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Original article

Evaluating the effectiveness of consolidation through laboratory and in situ tests for the conservation of frescoes in hypogean environments of Marsala (Italy)

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The conservation and restoration of frescos located in hypogeal environments require specifically tailored strategies to address critical thermo-hygrometric conditions, such as high humidity, poor ventilation, condensation, and capillary rise. These factors often lead to the accumulation of sulphate salts both on the surface and within their inner layers. Under such microclimatic conditions, the choice of a suitable consolidant is crucial to ensure material compatibility and long-term breathability. This study reports the results obtained by using barium hydroxide nanoparticles in hydroalcoholic solution for the consolidation of frescos in hypogeal environments, through a comparative evaluation with nanolime and nanosilica. The research involved both laboratory tests on artificially aged mock-up samples simulating frescoes and in situ applications on frescoes in the hypogea of Santa Maria della Grotta and of Crispia Salvia (Marsala, Italy). To evaluate the performance of the nanostructured consolidants, a series of standardized tests were carried out, including capillary water absorption, water vapor permeability, contact angle measurements, colorimetric analysis, surface cohesion (scotch tape test), and SEM-EDS analysis on the mock-ups. In situ, the consolidation effectiveness was evaluated using colorimetry, contact sponge test, and Scotch tape test, followed by a 12-months monitoring campaign. The results provide valuable insights into the relative performance, compatibility, and limitations of each consolidant under hypogeal conditions, contributing to the development of more effective conservation strategies for frescoes affected by moisture and sulphation.

1. Introduction

The conservation of frescoes in hypogeal environments represents one of the most complex challenges for conservators. The typical thermo-hygrometric conditions in such environments, high relative humidity, poor ventilation, condensation, and capillary rise, favor aggressive degradation processes such as sulphation, loss of material cohesion, salt migration, and the subsequent detachment of pictorial layers. The presence of soluble salts, in particular, is a critical variable that can compromise the effectiveness of consolidation treatments, especially when these form surface films or are not fully compatible with the mineral nature of the original constituent materials [1]. Traditionally, organic consolidants such as acrylic resins, polyvinyl acetates, or epoxy resins have been used. Although initially effective, they have shown long-term issues related to reversibility, chromatic alteration, and chemical incompatibility with lime-based substrates [2,3]. At the same time, the use of aqueous lime suspensions has shown poor penetration capacity and limited mechanical effectiveness, particularly in severely

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degraded substrates or those exposed to moisture cycles [4,5]. In the past two decades, the development of nanostructured consolidants [6] has opened new perspectives in the conservation of stone materials and decorated surfaces. Among these, nanolime dispersions, composed of $Ca(OH)_2$ nanoparticles in alcoholic media, have been widely used due to their high chemical compatibility with carbonate substrates [7,8]. However, the application of nanolime in hypogeal environments has revealed significant limitations: slow carbonation in the presence of high humidity, the appearance of white surface patinas, and doubts regarding long-term effectiveness in poorly ventilated conditions [9,10]. Silica-based consolidants, initially developed for siliceous stones, have shown good performance in terms of surface cohesion and water repellency. However, their tendency to form surface films and to reduce water vapor permeability can be problematic when used on porous lime-based materials such as frescoes, where breathability is fundamental to long-term stability [11]. Moreover, low penetration in fine-porosity materials and the superficial accumulation of silica particles result in mechanical incompatibility between consolidant and substrate, along with a film-like appearance from an aesthetic standpoint. The effects of these treatments can be particularly critical in hypogeal settings, where interactions between salts, moisture, and consolidant may lead to accelerated disintegration or optical alteration of the treated surface [11]. More recently, the use of barium hydroxide in nanometric form was considered as an alternative consolidant for carbonate substrates affected by sulphation [12]. This material, due to its ability to react with sulphates and form stable, insoluble barium sulphate, offers a dual function: consolidation and desalination [13]. Furthermore, $Ba(OH)_2$ nanoparticles exhibit good penetration, no chromatic alteration, and a reduced risk of forming occlusive surface films, making them particularly suitable for application in humid hypogeal environments [14]. Moreover, its application in hypogeal environments has been scarcely investigated.

2. Research aim chapter

The present study investigates the effectiveness of nanostructured barium hydroxide in hydroalcoholic solution, synthesized via a hydrothermal process, as an innovative consolidant for hypogeal frescoes, comparing its performance with two well-established materials: nanolime and nanosilica [15]. The main innovative contribution of this study lies in the methodological approach adopted. Before applying the developed formulation in situ, preliminary laboratory investigations were carried out on mock-up samples under controlled conditions simulating the thermo-hygrometric parameters of the sites where the experimentation would take place. The research was thus structured in two phases. The first involved laboratory testing on artificially aged mock-up samples reproducing the thermo-hygrometric conditions of hypogea. The second consisted of in situ applications on pilot areas of frescoes from Santa Maria della Grotta and the Crispia Salvia hypogeum (Marsala, Italy), monitored over 12 months to assess long-term stability. Standardized analyses—capillary water absorption, water vapor permeability, contact angle, colorimetry, Scotch tape test, and SEM-EDS evaluation of penetration depth—were used to compare the consolidants' performance. Two barium hydroxide systems were formulated to identify the most suitable dispersing medium for the in situ test: System A (75% water, 25% isopropanol) and System B (75% isopropanol, 25% water). In situ evaluation included colorimetry, Scotch tape, and contact sponge tests. The results highlight the relative performance, advantages, and limitations of the three consolidants, providing scientifically grounded and practical criteria for selecting suitable materials in highly vulnerable hypogeal environments.

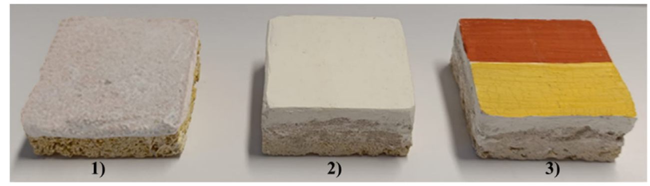

Fig. 1. Different steps for creating mock-ups samples of fresco: 1) Arriccio, 2) Tonachino, and 3) Pictorial layer.

3. Experimental part

3.1. Materials

The chemical reagent and solvent used for the synthesis was supplied by Sigma Aldrich; Barium hydroxide $Ba(OH)_2$ technical grade, Isopropyl alcohol ≥99.7%, FCC, FG. Deionised water was prepared with an ionised water purification system and was used in all procedures. The commercial consolidants were supplied by CTS Conservation; NANORESTORE (nanophasic calcium dispersed in isopropyl alcohol); NANOSILO OR (aqueous dispersion of nanosized fluorosilanes). For the realisation of the mock ups samples the lime was supplied by Codex; the calcarenite used originated from Marsala, while white white marble powder and medium- and fine-grained sand were employed as aggregates. The pigments red ochre and yellow ochre were supplied by Kremer Pigmente (red ochre #11273, yellow ochre #11272)

3.2. Synthesis of barium hydroxide nanoparticles

Barium hydroxide nanoparticles were synthesised via hydrothermal treatment. The synthesis was carried out in an autoclave system (Parr Instrument Company), equipped with a Model 4838 Reactor Controller and a Model 4793 general-purpose pressure vessel fitted with four valves. Micrometer-sized barium hydroxide particles were initially ground in a mortar to reduce their size and then dispersed in a hydroalcoholic medium (75% deionised water, 25% isopropanol) to promote homogeneous distribution and enhance dispersion stability. The hydrothermal reaction was conducted at 180 °C and 8 bar for 24 h. The synthesis procedure followed the method described by Tuccio et al. [15].

3.3. Preparation and aging of mock-up

To evaluate the effectiveness of the consolidant treatment, mock-up specimens reproducing the fresco technique were prepared according to the dimensional criteria defined by UNI EN standards (Fig. 1) [16,17]. Each mock-up consisted of a calcarenite base overlaid with three stratigraphic layers: 1)Arriccio, a preparatory layer composed of sand and lime in a 2:1 ratio; 2) Tonachino, a finishing layer made of lime and marble powder in a 1:1 ratio; and 3) the Pictorial layer, applied using yellow and red ochre pigments, consistent with those identified in the referenced hypogeal complex. The surface of the fresco was therefore mechanically abraded, and the dispersion was applied by brush until saturation.

Mockup accelerated ageing was conducted by placing the mockups inside a dryer, with the base filled with water to maintain a high relative humidity, mimicking the thermo-hygrometric conditions previously recorded at the monumental complex of Santa Maria della Grotta. A datalogger was allocated inside the dryer to continuously monitor temperature and humidity levels. The Temperature and Relative Humidity (RH) data obtained during artificial ageing were later compared with the in situ measurements to ensure that comparable conditions were reproduced in the laboratory (Figure S1 of Support Information, SI).

Details about the characterization methods are reported in the SI.

4. Results and discussion

4.1. Tests on mock-ups

The laboratory evaluation aimed to assess the effectiveness and compatibility of the barium hydroxide nanoparticles as a consolidant for frescoes, in comparison with two commercial nanostructured products: nanosilica and nanolime. The tests were conducted on artificially aged mock-up specimens reproducing the stratigraphy and materials of the original frescoes. Colorimetric measurements were performed according to the UNI EN 15886 standard. Measurements were acquired before, after treatment and after artificial ageing with the consolidants on the same three selected areas on the surface of each pigment of mock-ups (red ochre and yellow ochre). Variation in the colour coordinates and total colour of the paint surface after treatment and after ageing are reported in Tables S1 and S1 of SI. Before aging, the lowest ΔE^* values were recorded for system A, both on red ochre (6.3) and yellow ochre (6.0), indicating acceptable chromatic compatibility. However, these values remain above the commonly accepted threshold ($\Delta E \approx 5$), highlighting a limitation in chromatic compatibility despite the relative improvement compared to the other systems [18]. This limitation will be addressed in future developments, by optimizing the concentration or modifying the application solution/solvent.

System B showed slightly higher values ($\Delta E^* \approx 8$), while nanolime (C) and nanosilica (D) caused more pronounced shifts ($\Delta E^* > 10$), due to whitening and increased surface saturation, respectively. After aging, system A maintained a stable chromatic profile ($\Delta E^* = 7.0$ and 6.6), confirming its long-term compatibility. System B exhibited a moderate increase ($\Delta E^* \approx 9.4$–9.7), likely due to superficial carbonation and uneven reactivity, reflecting its reduced performance compared to A. Nanolime (C) showed the most significant chromatic variation after aging, with ΔE^* rising to 14.2 on red ochre and 15.6 on yellow ochre, confirming its tendency to form a whitish veil that becomes more pronounced over time. Nanosilica (D) also presented a measurable increase in ΔE^* (11.5–12.0), likely related to optical modifications induced by the fluorosilane film, which intensifies lightness and colour saturation but alters the original perception of polychrome surfaces. Overall, system A demonstrated the best balance between initial chromatic compatibility and long-term stability, supporting its selection as the most appropriate consolidant for in situ applications on painted surfaces with historical pigments.

To assess the change in surface wettability induced by the consolidation treatments, the drop test was carried out.

Wettability test was performed by depositing a 10 µL drop of distilled water on the treated surfaces. This test provides insight into the hydrophilic or hydrophobic nature of the surface and is a key parameter for predicting how the material will behave in relation to moisture and environmental agents over time. Measurements were conducted both before and after artificial ageing, and no significant variation was observed, confirming the stability of the surface properties over time for all tested consolidants. As shown in Fig. 2, the formulations containing barium hydroxide (A and B) exhibited relatively low contact angles, indicating hydrophilic behaviour compatible with vapor permeability. System A showed a slightly higher contact angle than B, suggesting lower wettability, but still within the acceptable range for conservation purposes in humid conditions. The nanolime (C) displayed a contact angle of 0°, indicating complete absorption of the water drop, confirmingan highly hydrophilic surface, where the consolidant has no barrier effect against moisture. While this property favours breathability, it may also increase the risk of water ingress into the substrate. The fluorinated nanosilica showed the highest contact angle, indicating a marked hydrophobic behavior, consistent with the film-forming nature of fluorosilanes, which tend to create a protective surface layer, reducing wettability and capillary absorption. In hypogeal environments, it is essential to select consolidants that maintain low contact angle values, ensuring material reinforcement without blocking vapor diffusion and avoiding internal moisture accumulation. Treatments that increase hydrophobicity, such as those with nanosilica (D), may hinder water vapour permeability, limiting the surface's ability to "breathe". In the long term, this could favour degradation phenomena associated with capillary rise, interstitial condensation, or salt crystallization within the porous network. The results confirm that the barium hydroxide formulation offers a good compromise between effective consolidation and preservation of vapor permeability, making it a suitable choice for conservation applications in humid and subterranean contexts.

Fig. 2. Test of wettability consolidant systems.**A**=Ba(OH) $_2$ in 75% water, 25% isopropanol; **B**=Ba(OH) $_2$ in 75% isopropanol, 25% water ; **C**=nanolime; **D**= nanosilica.

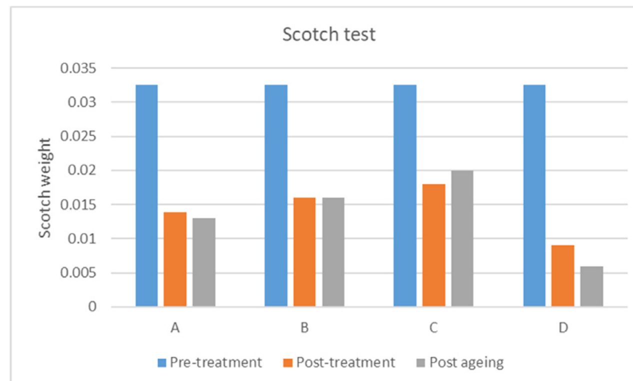

Fig. 3. Difference in scotch weight, pre- treatment, post treatment, post aging. **A**=Ba(OH)$_2$ in 75% water, 25% isopropanol; **B**=Ba(OH)$_2$ in 75% isopropanol, 25% water ; **C**=nanolime; **D**= nanosilica.

The peeling test was performed following the ASTM D3359 standard. The weight difference (Δ) before and after application was calculated and reported in Fig. 3.

The Scotch tape test was performed to evaluate the effectiveness of the consolidants in improving the superficial cohesion of the pictorial layer. The mass of material detached was measured before treatment, after application, and again after accelerated aging. All treatments led to a reduction in detached material compared to the untreated condition (≈ 0.032 g), indicating an improvement in surface stability. Among the tested products, nanosilica (D) exhibited the best performance, with a mass loss of 0.009 g after treatment and 0.006 g after aging. This confirms its effectiveness in consolidating the surface and maintaining cohesion over time. Nanolime (C) showed moderate performance, with a post-treatment value of 0.018 g, followed by an increase to 0.020 g after aging. These results are in line with existing literature, which reports reduced long-term effectiveness of nanolime in humid envi-

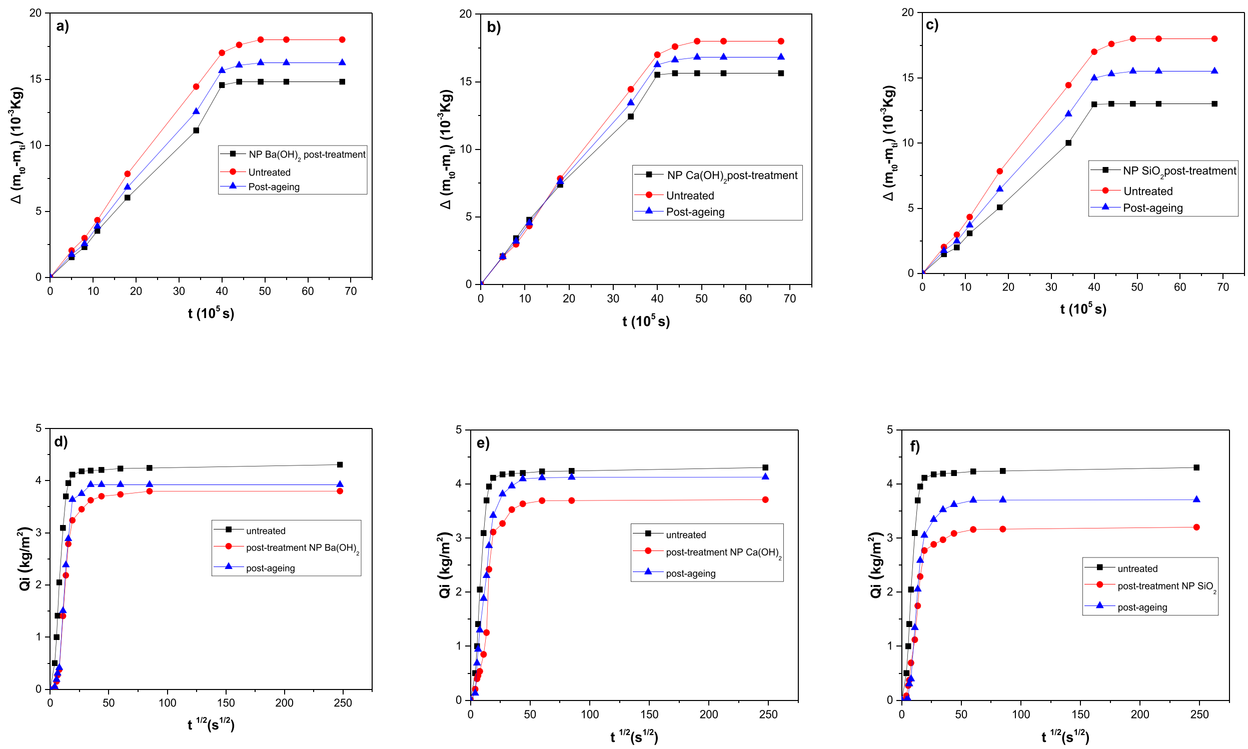

Fig. 4. UP). Amount of water absorbed per unit area, Qi, as a function of the square root of time at the three stages of analysis; before treatment, after treatment and after artificial ageing; a) nano barium hydroxide, b) nanolime, c) nanosilica. DOWN) Weight change, $\Delta(mt_0 - mt_i)$, versus time t_i at the three stages of analysis; before treatment, after treatment and after artificial ageing; a) nano barium hydroxide, b) nanolime, c) nanosilica.

ronments due to slow carbonation and surface whitening phenomena [ref]. The nano barium hydroxide systems also showed significant improvements. System A reduced the mass loss to 0.014 g after treatment and maintained a low value of 0.013 g after aging. In contrast, sample B showed a slightly higher post-treatment value of 0.016 g and a more evident increase after aging (0.016 g), suggesting reduced long-term stability. This may be attributed to superficial precipitation or less homogeneous penetration caused by the volatility of the solvent. In conclusion, the Scotch tape test highlights the importance of both initial consolidating performance and durability over time. While nanosilica (D) remains the most effective in enhancing surface cohesion, nano barium hydroxide (A) confirms its potential as a suitable and chemically compatible alternative for hypogeal environments.

Due to the above obtained results, the next test were performed only with the barium hydroxide dispersed in 75% water and 25% isopropanol (System A).

Water vapor permeability tests were conducted according to the UNI EN 15803 standard to assess the breathability of the substrate following treatment. The results, expressed as mass gain over time due to water vapor diffusion, are reported in Fig. 4-UP for the three consolidants.

In untreated samples, vapor transfer was consistent with the natural porosity of the lime substrate. Post-treatment results revealed varying degrees of reduction in vapor permeability, directly correlated with the pore blocking characteristics of each consolidant. The samples treated with nano barium hydroxide (Fig. 4A) maintained good vapor diffusion, with only a moderate decrease compared to the untreated samples. This suggests that the nanoparticle formulation preserves pore interconnectivity, likely due to a limited superficial deposition and a more internal interaction within the porous network. Nanolime (Fig. 4B) produced a similar trend, though slightly more vapor was retained. This behavior may be attributed to the carbonation process partially filling the pore spaces over time, especially after ageing. The nanosilica treatment (Fig. 4C) caused the most notable reduction in vapor permeability. The sharp decline indicates substantial surface pore obstruction, likely due to silica gel formation near the surface. While this enhances water resistance, it may adversely affect the long-term breathability required in hypogeal conservation. Among the tested treatments, nano barium hydroxide achieved the best balance, reducing excessive vapor flow while maintaining sufficient permeability to avoid moisture accumulation within the substrate, a crucial factor in preserving frescoes under hypogeal microclimatic stress.

The *capillary water absorption* behavior of treated and untreated mock-up specimens was evaluated according to UNI EN 15801. The results are reported in Fig. 4, where the cumulative water absorption (Q_i in kg/m²) is plotted against the square root of time, highlighting differences in absorption due to the applied consolidants. The untreated mock-up showed the highest absorption values, stabilizing at approximately 4.4 kg/m². This confirms the high capillarity and open porosity typical of lime-based substrates, which under hypogeal conditions can promote moisture transport and salt crystallization.

Treatment with nano barium hydroxide (Fig. 4D) led to a noticeable reduction in water uptake. The absorption curve reached a plateau earlier and at lower Q_i values (~3.9 kg/m²), indicating that the treatment effectively reduced capillary rise without completely obstructing the porous network. This suggests a pore lining action that is favorable in conserving both cohesion and vapor permeability. Nanolime (Fig. 4E) also exhibited reduced capillary absorption compared to the untreated control. However, the final absorption remained slightly higher (~4.0 kg/m²) than that of nano barium hydroxide. This may reflect incomplete carbonation in humid conditions or the formation of polymorphs with limited densification. The nanosilica (Fig. 4F) showed the most significant decrease in capillary water absorption, with a plateau around 3.6 kg/m². This reduction is attributed to the strong hydrophobic and pore blocking properties of silica nanoparticles. While effective in limiting water ingress, such occlusion could hinder vapor exchange, raising concerns about long-term compatibility in environments with fluctuating humidity. In all cases, post-aging measurements showed slight increases in absorption values compared to freshly treated mock-up, particularly in nanolime samples, possibly due to progressive carbonation or microcracking. Nevertheless, nano barium hydroxide maintained stable performance, reinforcing its suitability as a consolidant in humid microclimates where both moisture management and breathability are essential.

The SEM-EDS investigation was carried out on cross-sections of the mock-up treated with system A (barium hydroxide dispersed in 75% water and 25% isopropanol), in order to assess the distribution and penetration depth of the consolidant within the fresco matrix. A SEM micrographs and the EDS spectra acquired from different areas of the sample, from the surface to the deeper layers are reported in Figure S2 of SI. For each spectrum, the barium content was expressed as weight percentage (% Ba), used as a direct indicator of the consolidant's presence**.** The results show a progressively decreasing distribution of barium as a function of depth: average values start above 28 wt% in the outermost layer (Spectrum 1) and gradually decrease to around 12 wt% in the deeper zones (Spectrum 5). This trend confirms an effective yet controlled penetration, consistent with the low-viscosity formulation and its good affinity with the porosity of the substrate. The absence of surface accumulation or structural discontinuities, as observed in SEM micrograph, further supports the hypothesis of a homogeneous and well-distributed consolidation, capable of reinforcing the material without clogging the pores or impairing the breathability of the substrate. Overall, the analysis confirms that system A achieves a balanced performance between consolidation efficacy and physicochemical compatibility.

4.2. Test in situ

The test in situ were performed on selected areas of to hypogea contests, Santa Maria della Grotta and Crispia Sanvia, belonging to the Lilibeum Archeological Park (Italy) [19]. Santa Maria della Grotta is an hypogea complex composed of interconnected rock-cut chambers, preserving several medieval mural paintings dated between the 12th and 14th centuries A.D. The hypogeum, which originally served as a monastic space for a Basilian community of the Greek rite, is now partially incorporated into an 18th-century semi-hypogeal church [20,21]. Access to the underground rooms is currently through the main entrance of the church, which connects the upper and lower spaces via a staircase carved into the rock. The subterranean location and partial isolation from the external environment define this site as a hypogeum. A microclimatic survey revealed consistently high levels of relative humidity throughout the year, due to the porous nature of the local calcarenite and the presence of capillary water rise, infiltration, and condensation. These environmental conditions pose critical challenges to the preservation of mural paintings. Salt efflorescence, sub-efflorescence, and chromatic alteration have been observed, mainly constituted by sulphates, often resulting in plaster detachment, flaking, and loss of the pictorial layer. The degradation phenomena are consistent with those typically encountered in rupestrian hypogea and significantly impact conservation strategies. For application in situ of the three consolidants, two frescoes were selected, a fresco located in the south room (Virgin and St. Vitus) and a fresco located in the north room (The Theory of the Saints). The barium hydroxide system selected for the in situ applications was System A ($Ba(OH)_2$ in 75% water / 25% isopropanol), as it demonstrated superior performance compared to System B during laboratory testing. In particular, system A showed better wettability, more stable colorimetric coordinates, and improved surface adhesion, making it the most suitable choice for application on site. The used dispersion (10 g/L, 75:25 water:isopropanol) contains three barium hydroxide particle morphologies. Type 2 and Type 3 show acicular shapes: Type 2 consists of long, radially arranged needles (∼163 nm), while Type 3 forms shorter bundled nanocrystals (∼53 nm). Type 1 displays disordered nanosheet aggregates with the smallest dimensions (∼50 nm), indicating less oriented growth. The performance of the consolidants was evaluates carring out pre- and post-treatment through scotch tests to assess the consolidation of the paint film, through contact sponge tests to assess the consolidation of the constituent layers of the fresco and through colorimetry to assess the variation of the surface colour. Monitoring after 12 months was carried out through contact sponge test. Three areas measuring 20 × 20 cm were selected on each fresco where the consolidating systems were applied (Fig. 5).

Prior to the application of the three consolidating systems, the intervention phases initially included the removal of the surface deposit by means of pads soaked in deionised water (Fig. 5, left) and the subsequent desalination with desalinating extractive compresses to remove as much as possible of the salts present in the constituent layers of the fresco. The desalinating extractive compresses, consisting of a mixture of sepiolite and cellulose pulp in a 1:1 ratio (Fig. 5, right), were applied to the surface of the fresco, placing Japanese paper between the compress and the surface to facilitate the removal of the compress once dry (Fig. 5, center). The salt extraction was monitored using conductivity measurements (not reported). Once the cleaning phase was completed, the consolidating solutions (nanolime, nanosilica and nano barium hydroxide) were applied to the respective test areas by brush. Below are the results obtained pre-application, post-application, after six months and after 12 months.

The average values of ΔL^*, Δa^* and Δb^* and ΔE^* are shown in Tables S3 and S4 of SI and provide a quantitative assessment of the visual impact of the intervention. The chromatic variations ΔE^* observed after treatment show different behaviors depending on the type of pigment and the consolidant used. On the Theory of the Saints fresco, the lowest alterations were recorded for pigments yellow A ($\Delta E^* = 3.8$) and grey A ($\Delta E^* = 2.6$), both treated with nanolime, confirming the good chromatic compatibility of this product on cool and neutral tones. However, still with nanolime, red shows a significant variation ($\Delta E^* = 11.9$), associated with considerable lightening ($\Delta L^* = 6.5$), suggesting that red pigments may be more sensitive to interaction with this consolidant, possibly due to the whitish veil caused by lime carbonation. The area treated with nano barium hydroxide shows intermediate variations: the orange pigment displays a $\Delta E^* = 5.4$, while red B reaches $\Delta E^* = 6.8$.

In the Virgin and St. Vitus mural, the chromatic changes are more pronounced. In particular, pigments treated with nanosilica show the highest ΔE^* values: red C ($\Delta E^* = 19.5$) and yellow ($\Delta E^* = 31.7$), with significant increases in lightness ($\Delta L^* = 14.1$ and 21.4), indicating a strong whitening effect and intense chromatic alteration. This behavior can be attributed to optical modifications induced by the nanosilica film, which increases brightness and saturation but alters the original perception of polychrome surfaces. Pigments treated with nano barium hydroxide on the other hand, exhibit more limited variations, such as yellow ($\Delta E^* = 8.6$), brown ($\Delta E^* = 7.9$), and red ($\Delta E^* = 6.8$), suggesting good chromatic compatibility with minimal visual changes. Finally, nanolime shows heterogeneous behavior: low ΔE^* values for some pigments ($\Delta E^* = 3.8$ for yellow), but values above 11 in

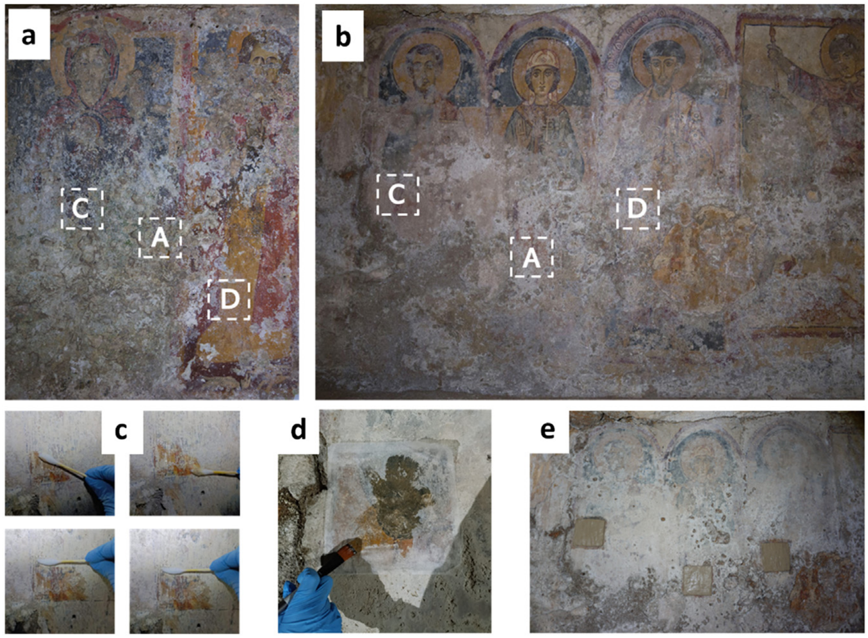

Fig. 5. UP) Areas of the frescoes depicting the Virgin and St. Vitus (a) Theory of the Saints (b) on which the experimentation was carried out. (A= $(Ba(OH)_2$ in 75% water / 25% isopropanol; C=nanolime; D= nanosilica). DOWN) Removal of surface deposits using swabs soaked in deionised water (c); application of Japanese paper (d); extractive desalting compresses (cellulose pulp and sepiolite mixed in a 1:1 ratio with deionised water) (e).

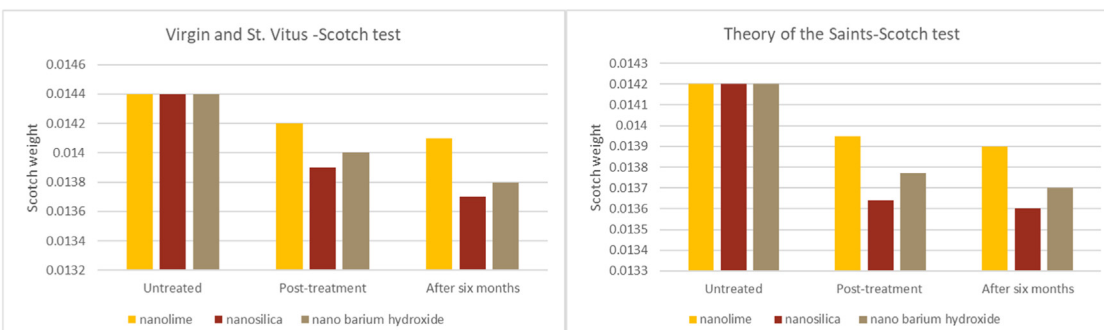

Fig. 6. Scotch test pre-, post-treatment and monitoring after six months.

other cases (red and grey), confirming its tendency to interact variably, especially on red and dark surfaces. The Scotch test was performed by weighing the tape both before and after treatment and 6 months after treatment on three different areas of the treated surface in order to average the three measurements (Fig. 6).

All three nanostructured consolidants reduced the amount of material removed compared to the initial condition, indicating an improvement in surface cohesion. Nanosilica showed the best performance, with a stable reduction in detachment both immediately after application and after six months. Nanolime had positive initial effectiveness, but a slight loss of performance over time, probably due to slow carbonation in a humid environment. Nano barium hydroxide offered intermediate results, maintaining good long-term stability.

The weight of sponge before, after application, after six months and after 12 months, obtained through the contact sponge method, is shown in Fig. 7.

The Contact Sponge Test was performed to estimate the reduction in surface water absorption following the application of three consolidants: nanolime, nanosilica and nano barium hydroxide. Under the initial conditions, all treated surfaces showed a significant reduction in absorption compared to the untreated area, which had values above 5 g. Among the products, nanosilica showed the greatest effectiveness in limiting absorption, followed by barium hydroxide and finally nanolime. After six months, the results remain stable, with slight variations. Nanosilica continues to show excellent resistance to water absorption, indicating a good durability of the treatment. Nano barium hydroxide also maintains consistent performance over time. On the contrary, the nanolime, while showing an initial improvement, shows a slight increase in absorption after six months, especially on the painting Theory of Saints, suggesting a partial loss of effectiveness. After 12 months, the results show a further general decrease in water absorption in all treated areas, confirming the lasting effect of the consolidants. In particular, nanosilica shows almost zero absorption values, indicating a protective barrier on the surface. Nano barium hydroxide also maintains low absorption values, proving to be an effective and durable treatment. Nanocalcium, on the other hand, shows a more marked decline in performance, with slightly higher absorption values than the other consolidants. The tests performed, scotch test, contact sponge test and colour measurements, made it possible to evaluate the effectiveness of three treatments for the consolidation of the frescoes in Santa Maria della Grotta. Nanolime showed good efficacy for the consolidation of the inner layers. However, poor effectiveness in consolidating the paint film and variable results in colour change were evident, with some areas

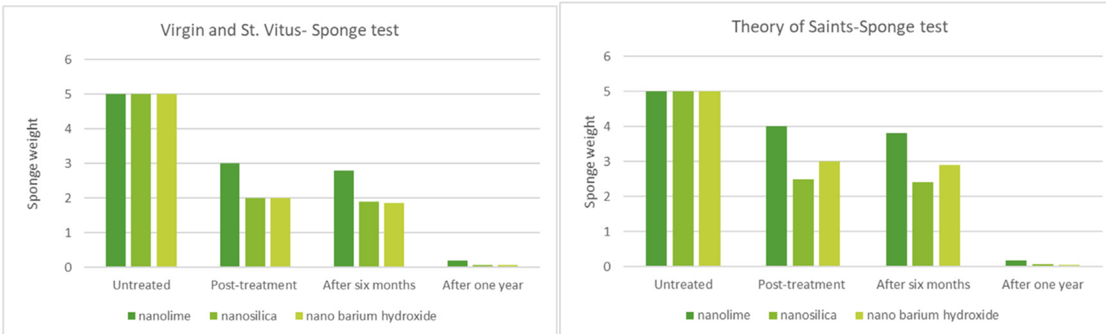

Fig. 7. Contact sponge test pre, post application after six months, and after one year.

where the change was visible. In detail, the nanosilica was very effective in reinforcing the cohesion of the paint film and reducing water absorption, but at the same time it gave water repellency to the surface, an aspect that can block the natural breathability of the frescos, which is not suitable in hypogeal environments. It also caused the most noticeable colour changes, especially in the red and yellow pigments. Barium hydroxide proved to be the nanostructured system with the best performance. It offers good consolidation, reduces water absorption without creating impermeable barriers and maintains the original appearance almost unchanged, with limited colour changes. This makes it particularly suitable for frescoes located in environments where it is essential that moisture can circulate freely. In conclusion, among the three treatments, barium hydroxide is the most suitable choice to guarantee protection, stability and respect for the original material in critical environmental conditions.

In situ applications were also carried out at the Crispia Salvia hypogeum, with the aim of comparing the results obtained with those recorded at the Santa Maria della Grotta Monumental Complex. At this site, it was decided to test System A ($Ba(OH)_2$ in 75% water / 25% isopropanol), once again. The decision to test the same consolidant was motivated by the similar nature of the two environments, both underground, characterised by similar thermo-hygrometric conditions and comparable degradation phenomena. The main objective of the intervention was therefore to evaluate the behaviour of nano barium hydroxide on frescoes located in two different conservation contexts but sharing the same degradation problems, in order to compare the effectiveness of the treatment and its durability over time. The painted hypogeum of Crispia Salvia [22,23] dates back to the 2nd-4th century AD. Access is via a dromos carved into the rock, which leads to a burial chamber with six tombs arranged along the walls. The interior surfaces are decorated with polychrome frescoes. For the experiment with barium hydroxide, an area was selected that showed active signs of deterioration, such as pulverisation and partial detachment of the surface paint layer. The effectiveness of the treatment was evaluated in situ through three tests carried out in accordance with current standards: Colorimetric measurements (UNI EN 15886) to assess color variations on the surface; the Scotch Tape Test to evaluate surface cohesion; and the Contact Sponge Test (UNI 11432:2011) to determine water absorption capacity. Three months after the intervention, a monitoring campaign was conducted, repeating the Scotch Tape Test and the Contact Sponge Test in order to verify the long-term stability of the consolidating effect.

The following sections describe in detail the operational phases of the intervention and the results obtained. The application was carried out on an area measuring 20 × 20 cm, after a preliminary mechanical cleaning of incoherent surface deposits using soft-bristle brushes. In this case, it was not necessary to perform cycles of extractive poultices, as no significant efflorescence or saline concretions were observed. The dispersion was applied by brush onto the selected area to saturation, in order to ensure adequate penetration of the consolidant into the substrate. The results obtained before the application and three months after the treatment are reported below. The testing procedures followed were the same as those previously described for the Santa Maria della Grotta Complex. The average values of ΔL^*, Δa^* and Δb^* and ΔE^* are shown in Table S5 of SI provide a quantitative assessment of the visual impact of the intervention. Colorimetric analysis revealed limited variations after application of system A. The yellow and red pigments showed an increase in brightness (ΔL^*) and higher ΔE^* values, indicating a slight lightening effect, while the brown pigment showed a shift towards cooler tones (negative Δb^*). The background showed minimal variations ($\Delta E^* = 3.1$).

The Scotch Test was performed to evaluate the effectiveness of the consolidating system in improving surface cohesion. Measurements were taken on three different areas to ensure reliable and representative results, and the average value was calculated. The difference in weight (Δ) before and after application, and after three months, is shown in Figure S3 of SI. The Scotch test results show a clear decrease in the weight of the tape after treatment with barium hydroxide, from approximately 0.014 g to 0.010 g, with values remaining stable after three months. The Contact Sponge Test was performed to assess the water absorption of the substrate. The Sponge Test results show a marked decrease in water absorption after treatment with barium hydroxide, with sponge weight dropping from 6 g to 4 g. The tests carried out, including the Scotch Test, Sponge Test and colorimetric measurements, made it possible to evaluate the performance of the barium hydroxide-based consolidant at the Crispia Salvia hypogeum and also to compare the results with those obtained at the Monumental Complex of Santa Maria della Grotta. The data indicate a significant improvement in surface cohesion and a marked reduction in water absorption, both of which were maintained after three months, demonstrating the long-term stability of the treatment. Colorimetric measurements showed only limited variations, in particular a slight lightening of the yellow and red pigments, without compromising the visual appearance of the frescoes. Overall, the barium hydroxide-based system confirmed its effectiveness and compatibility in underground environments, ensuring consolidation without hindering the natural moisture exchange of the substrate.

5. Conclusions

The conservation of wall paintings in hypogeal environments requires specific approaches capable of dealing with the extreme conditions that characterise these contexts: high humidity, low ventilation, presence of soluble salts and continuous cycles of condensation and drying. Under such conditions, the choice of a consolidant cannot be limited to mechanical effectiveness, but must take into account chemical compatibility with the substrate, breathability of the treated material and stability over time. This study proposed an comparison of three nanostructured consolidants, nanolime, nanosilica and nano barium hydroxide, through a combination of laboratory tests and in situ applications on the two hypogea complex of Santa Maria della Grotta and Crispia Salvia in Marsala (Italy). The integrated approach made it possible to evaluate the behaviour of the products under controlled analysing fundamental parameters such as capillary absorption, colour variation, surface cohesion, vapour permeability and the distribution of the consolidant within the substrate. The results obtained indicate that barium hydroxide, (75% water and 25% isopropanol), guaranteed a balanced combination of consolidation effectiveness, aesthetic compatibility and maintenance of breathability. Compared to the other consolidants tested, it showed good penetration, less colour alteration and more stable behaviour over time, even after six months of monitoring in an underground environment. Nanosilica, although very effective in terms of cohesion, showed limitations related to the formation of surface films and reduced breathability, critical aspects in damp contexts. Nanolime, although chemically compatible, showed inferior performance in terms of stability and adhesion and high colour variation, with formation of surface whitening. In conclusion, the nano barium hydroxide consolidant proved to be a promising solution for the conservation of frescoes in hypogea environments. These results open new perspectives for the use of innovative materials in the conservation of cultural heritage in contexts characterised by critical thermo-hygrometric values and high humidity.

Author contributions

MLS: Conceptualization and methodology, writing–review and editing. CT: Mock-up preparation and aging, characterization. FA: Colorimetric measurements. GC and SMM: SEM investigation. All authors contributed to the article and approved the submitted version.

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Data availability statement

The datasets generated during and/or analysed during the current study are available from the corresponding author on reasonable request.

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.culher.2026.05.005.

References

[1] K. Elert, B. Biçer-Simşir, E. Correa, C. Rodriguez-Navarro, D. Gulotta, Surface characterization of consolidated earthen substrates using an innovative multi-analytical strategy, Constr. Build. Mater. 438 (2024) 137154, doi:10.1016/j.conbuildmat.2024.137154.

[2] B. Sena da Fonseca, Current Trends in stone consolidation research: an overview and discussion, Buildings 13 (2023) 403, doi:10.3390/buildings13020403.

[3] D. Pinna, B. Salvadori, S. Porcinai, Evaluation of the application conditions of artificial protection treatments on salt-laden limestones and marble, Constr. Build. Mater. 25 (2011) 2723–2732, doi:10.1016/j.conbuildmat.2010.12.023.

[4] S. Iafrate, G. Sidoti, F.E. Capasso, M. Giandomenico, S. Muca, V. Daniele, G. Taglieri, New perspectives for the consolidation of mural paintings in Hypogea with an innovative aqueous nanolime dispersion, characterized by compatible, sustainable, and Eco-friendly features, Nanomaterials 13 (2023) 317, doi:10.3390/nano13020317.

[5] G. Borsoi, B. Lubelli, R. van Hees, R. Veiga, A.Santos Silva, Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties, Constr. Build. Mater. 142 (2017) 385–394, doi:10.1016/j.conbuildmat.2017.03.097.

[6] M.E. David, R.-M. Ion, R.M. Grigorescu, L. Iancu, E.R. Andrei, Nanomaterials used in conservation and restoration of cultural heritage: an up-to-date overview, Materials 13 (2020) 2064, doi:10.3390/ma13092064.

[7] C. Rodriguez-Navarro, A. Suzuki, E. Ruiz-Agudo, Alcohol dispersions of calcium hydroxide nanoparticles for stone conservation, Langmuir 29 (2013) 11457–11470, doi:10.1021/la4017728.

[8] A. Martínez-Arredondo, V.E. García-Vera, D. Navarro-Moreno, A.J. Tenza-Abril, M. Lanzón, Calcium hydroxide, magnesium hydroxide, silicon dioxide nanoparticles and their combinations as consolidants for lime mortars and gypsum plasters, J. Cult. Herit. 68 (2024) 17–27, doi:10.1016/j.culher.2024.05.004.

[9] R. Albini, L. Campanella, B. Mazzei, Il consolidamento con idrossido di calce nano strutturata in ambiente ipogeo, Lo Stato Dellarte 10 X Congr. Naz. IGIIC, 2012 https://www.academia.edu/25602933/Il_consolidamento_con_idrossido_di_calce_nano_strutturata_in_ambiente_ipogeo accessed October 16, 2025.

[10] B. Baiza, M. Gil, C. Galacho, A. Candeias, P.I. Girginova, Preliminary studies of the effects of nanoconsolidants on mural paint layers with a lack of cohesion, Heritage 4 (2021) 3288–3306, doi:10.3390/heritage4040183.

[11] J.S. Pozo-Antonio, J. Otero, P. Alonso, X. Mas i Barberà, Nanolime- and nanosilica-based consolidants applied on heated granite and limestone: effectiveness and durability, Constr. Build. Mater. 201 (2019) 852–870, doi:10.1016/j.conbuildmat.2018.12.213.

[12] E. Tesser, A. Conventi, F. Majerle, Characterization of barium hydroxide used as consolidating agent for monumental surfaces in Venice, Heritage 5 (2022) 3280–3297, doi:10.3390/heritage5040168.

[13] Y. Rong, J. Yang, S. Huang, Y. Li, Barium hydroxide nanoparticle–phosphoric acid system for desalination and consolidation of tomb murals, Crystals 12 (2022) 1171, doi:10.3390/cryst12081171.

[14] P. Baglioni, Nanoparticles for cultural heritage conservation: calcium and barium hydroxide Nanoparticles for wall painting consolidation, Chem. - Eur. J. (2010), doi:10.1002/CHEM.201001443.

[15] Chiara Tuccio, Francesco Armetta, Delia Francesca, Chillura Martino, Ramunas Skaudžius, Maria Luisa Saladino, Controlled synthesis of alkali metal hydroxide particles via solvothermal processing, (2025).

[16] UNI EN 15801 - Liquid water absorption, (n.d.) 2000.

[17] UNI EN 15803 - Water vapour permeability, (n.d.) 2000.

[18] A. Lo Monaco, M. Marabelli, C. Pelosi, R. Picchio, Colour measurements of surfaces to evaluate the restoration materials, SPIE Proc. (2011), doi:10.1117/12.889147.

[19] P. Tisseyre, Un'abbazia basiliana nel XIII secolo : santa Maria della Grotta a Marsala ; lo scavo e i materiali /Philippe Tisseyre. –1995 In: Federico e la Sicilia : dalla terra alla corona. – [Siracusa], Ediprint (1995) n.d. https://www.academia.edu/2066829/Unabbazia_basiliana_nel_XIII_secolo_Santa_Maria_della_Grotta_a_Marsala_lo_scavo_e_i_materiali_Philippe_Tisseyre_1995_In_Federico_e_la_Sicilia_dalla_terra_alla_corona_Siracusa_Ediprint_1995 . accessed October 16, 2025.

[20] R. Giglio, Lilibeo (Marsala): nuove scoperte archeologiche nell'area di Santa Maria della Grotta e del complesso dei Niccolini, Sicil. Archeol. (1997) 45–58 XXX 939495 1997.

[21] R. Abate, G. Lauria, M.G. Griffo, L. Sineo, The «painted» hypogeum of Crispia Salvia (Marsala-TP) – 2nd century C.E. Preliminary anthropological and archaeological report of tomb 3 and tomb 4, Arch. Antropol. E Etnologia 151 (2021) 109–124, doi:10.36253/aae-2230.

[22] R. Giglio, Marsala : recenti rinvenimenti archeologici alla necropoli di Ulibeo : l'ipogeo dipinto di Crispia Salvia, Sicil. Archeol. (1996) 31–51 XXIX 909192 1996.