase of RH and CO₂ in the environment, giving rise to more homogeneous chromatic surfaces, where the variations are produced in a similar way in the whole surface. However, in Bateig stone specimens consolidated at 5 g/l, the total color difference (ΔE^*) increases with the increase of RH and CO₂ of the environment. The differences on chromatic variations after consolidation, besides the porosity, can be explained because the application of nanoparticles produce an increase of WI, which rises with the

carbonation rate, being more remarkable in Bateig stone with an original lower WI compared to Lecce stone.

Due to the suitability criteria used to assess conservation treatments, the variations produced at 5 g/l would not be visually detectable by the human eye and these would not significantly affect the colorimetric parameters of the substrate in any case, because ΔE^* is lower than 5 [55], or lower than 3 according to other authors [56,57]. In the case of treated stones at a concentration of 25g/l, the chromatic variations are greater than the suitability criteria in both type of substrates, producing detectable visually changes. Both in Lecce and Bateig stone specimens, ΔE^* is much greater in the case of the specimens exposed to the laboratory conditions. ΔE^* value decreases in the closed environment and increase again in the yeast system environment, although ΔE^* is still lower than the difference produced in the laboratory environment. In both stone types, an agglomeration of nanoparticles is produced on the surface of the substrates giving rise to a homogeneous white crust that makes those parameters to increase (Fig.6). In the closed environment, small agglomerations are produced, giving rise to small crusts heterogeneously distributed on the surface (Fig.7). However, in the yeast system environment there are no crusts, just a white glazing only observed in Bateig stone at 25 g/l (Fig. 8). This effect is produced by initial bigger pores sizes and lower open porosity values compared to Lecce, giving rise to higher chromatic variations.

The SEM images (Fig. 6-8) show that the nanoparticles are aggregated and display signs of amorphization. Moorehead [58], reported that the increase of CO_2 concentration during carbonate cementation increase the rate of transformation from portlandite into calcite, showing how the carbonation of hydrated lime ($\text{Ca}(\text{OH})_2$) gives rise to mostly amorphous or very poor crystalline forms of CaCO_3 . This was also observed in $\text{Ca}(\text{OH})_2$ nanoparticles showing ACC formation on the faces of portlandite [20,21,50]. This can be seen in the SEM images, especially in the cases of nanoparticles applied at 5g/l and exposed to the three environments, where nano and microcrystals together with large amounts of ACC are observed. Colloidal particles may undergo aggregation of plate-like $\text{Ca}(\text{OH})_2$ nanoparticles ranged from 30 nm up to 200 nm that aggregate into micron-sized clusters [20,21,59]

The initial higher open porosity of Lecce stone (Table 1) has favor a higher penetration of the product, avoiding its saturation on the surface and the agglomeration of the nanoparticles, with less white deposits left on the surface, especially in the yeast system environment. Bulk and real density values barely change in both stone types

exposed to the three environments. The open porosity values slightly decrease in a similar way (3% in Lecce stone and 5% in Bateig stone) in the closed and yeast system environments, whereas, no changes are produced in the laboratory environment. These results are in agreement with previous works, both in a short [7] and in a longer term [16], where it was demonstrated that consolidation process with $\text{Ca}(\text{OH})_2$ nanoparticles improved the physical and hydric properties of limestone specimens exposed to dry and humid environments. An initial high RH and a higher and larger porosity favor the consolidation in a longer term.

After consolidation, water absorption and desorption capillarity coefficients barely change (Table 3). Regarding to the quantity of absorbed water in Lecce and Bateig stone specimens consolidated at 5g/l, a 3% and 6% increase is produced in the three environments. Whereas, no changes are obtained at a concentration of 25g/l, with the exception of specimens exposed to the laboratory environment (6% increase). Although the values are variable, generally higher variations in the capillarity coefficients (C) are produced in Bateig specimens, especially at 25 g/l. An increase in the C coefficient means that specimens absorb water at a faster rate. Due to the decrease of pore sizes, the suction force increases, so the higher the volume of capillary pores the higher the C coefficient [60]. This could be related to the generation of micropores with a diameter in the range between 0.1 and $1\mu\text{m}$ at the expense of pores between 1 and $10\mu\text{m}$ and between 10 and $100\mu\text{m}$. So, the sizes within these latter ranges are reduced by the application of nanoparticles and give rise to higher C coefficients, especially in the case of Bateig stone with higher amount of pores in these ranges (Table 1). This supposition is in agreement with the MIP data obtained in previous works before and after application of same type of nanoparticles under similar conditions in dolostones specimens [16]. When comparing the PSD of the blanks of both stones (Fig.5) and the C coefficients of both stones (Table 3), the main difference can be found in the amount pores in the range between 0.1 and $1\mu\text{m}$. In the case of Lecce stone, this amount is approximately double than the obtained in Bateig stone for this range, as well as the C coefficient and desorption rates. Therefore, it seems that the ranges of pores that mostly influence the C coefficient are those comprised between 0.1 and $1\mu\text{m}$. The results on capillary desorption rates of Lecce stone specimens after consolidation, (Table 3) show a slight increase of this coefficient, i.e. increase of evaporation rate of capillarity water, which supposes lower water retention during drying. However, in Bateig specimens, the capillarity desorption rate is reduced in the three environments, independently of the product's concentration. Although, as the same time the environment has a higher humidity and CO_2 concentration, the water

evaporation is speed up, from 13% decrease in the laboratory environment down to 7% decrease in the yeast system environment. Comparing the results obtained at both concentrations of nanoparticles depending on the consolidation environment, the improvement of hydric properties after consolidation (decrease of amount of absorbed water and increase of capillarity and desorption coefficients) is obtained in the yeast system environment. Nevertheless, the slight increase in the amount of absorbed water (more pronounced in Bateig stone) and the decrease in the water evaporation rate (in Bateig specimens) should be assessed. Although these are minor variations, they could have adverse effects in the durability of the stone, because the presence of water inside the rocks gives rise to a durability decrease since it can favor salt and ice crystallization processes, dissolution, adsorption of pollution particles and biodeterioration [61].

In a similar way to the spectrophotometry results, the decrease of standard deviation on the surface hardness values after consolidation (Table 1 and Table 4) suggests a homogenization of the surface of the stone specimens and hence of the surface hardness with almost none increase of this value in the specimens exposed to the laboratory and closed environments. However, in the yeast system surface hardness increases at both concentrations of the product, and this is higher in Lecce compared to Bateig. The drilling resistance values also increase after consolidation of Lecce specimens, especially at 25g/l. However, in Bateig specimens these values barely change. The microdrilling results can be affected by the presence of microfossils that in the case of Lecce stone provoke a higher heterogeneity of the measurements compared to Bateig stone. This latter stone shows a homogeneous drilling resistance increase with the rise of humidity and CO₂ of the environment and with the increase of the product's concentration.

According to Moorehead [58], the main factors involved in controlling the carbonation reaction, are CO₂ gas concentration, moisture content and the permeability of the substrate. From the SEM images, it can be inferred that porosity and permeability values are more favorable and prone to the penetration of these nanoparticles in the case of Lecce stone, especially when the concentration of the product is higher (25g/l) and is exposed to the yeast system environment (Fig.6, Fig.7 and Fig.8). At 5g/l both stone types apparently better absorb the product because no white deposits seem to be left over the surface of the specimens in the three environments. However, at this concentration the mechanical properties barely change in Bateig stone compared to Lecce stone. Even though the changes in the mechanical properties are higher at 25g/l for both stone types, this increase is not directly proportional to the product's

concentration, being these properties just slightly increased. Besides, the white deposits left by the nanoparticles are larger when the product is applied at 25g/l concentration, especially in Bateig stone, because it has larger pore sizes but lower total open porosity and C coefficients compared to Lecce stone. Eventually, the appearance of these white deposits decrease from the laboratory to the closed environment, and these are almost inexistent in the yeast system environment, especially in Lecce stone. A second application at 5g/l (two applications instead of just one) should be studied, after the carbonation of the first one, 28 days later, to know if is there a similar increase on the mechanical properties, or even higher, that the obtained with concentration at 25g/l but avoiding the formation of white deposits left on the surface.

MIP results of Lecce stone show a higher total connected porosity and higher amount of pores with smaller pore diameters (below 1 μm , and mainly between 0.1 and 1 μm) compared to Bateig. According to all the obtained results on the different physical properties, it seems that the size of these nanoparticles (60-130 nm) better fit with the bimodal PSD of Lecce stone compared to the polymodal PSD of Bateig stone (with higher amount of pores above 1 μm). The size of this type of nanoparticles can increase from nanometer sizes (<100 nm) up to micrometric size (2 μm) at high RH [20]. Besides, a higher open and more connected porosity improve the access of CO_2 and H_2O to the interior of the stone, and therefore ease the carbonation process. It is important not only to take into account the open porosity values of the substrate, but the PSD as well, since depending on the size of the initial nanoparticles and the final formed crystals, related to the environmental conditions during the crystallization process, the filling of different pore sizes can be better or worse, increasing or decreasing the consolidating/cementing efficacy of the nanoparticles.

The carbonation process and the improvement in the petrophysical properties seem to be stopped (or slowed down) at low RH, whereas these processes keep going (or are speed up) in a longer term at higher RH. So, the influence of the RH of the environment during the first stage of consolidation is a key factor for the transformation of Ca(OH)_2 nanoparticles into CaCO_3 and for the improvement of petrophysical properties of the treated stones in a longer term [16]. Besides the high humidity, the addition of CO_2 and a source of ethanol also speed up the carbonation rate and the mechanical properties of limestone. However, accelerated ageing tests should be the next step in order to assessing the durability of the stones initially exposed to these different environments.

4 Conclusions

A high humidity environment together with the CO₂ and ethanol released by yeast fermentation favors and accelerates the carbonation process of colloidal Ca(OH)₂ nanoparticles (60-130 nm) dispersed in 2-propanol. These nanoparticles are transformed into vaterite, aragonite and calcite (CaCO₃ polymorphs), after 21 days of exposure to this system, and achieve 100% CaCO₃ yield (aragonite and calcite) after 28 days. Samples under high humidity but without the yeast system, display the same mineral phases together with portlandite after 21 days, and reach 95% CaCO₃ yield (aragonite and calcite) vs. 5% Ca(OH)₂ (portlandite) after 28 days. Whereas samples exposed to laboratory room conditions barely carbonate, displaying almost the total amount of initial portlandite nanoparticles, 85% Ca(OH)₂ (portlandite) vs. 15% CaCO₃ yield (calcite) after 28 days.

In the three environments all the limestone specimens consolidated with these nanoparticles show an increase in the drilling resistance and surface hardness values with variable results in the capillarity absorption and desorption coefficients, especially when the nanoparticles were applied at a concentration of 25g/l. Besides, at this concentration white crusts and glazing are left by the nanoparticles on the surface of the stones, composed of a mixture of amorphous, nano and microcrystals of CaCO₃.

The largest increase in these mechanical properties, with slight rise in the capillarity absorption and desorption coefficients and with lesser stone color changes (with total color differences lower than the established for stone conservation treatments) are produced at a concentration of 5g/l, in the yeast system environment and especially in stone specimens initially with bimodal pore size distributions (PSD), more amounts of pores in the range between 0.1 and 1µm diameters, higher open porosity values and faster capillary coefficients compared to Bateig stone with a polymodal PSD and more amount of pores above 1µm. In both types of stone, density and open porosity values barely change.

This research show the importance of controlling the environmental conditions during the phase transformations of these nanoparticles used as cementing materials and during their application as a consolidating product, both in laboratory and in the field. A simple, inexpensive and reliable method that can be easily applied in the laboratory and on-site, based on water and a yeast-sugar solution to create a microclimate saturated on high humidity, CO₂ and ethanol released to speed up carbonation of Ca(OH)₂ nanoparticles, is presented to improve the mechanical properties of decayed limestone frequently used in archaeological and architectural heritage.

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909 **FIGURE CAPTIONS**

910 **Fig.1** Set up of the experiment at the laboratory showing the limestone specimens and the
911 consolidating product based on Ca(OH)₂ nanoparticles, in the three environmental conditions.
912 a) to the left, stone specimens (5cm³) connected to the flask with the yeast fermentation; in the
913 back, specimens inside the closed container at high humidity; to the right and front, stone
914 specimens exposed to the ventilate laboratory conditions

915 **Fig.2** XRD and DTA-TG analyses of Ca(OH)₂ nanoparticles exposed to ventilate laboratory
916 room conditions (59 ± 11 %RH). a) XRD patterns of samples after 7, 14, 21 and 28 days

exposure; b) DTA, TG and dTG curves after 7 days exposure; c) DTA, TG and dTG curves after 28 days exposure

Fig.3 XRD and DTA-TG analyses of $\text{Ca}(\text{OH})_2$ nanoparticles exposed to a closed container with high humidity ($87\pm 1\%$ RH). a) XRD patterns of samples after 7, 14, 21 and 28 days exposure; b) DTA, TG and dTG curves after 7 days exposure; c) DTA, TG and dTG curves after 28 days exposure

Fig.4 XRD and DTA-TG analyses of $\text{Ca}(\text{OH})_2$ nanoparticles exposed to a yeast fermentation system connected to a closed container with high humidity ($87\pm 7\%$ RH). a) XRD patterns of samples after 7, 14, 21 and 28 days exposure; b) DTA, TG and dTG curves after 7 days exposure; c) DTA, TG and dTG curves after 28 days exposure

Fig.5 Pore size distribution, PSD (pore diameter), obtained with mercury intrusion porosimetry of limestone specimens. a) PSD of Lecce stone; b) PSD of Bateig stone

Fig.6 Limestone specimen showing the product application face (from the bottom), after 28 days of the application of $\text{Ca}(\text{OH})_2$ nanoparticles at 25 g/l, exposed to ventilate laboratory room conditions ($59 \pm 11\%$ RH). a) macroscopic view of Lecce stone with nanoparticles at 5g/l; b) SEM image (1000x magnification) of former sample; c) SEM image of former sample (6000x magnification); d) macroscopic view of Lecce stone with nanoparticles at 25g/l; e) SEM image (1000x magnification) of former sample; f) SEM image (6000x magnification); g) macroscopic view of Bateig stone at 5g/l; h) SEM image (1000x magnification) of former sample; i) SEM image (6000x magnification); j) macroscopic view of Bateig stone at 25g/l; k) SEM image (1000x magnification) of former sample; l) SEM image (6000x magnification)

Fig.7 Limestone specimens showing the product application face (from the bottom), after 28 days of the application of $\text{Ca}(\text{OH})_2$ nanoparticles exposed to a closed container with high humidity ($87\pm 1\%$ RH). a) macroscopic view of Lecce stone with nanoparticles at 5g/l; b) SEM image (1000x magnification) of former sample; c) SEM image (6000x magnification); d) macroscopic view of Lecce stone with nanoparticles at 25g/l; e) SEM image (1000x magnification) of former sample; f) SEM image (6000x magnification); g) macroscopic view of Bateig stone at 5g/l; h) SEM image (1000x magnification) of former sample; i) SEM image (6000x magnification); j) macroscopic view of Bateig stone at 25g/l; k) SEM image (1000x magnification) of former sample; l) SEM image (6000x magnification)

Fig.8 Limestone specimens showing the product application face (from the bottom), after 28 days of the application of $\text{Ca}(\text{OH})_2$ nanoparticles exposed to a yeast fermentation system connected to a closed container with high humidity ($87\pm 7\%$ RH). a) macroscopic view of Lecce stone with nanoparticles at 5g/l; b) SEM image (1000x magnification) of former sample; c) SEM image (6000x magnification); d) macroscopic view of Lecce stone with nanoparticles at 25g/l; e) SEM image (1000x magnification) of former sample; f) SEM image (6000x magnification); g) macroscopic view of Bateig stone at 5g/l; h) SEM image (1000x magnification) of former

954 sample; i) SEM image (6000x magnification); j) macroscopic view of Bateig stone at 25g/l; k)
955 SEM image (1000x magnification) of former sample; l) SEM image (6000x magnification)

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Figure1

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1 TABLES

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Table 1 Physical properties of blank stone specimens of Lecce and Bateig without nanoparticles			
Physical properties	Lecce specimens	Bateig specimens	
Chromatic parameters			
Lightness (L*)	78.93±4.87	76.55±1.63	
a* and b* color coordinates	2.96±1.25 and 13.25±3.91	2.6±0.41 and 13.79±1.26	
Chroma C*	13.64±3.88	14.04±1.31	
Brightness	43.73±7.68	39.41±3.11	
White index (WI)	5.98±3.82	1.79±4.94	
Yellow index (YI)	22.70±6.60	24.23±2.33	
Pore size distribution			
Total open porosity (%)	31±5	19±0.5	
< 0.01 µm	1	1	
0.01 - 0.1 µm	7±2	12	
0.1 - 1 µm	41±5	22	
1-10 µm	49±2	58±3	
10 - 100 µm	-	4±1	
>100 µm	1	4±2	
Water absorption			
Apparent density (kg/m ³)	1,669±5	2,155±14	
Real density (kg/m ³)	2,714±0	2,710±7	
Open porosity (%)	39	21	
Water saturation (%)	23	10	
Capillarity absorption			
Total water absorption (g)	32	18	
Capillarity coefficient g/(m ² s ^{0.5})	98±4	41±0	
Desorption coefficient g/(m ² s ^{0.5})	24±2	15±0	
Surface hardness			
HDL values	234±21	342±30	
Microdrilling resistance			
Force values (N)	3.96±0.43	9.50±1.11	

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Table -2 Average variations (Δ) promoted on chromatic parameters (L*, lightness; C*, Chroma; E*, total color; YI, yellow index; WI, white index) on the stone specimens after 28 days of consolidation with Ca(OH) ₂ nanoparticles exposed to different environments							
Environment	Specimen	ΔL*	ΔC*	ΔE*	ΔYI	ΔWI	ΔBrightness
Laboratory conditions	Lecce 5g/l	4.34±1.65	-0.61±02.01	4.67±1.77	-1.47±3.31	3.81±8.88	6.65±4.45
	Lecce 25g/l	15.34±0.8	-13.09±0.1	20.85±0.6	-23.7±0.03	83.32±2	42.85±1.85
	Bateig 5g/l	-0.08±0.65	-0.81±0.28	0.95±0.18	-1.27±0.6	2.41±1.3	0.42±1.12
	Bateig 25g/l	14.69±0.1	-11.96±0.44	20.29±1.8	-24.03±4.5	78±11.7	40±2.1
Closed container	Lecce 5g/l	3.85±0.85	0.15±1.48	4.13±0.69	-0.23±2.4	0.44±6.14	5.13±2.65
	Lecce 25g/l	4.27±0.11	-3.73±0.26	5.63±0.26	-6.3±0.42	15.8±1.11	9.21±0.42
	Bateig 5g/l	-0.37±0.27	-1.19±0.91	0.32±0.75	-1.76±1.5	3.59±2.9	0.35±0.9
Yeast system	Bateig 25g/l	5.57±0.3	-7.52±0.81	9.36±0.83	-13±1.38	31.86±3.7	14.78±1.3
	Lecce 5g/l	3.11±0.89	1.37±0.95	3.71±0.43	1.74±1.58	-4.46±3.79	2.96±2.13
	Lecce 25g/l	6.63±1.73	-4.83±1.44	8.18±2.23	-8.26±2.47	22.8±8.12	14.38±4.52
	Bateig 5g/l	1.40±0.32	-2.42±0.9	2.85±0.9	-13.4±0.2	18.2±2.8	3.84±2.2
	Bateig 25g/l	6.36±2.61	-9.35±1.96	11.37±3	-16.3±3.48	41.23±12	18.14±6.6

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Table 3 Water absorption by capillarity and water desorption values and variations (Δ) of stone specimens before and after 28 days of consolidation with $\text{Ca}(\text{OH})_2$ nanoparticles (NC: No change)

Environment	Specimens	Total water absorption by capillarity (g)			Capillarity coefficient ($\text{g}/(\text{m}^2\text{s}^{0.5})$)			Capillarity desorption coefficient ($\text{g}/(\text{m}^2\text{s}^{0.5})$)		
		Before	After	Average Δ (%)	Before	After	Average Δ (%)	Before	After	Average Δ (%)
Laboratory conditions	Lecce 5g/l		33	3.0		107 $\pm$ 0	9		25 $\pm$ 1	4
	Lecce 25g/l	32	32	NC	98 $\pm$ 4	98 $\pm$ 0	NC	24 $\pm$ 2	24 $\pm$ 0	NC
	Bateig 5g/l		19	5.5		38 $\pm$ 1	-7		13 $\pm$ 1	-13
	Bateig 25g/l	18	19	5.5	41 $\pm$ 0	47 $\pm$ 1	15	15 $\pm$ 0	13 $\pm$ 0	-13
Closed container	Lecce 5g/l		33	3.0		101 $\pm$ 2	3		24 $\pm$ 0	NC
	Lecce 25g/l	32	32	NC	98 $\pm$ 4	88 $\pm$ 6	-10	24 $\pm$ 2	26 $\pm$ 2	8
	Bateig 5g/l		19	5.5		43 $\pm$ 2	5		13 $\pm$ 0	-13
	Bateig 25g/l	18	18	NC	41 $\pm$ 0	43 $\pm$ 1	5	15 $\pm$ 0	14 $\pm$ 1	-7
Yeast system	Lecce 5g/l		33	3.0		100 $\pm$ 3	2		25 $\pm$ 1	4
	Lecce 25g/l	32	32	NC	98 $\pm$ 4	100 $\pm$ 2	2	24 $\pm$ 2	25 $\pm$ 0	4
	Bateig 5g/l		19	5.5		44 $\pm$ 6	7		14 $\pm$ 0	-7
	Bateig 25g/l	18	18	NC	41 $\pm$ 0	38 $\pm$ 2	-7	15 $\pm$ 0	14 $\pm$ 0	-7

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Table 4 Drilling resistance values (Force, N) and surface hardness (HLD) values and variations (Δ) of stone specimens after 28 days of $\text{Ca}(\text{OH})_2$ nanoparticles application at a concentration of 5g/l and 25 g/l

Environment	Stone	5g/l concentration				25g/l concentration			
		Force (N)	Δ (%)	Surface hardness (HLD)	Δ (%)	Force (N)	Δ (%)	Surface hardness (HLD)	Δ (%)
Laboratory conditions	Lecce	4.71 $\pm$ 0.1	19	245 $\pm$ 0	5	4.41 $\pm$ 0.1	11	254 $\pm$ 7	8
	Bateig	9.61 $\pm$ 0.7	1	346 $\pm$ 6	1	9.94 $\pm$ 1	5	354 $\pm$ 3	4
Closed container	Lecce	4.3 $\pm$ 0.1	9	253 $\pm$ 3	8	4.62 $\pm$ 0.2	17	251 $\pm$ 4	7
	Bateig	9.73 $\pm$ 0.5	2	351 $\pm$ 10	3	10.29 $\pm$ 1	8	359 $\pm$ 2	5
Yeast system	Lecce	4.26 $\pm$ 0.3	8	257 $\pm$ 13	10	4.61 $\pm$ 0.2	16	259 $\pm$ 7	11
	Bateig	9.93 $\pm$ 1	5	361 $\pm$ 15	6	10.46 $\pm$ 1	10	368 $\pm$ 13	8

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