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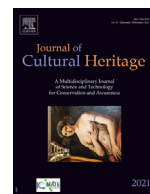
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Original article

Applicability and efficacy of an enhanced nanolime consolidation technique for British Museum limestone objects

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ABSTRACT

Stone consolidation is one of the most important and complex treatment actions performed in museums. However, products routinely applied on limestone objects are often chemically incompatible with the treated substrate. Despite the established efficiency of nanolime for outdoor conservation and its chemical compatibility with the carbonate mineral matrix, its performance in a museum context needs to be verified. As a result, this work addresses a shortcoming in the field of Stone Conservation as nanolime has never been officially introduced in museums before. Three British Museum limestone objects affected by superficial damages were treated using an Enhanced Nanolime Consolidation Technique (En–NCT) which was developed in the Materials Engineering Research Institute (Sheffield Hallam University) and tested for the first time in a museum context. The results show that the use of alcoholic nanolime by means of a tailored consolidation technique is a realistic and promising museum conservation approach. The En–NCT does not impair the aesthetical appearance of the objects and restores the mineral cohesion of the treated surface by increasing the hardness of the near-to-surface layers.

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Introduction

Stone consolidation is one of the most important and complex treatment actions performed in museums. However, organic products applied to consolidate limestone objects are often chemically incompatible with the treated carbonate substrate. Besides, in addition to this lack of compatibility, the use of acrylics, (alkoxy)silanes, poly-vinyl/butyl acetate-based polymers, and epoxy resins used to consolidate carbonate stones can lead to the following issues: irreversibility of the treatment [1]; limited penetration; poor chemical bonding with the carbonate mineral matrix and difficulty to control the spreading and the migration of the product in the stone [2]; cross-linking, brittleness, and cracks affecting the consolidating film during polymerisation [3,4]; and finally, alteration at a varied extent of physical properties (e.g.

thermal expansion, water vapour permeability, drying kinetics, and chromatic variation) of the treated substrate [5–7]. Nowadays, the conservation of carbonate stones benefits from the development of new consolidation techniques. Indeed, the use of diammonium hydrogen phosphate (DAP) and ammonium (phenyl/monomethyl) oxalate [8,9], tetraethyl orthosilicate-based products (KSE 100, KSE 300 E/HV, for instance) [10], or hybrid treatments using modified alkoxy-silane-based polymer (TEOS) doped with hydroxyapatite and SiO₂ nanoparticles, showed promising outcomes [11–13]. Unfortunately, examples of application of these products in museums are scarce and their performance remains to be established in such context of conservation. Nanolime offers a promising alternative to the previously listed products. The consolidation of porous calcareous substrates with nanolime is a conservation approach which showed a growing importance since the 2000's [14]. Nanolime restores the cohesion of the carbonate matrix by regenerating mineral bridges with new calcite crystals [15–17]. Nanolime offers other advantages related to the size of lime particles [18]. Indeed, surface area per unit volume increases when the size of the particles is reduced, therefore, the reactivity of the nanoparticles is enhanced [19]. During the past decades, research have been conducted to optimise the performance of the nanolime with the view of improving the penetration and

Abbreviations: DIW, De-Ionised Water; En–NCT, Enhanced Nanolime Consolidation Technique; EvR, Evaporation Rate; hbp, HighBoiling Point; hks, High Kinetic Stability; IMS, Industrial Methylated Spirit; lbp, Low Boiling Point; lks, LowKinetic Stability; N/MDT, Non/Minor Destructive Techniques; UAH, Ultrasonic Air Humidification.

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carbonation processes [20–29]. Recently, an innovative nanolime dispersion patented by the University of L'Aquila has also been developed to overcome the limitations of nanolime synthesised with the “bottom-up” route [30,31]. This new nanolime dispersion synthesised by mixing a calcium chloride (CaCl_2) aqueous solution with an anionic (CaCl_2) aqueous solution with an anionic exchange resin (in OH^- form) allows a complete carbonation of nanolime in a couple of hours, using a green approach which avoids the use of organic and volatile chemical compounds. Applications of this new aqueous nanolime dispersion in the field of built heritage conservation show promising outcomes when applied on biocalcarenites [32], historical mortars [33,34], and earthen plasters [35]. Despite its well-established efficiency for the consolidation of wall paintings and frescoes [15,36–39], plasters and renders [40–43], lime-mortars [44,45], and architectural limestone works [46], alcoholic commercial nanolime has never been officially used on museum limestone objects. This study aims to address this shortcoming by presenting the work carried out at the British Museum and in collaboration with Sheffield Hallam University (SHU). An Enhanced Nanolime Consolidation Technique (*En-NCT*) developed in the Materials & Engineering Research Institute at SHU and tailored for museum applications was applied for the first time in a museum context to consolidate deteriorated objects kept in storage because of their unstable condition. This paper introduces the *En-NCT* and provides details regarding its application on three British Museum limestone objects characterised by powdering and crumbling surfaces affected by peeling, flaking, scaling, and hairline cracks. Results show that the use of the *En-NCT* on museum collections is possible and confirm that alcoholic nanolime could be used for the consolidation of precious limestone objects in order to ensure their reintroduction into galleries for the benefit of future generations.

Research aim

Existing museum consolidating techniques for enhancing the strength of limestone objects are incompatible from both a material mismatch point of view and aesthetical reasons. This gives museum curators a problem in that their options are either to use incompatible products for conservation treatments or to keep priceless objects in storage, for fear of further damage to the already fragile surface. The aim of the *En-NCT* is to overcome both the material incompatibility and aesthetical issues. This will enable museum collections to be confidently strengthened in a safe and reliable manner for future generations to enjoy. Finally, research carried out at the British Museum aims to show that the introduction of nanolime in a museum context is a promising conservation approach.

Material and methods

Limestone objects

In agreement with the Keepers of the Department of Greece and Rome and the Department of Egypt and Sudan, the curators and the Head of Inorganics Conservation; three British Museum limestone objects (referred as Objects A, B, and C) from the Greek, Roman and Egyptian storage collections (Fig. 1), were selected for consolidation by the *En-NCT*. Objects A–C shows decay patterns such as powdering and crumbling surface with the presence of scaling, flaking, and peeling, and hairline cracks [47].

Nanolime and chemicals

Two commercial alcoholic nanolime dispersions were used for the conservation treatments, these are : CaLoSiL® E5 (5 g/L of $\text{Ca}(\text{OH})_2$ in ethanol) and Nanorestore Plus® E5 and E10 (5



Fig. 1. Selected British Museum objects consolidated by the *En-NCT*.

and 10 g/L of $\text{Ca}(\text{OH})_2$ in ethanol, respectively. Particle size of CaLoSiL® and Nanorestore Plus® dispersions range from 50 nm to 150 nm and from 100 nm to 300 nm, respectively. A description of the physical-chemical properties of CaLoSiL® and Nanorestore Plus® nanolime can be found in the literature [14,18,48,49]. Three types of alcohols were also used to dilute the nanolime dispersions, these are: ethanol (96%), 1-butanol (99.8%), and 2-propanol (99.5%), all supplied by Merck® Chemical.

Description of the *En-NCT*

En-NCT has been developed by taking into consideration the different practical recommendations mentioned in the literature [31–34,43,50–54]. The technique, summarised in Fig. 2, is divided in four steps, these are steps: (i) Assessment of the nature and condition of the object, (ii) Pre-wetting the surface, (iii) Consolidation of the pre-wetted surface, and (iv) Curing of the treated substrate.

Assessment of the nature and condition of the object

An assessment of the type(s) and extent of the damage affecting the object is the first step of the treatment. Macroscopic observations using visible or UV light should primarily be used. More thorough examination of the structural cohesion with Non/Minor Destructive Technique could be considered [55–58]. Then, the area to be treated should be examined and any materials left by previous restoration, salt (sub)efflorescence, microbiological growth, or any deposits encrusted over the surface should be removed, as they could create a barrier layer which could prevent the penetration of the nanolime. The penetration of the nanolime from the treated surface is also influenced by the porosity, the type of the mineral matrix (i.e. grain size), and the surface wettability. Ideally, these properties should be determined before applying the *En-NCT* as they can influence the treatment performance. The use of analytical techniques (i.e. Mercury Intrusion Porosimetry, stereomicroscopy and polarised light microscopy, for instance) or standards BS EN 1936:2006 [59] and ASTM C-20 (2015) [60], EN 15,801 (2009) [61] and EN 16,322 (2013) [62] could be considered. However, the analytical techniques or the standards previously mentioned involve a destructive testing process and the necessity to work on samples with specific size and shape. Therefore, an alternative approach allowing a less invasive assessment was proposed, to carry out tests directly on the museum objects without further deteriorating the stone matrix.

Observation of the surface to be consolidated using a portable Dino-Light® digital microscope can help in determining the grain-size of the limestone matrix at the near-to-surface layers. In

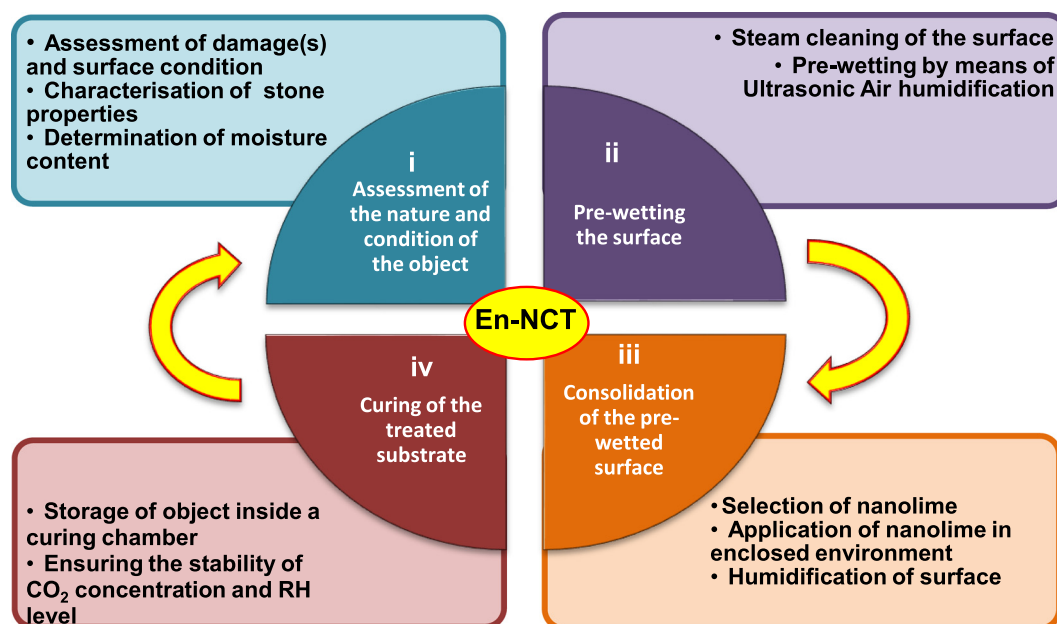


Fig. 2. Synopsis presenting the four main practical steps of the *En – NCT*.

In addition to this, a wetting test using de-ionised water (DIW) applied with a pipette determines the permeability of the mineral matrix near to the surface. For this test, a droplet of DIW is pipetted over the surface and both the adsorption (the binding mechanism of liquid molecule to a solid substrate) and drying kinetics are assessed during the first 2 mins. It will be noted that this method relies on a visual assessment and to be as accurate as possible, the surface of the object should be cleaned, and the test should be carried out in an enclosed environment and at room temperature. DIW was selected for the test because of its evaporation rate (*EvR*) which is similar to *n*-butyl acetate (*EvR* of *n*-butyl acetate = 1). *EvR* > 1 indicates a more rapid evaporation rate, whereas *EvR* < 1 translates a slower evaporation rate. Lastly, the conservator should ensure that there is a reduced moisture content in the object. Indeed, applying the nanolime on a wet porous matrix, or pre-wetting the surface with a high quantity of solvent that takes time to evaporate, might affect the penetration of the product. In this case, the pores located near to the surface could be overfilled with the solvent molecules, thus preventing the migration of nanolime through the treated surface [28]. Although the presence of moisture helps to limit the back-migration of alcoholic nanolime toward the treated surface [20–23,63,64], it was demonstrated that applying an alcoholic dispersion on a wet porous substrate might cause adverse effects. Previous work [22,23,65] established that water can affect the kinetic stability of alcoholic nanolime due to the action of short-range attractive Van der Waals forces, which could cause a risk of sedimentation and aggregation of the $\text{Ca}(\text{OH})_2$ nanoparticles. Rodríguez-Navarro et al. [66] acknowledged that $\text{Ca}(\text{OH})_2$ nanoparticles dispersed in ethanol react with the water forming a hydro-alcoholic layer of calcium alkoxide which drastically reduces the carbonation rate of the nanolime. Consequently, a too high moisture content inside the porous limestone matrix could facilitate the formation of calcium alkoxides which could affect the nucleation of the nanolime into stable calcite over time. This excess of humidity in the stone could also increase the yield of hydrated and anhydrous CaCO_3 phases, and if calcium alkoxide is present in the system, the yield of unstable polymorphs which possess different crystallinities and are more unstable than calcite is likely to increase even more after the hydrolysis of calcium alkoxides [67,68]. This could affect the whole nucleation process of the nanolime which follows the Ostwald's

step rule [69]. Therefore, although the use of alcoholic nanolime with reduced kinetic stability (i.e. nanolime diluted in water) [21,63] and aqueous nanolime dispersions [32–35] proved to be efficient when applied on different calcareous substrates, museum conservators should be aware that applying alcoholic nanolime on a wet limestone substrate can affect the treatment performance. If the condition of the surface is stable enough and if there is only residual dampness, the area to consolidate could be dried with a hair drier on a low setting (i.e. low airflow and safe working distance). To measure the moisture content, the conservator can use a digital protimeter calibrated to monitor the humidity inside building materials. If the limestone is too damp, and if the object is not affected by salts issue, it is recommended to leave the object in a dry and ventilated environment for couple of days (period to be adapted in relation to the size of the object/damp area).

Pre-wetting the surface

Before applying the nanolime, the stone surface should be pre-wetted. It has been acknowledged that this action can improve the adhesion and penetrability of the nanolime [20–23,28,52]. Based on the experiments carried out in the laboratory on fine-grained limestones, it was decided that the pre-wetting technique would be a combination of steam cleaning (~3 bars, 120 – 130 °C) and ultrasonic air humidification (UAH- humidifier with a spray volume capacity of 25 – 35 mL/h). UAH provides a fine wet mist and avoids inserting too much moisture into the pores. The pre-wetting technique is described as follows: first, the surface is steam cleaned for a period of five minutes maximum, followed by a cooling period of one to two minutes. The conservator should ensure a safe working distance (WD) between the nozzle of the steam cleaner and the surface of the object (i.e. WD > 30 cm). Then, the area is submitted to an enclosed damp environment for a period of 30 mins, by means of UAH. Periods selected for the steam cleaning and the UAH were determined upon completion of assessment tests carried out in the laboratory on fine-grained Lavoux limestone samples. Results obtained with the phenolphthalein (pH indicator showing the presence of the nanolime by turning purple) revealed that depending on the pre-wetting periods observed, the penetration of nanolime through the treated surface was affected to different extents (see Fig. A - Supplementary materials). Following UAH, a drying period should be observed to allow the evaporation of

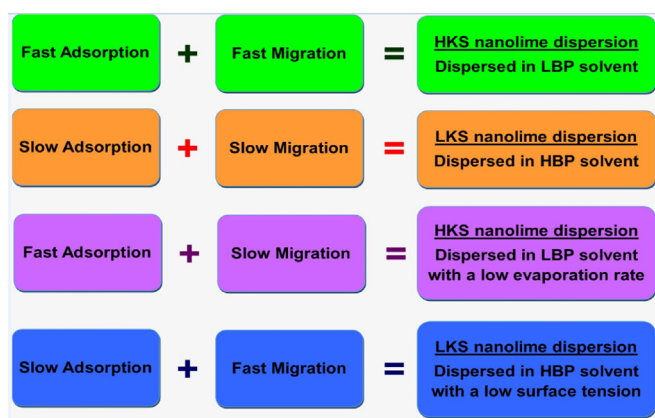


Fig. 3. Kinetic model used to select the optimal nanolime dispersion based on the sorptivity property of the substrate. “HKS” and “LKS” stand for “High” and “Low” Kinetic Stability, and “HBP” and “LBP” stand for “High” and “Low” Boiling Point, respectively.

the excess water at the surface. The evaporation period varies depending on the size of area pre-wetted, type of mineral matrix and porosity, and the environmental conditions. Finally, if the object is affected by salt (sub)efflorescence issues, desalination action should be carried out prior to the pre-wetting as it might solubilise the salts.

Consolidation of the pre-wetted surface

The concentration of nanolime and the type of dispersion to be used should be tailored to the type of mineral matrix (i.e. porosity and grain-size) to be consolidated [6]. Previous work [70] showed that in comparison with commercial alcoholic nanolime (i.e. Nanorestore Plus® propanol 5), hydro-alcoholic nanolime synthesised in water and isopropanol (1:1 V/V) and characterised by particle-size ranging from 20 to 80 nm, could be more efficient in consolidating fine-grained porous substrate. Authors also demonstrated that nanolime with larger particle-size (150–300 nm) tends to be more efficient in the consolidation of coarse-grained porous substrate, as they lead to a migration and nucleation of nanoparticles in larger pore-size. Depending on the moisture transport characterising the limestone (i.e. slow/fast adsorption and migration processes), the kinetic stability of the dispersion should be adapted too. For this, the conservator can refer to the kinetic model described in Fig. 3 to help in selecting the optimal nanolime dispersion. The proposed kinetic model was developed in taking into consideration the advice given in the literature [30,39–42] and is based on the laboratory experiments carried out on different limestones, with some of the solvents routinely used in stone conservation (ethanol, butanol, and propanol were used in this research). According to the kinetic model, two types of nanolime dispersion can be selected, these are high and low kinetic stability dispersions (referred as “hks” and “lks”, respectively). Previous works which studied the kinetic stability of the nanolime and its impact on the wettability and penetration process [23,28,71,72], indicate that *hks* should be dispersed in low boiling point (*lbp*) solvents such as ethanol or Industrial Methylated Spirit (IMS), for instance, and would be more suitable for the consolidation of fine-grained porous limestone [65]. The conservator has also the possibility to dilute the *hks* nanolime with a *lbp* solvent which is different than the solvent carrier used to synthesise the dispersion. For instance, the use of an ethanol-based dispersion diluted in isopropanol or in a mix of isopropanol/ethanol at different ratios, could be considered for the consolidation of a substrate characterised by a fast adsorption and fast migration. Indeed, the low surface tension of both ethanol and isopropanol could im-

prove the surface wettability [73]. Conversely, *lks* nanolime should be dispersed in high boiling point (*hbp*) solvents (such as DIW or butanol, for instance) and should be applied for the treatment of coarse-grained porous limestone [65].

Although the studies mentioned in the literature and the kinetic model described in Fig. 3 can be used as empirical standards, it is important to stress that the information communicated is not unchallengeable. Indeed, in the decision-making process for selecting the optimal nanolime dispersion, the conservator should consider the impact of other solvent properties such as the evaporation rate, the dynamic viscosity, and the surface tension, all known to affect the wettability of porous surface [74,75]. Besides, it is worth noting that in addition to the solvent properties, the impact of the substrate roughness, type of mineral matrix, and the porosity, can equally affect the surface energy of the limestone surface, thus its wettability [76,77]. To avoid any issues related to the formation of alkoxides that might have developed over time and could affect the rate and yield of the carbonation process [26,66,78,79], the conservator should ensure that the alcoholic dispersion used is not more than 6–8 months old and is stored in the fridge. Alternatively, the conservator could synthesise its own nanolime using the patented anionic exchange process developed by the University of L'Aquila (Italy) [80,81]. This novel synthesis technique allows the production of nanolime at room temperature using a simple, rapid, and scalable method [32–35]. For the consolidation of damage as seen on Objects A–C, alcoholic nanolime with a low concentration (<10 g/L) should be considered. A lower concentration (i.e. <5 g/L) should be applied first as pre-consolidation, then the concentration of the other applications can gradually be increased afterwards [40]. However, it is vital for the methodology to be adapted to the condition of the surface, the specific damage, and properties of the treated artefact. As examples, the conservator has the possibility to apply successive coatings (up to 10, for instance) by brushing a same low concentration (i.e. 5 g/L) of nanolime [6], injecting a higher concentration (i.e. 25 g/L) with a reduced number of applications (up to 6, for instance) [51], or again, using one application at a high concentration (i.e. >25 g/L) by capillary adsorption until the full saturation of the surface [63]. Once selected, the dispersion must be shaken and put in a sonication bath (60 Hz) for 15 mins to prevent the aggregation of nanoparticles, thus avoiding the deposit of nanolime clusters over the treated surface.

Although the treatment methodology varies according to the environmental context (i.e. relative humidity and temperature, location and access to objects) as well as the size and the condition of the object [72,82–85], a less invasive application of nanolime is generally carried out by brushing [28,48,64,86,87], nebulisation with a spray or an airbrush [20,32–35,52,88], or injection using a medical drip system [89]. If the surface can endure pressure, a thin Japanese tissue (2 to 5 gr/m²) dampened in the same solvent used for the dispersion should be brushed over the surface before applying the nanolime. The Japanese tissue will act as a filter layer, thus limiting the deposit of nanolime clusters over the surface. Conversely, the use of Japanese tissue should be avoided for the treatment of fragile surfaces as loose fragments could become trapped into the fabric. In addition to this, the total amount of nanoparticles that penetrates the surface can be reduced if the tissue is too thick and if a high concentration of nanolime is applied. Application of the nanolime should be done in an enclosed environment to prevent the impact of draught that could induce the back-migration of the nanoparticles toward the treated surface. The number of applications vary depending on the type and extent of damage, and the substrate properties [6,20–23,28,51]. The consolidation of an object affected by superficial damage (powdering and flaking surface, for instance) and requiring localised applications (i.e. treatment of small area), necessitates a tailored number of applications which can go up to ten as illustrated by

this research. It is important to stress that the amount of nanolime applied for each centimetre square of treated surface varies depending on the condition and porosity of the substrate, as well as the size of area to be consolidated [50,65,70]. A 24h-time interval between each application should be observed to allow the evaporation of the alcohol (ethanol in this case) present in the pores. Application of the nanolime should be stopped as soon as a white haze is formed over the treated surface. It will be noted that the higher the concentration, the more the surface is likely to be affected by the whitening issue. If a white haze appears, a combination of mechanical and chemical cleaning actions [90] can be considered to attenuate its formation. Wiping the lime deposit formed over the treated surface directly after the application of nanolime should primarily be considered. For this, a cotton wool swab or a medical gauze swab dampened with IMS could be used. Nanolime should be applied until rejection, meaning that the surface is saturated by the nanolime. At this point, no further nanolime should be applied, as the surface will be oversaturated by the nanolime. As a guideline, the surface is deemed saturated if it stays wet and glittery for one minute after the application of nanolime [48,91]. After each application, the surface should be humidified to reduce the evaporation rate of the ethanol, thus preventing the back-migration of nanolime during the drying phase. Upon completion of laboratory tests, the use of a humidification pad applied over the treated surface proved to be very efficient. The humidification pad was made of a medical absorbent cotton gauze swab dampened in DIW and filled with hydrogel (40% W/V in DIW).

Curing of the treated substrate

Once nanolime particles have penetrated the porous stone matrix, time needs to be given to the nanoparticles to carbonate. Over time, the alcohol contained in the dispersion evaporates, the calcium hydroxide nanoparticles react with the moisture in the air and in the stone pores, and the atmospheric carbon dioxide. This reaction triggers the carbonation process of the nanolime which can take several weeks. At the end of the carbonation period, nanolime will have become calcium carbonate, and the newly formed calcite crystals will fill the pores. During the carbonation period, the nucleation of different calcium carbonate polymorphs takes place [69,80,92]. It has been established that the nucleation of alcoholic nanolime from amorphous calcium carbonate to stable calcite follows the Ostwald's kinetic step rule [69,93]. Depending on the relative humidity (RH) level, a variation in the nucleation rate and yield of calcium carbonate polymorphs can be observed [94,95]. Therefore, polymorphs with dissimilarities in term of density, crystallinity and particle-size can be obtained. Indeed, higher RH conditions (RH > 80%) tend to accelerate the carbonation kinetics and yield to the formation of larger particles with higher crystallinity. Conversely, lower RH conditions (RH < 70%) reduces the carbonation rate and leads to the formation of smaller particles with a lower degree of crystallinity [25,65,91,96].

To enable the proper carbonation of alcoholic nanolime, the treated area should be subjected to specific environmental conditions for at least one month. Depending on the condition and the size of the object, a curing chamber built using a heavy-duty plastic storage box could be considered to store the object during the carbonation period. If the object is too large, fragile or cannot be moved, a tent made of Moistop® aluminium laminated barrier foil could be built to house the object. Although the consolidation effectiveness increases over time [6], the carbonation of alcoholic nanolime generally takes a couple of weeks, though it can be far quicker depending on the RH level [17,25,94] and CO₂ concentration [25]. To ensure an optimal carbonation process, RH needs to be around 70% (± 5%), air temperature between 18 °C and 20 °C, and CO₂ concentration between 0.1% and 1%. However, it will be recalled here, that the information aforementioned

are verified only for alcoholic dispersions. Indeed, recent research [32,33,71,78] proved that aqueous dispersion can lead to the complete carbonation of nanolime after a couple of hours at room temperature (20 °C) and dry environmental conditions (RH at 40%). To maintain the RH at the required level, a container placed inside the curing chamber and filled with a saturated salt solution of sodium chloride (NaCl) in DIW should be prepared as described in the literature [97,98]. To increase the CO₂ concentration from 0.5% to 1%, the sugar-yeast fermentation process was considered in this project [78]. The CO₂ generator filled with a sugar-yeast mixture should be placed outside the curing chamber and refilled on a weekly basis to ensure a stable CO₂ concentration.

Application of the En-NCT in a museum context

Overview of the methodology

Two areas measuring approximately 10 cm x 10 cm, were selected on each object. Area #1 was treated with the En-NCT, whereas Area #2 was treated by the control treatment, that is consolidation with the nanolime following the treatment guidelines as described in the literature [18,49–54]. A summary of the strategy followed for the treatment of Areas #1 & #2 is given below.

Area 1 (consolidated with the En-NCT)

- Pre-wetting of surface with steam cleaning and UAH
- Application of the nanolime in enclosed chamber
- Removal of the nanolime excess with an absorbent medical gauze swab (dampened with IMS)
- Humidification for 24 h of the treated surface with a retention pad (hydrogel 20% W/V in DIW)
- Object in curing chamber (slightly ventilated) between each application.

Area 2 (control treatment)

- Pre-wetting of surface with IMS
- Application of similar nanolime dispersion and quantity as for Area #1, using the same method of application.
- Removal of the nanolime excess with an absorbent medical gauze swab (dampened with IMS)
- Humidification of the treated surface by spraying DIW
- Object in curing chamber (slightly ventilated) between each application.

Application of the En-NCT on objects A-C

The assessment of the nature and condition of the objects revealed that Object A is affected by superficial damages, whereas Objects B and C show the presence of structural damage (Fig. 4, a-f). Microscopic observations with a portable digital microscope Dino-Light® - AD7013MTL (Fig. 4, g-i) showed that the surface of Object A is characterised by a fine-grained compact matrix with superficial dirt ingrained. Object B is characterised by a coarser mineral matrix which looks waxy as the result of treatments carried out during the 1960's with Polyethylene Glycol (PEG) 6000. Object C exposes a powdering surface composed of a fine-grained mineral matrix with ingrained dirt and the presence of scaling. UV examination (Fig. 4, j-l) using a long-wave UV lamp ($\lambda = 365$ nm) revealed that Object A fluoresced in dull and light purplish hues. No visible traces of previous restoration could be spotted on Area #1 & #2 of Object A. The eroded and exposed mineral matrix on Area #1 was characterised by a light beige fluorescence, whereas Area #2 showed dull purple hue because of the grounding and soiling material that covers the surface and inhibits the fluorescence (it will be recalled that Object A was found buried in the Idalion Archaeological Site, Lanarka District, Cyprus). Object B is characterised by a blueish fluorescence which could confirm the presence of PEG 6000 over the surface [78]. Some parts fluoresced

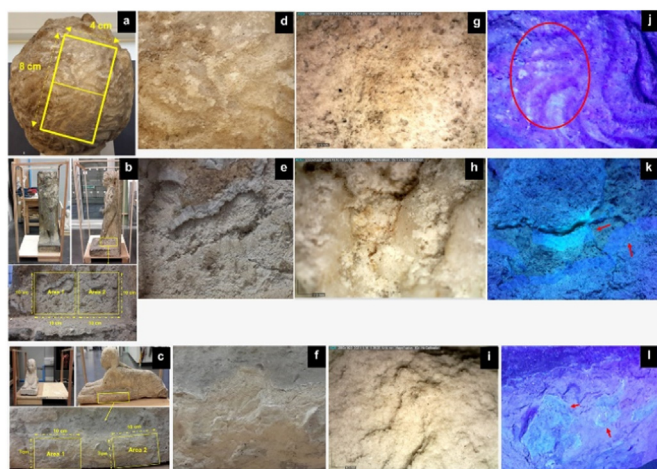


Fig. 4. Condition assessment of Objects A-C (a-c) showing details of damage (d-f) and pictures obtained after observations with digital microscope Dino-Lite AD7013MTL (g-i) and UV light (j-l).

in bright blue and yellowish hues, this is the reaction with the materials used during previous conservation work. Finally, Object C exhibits a light purplish and blue fluorescence, which could be related to the presence of pigment(s), coating, or maybe material(s) left by previous restoration.

Wettability tests carried out on the objects (Fig. B–Supplementary materials) showed that the surface of Object A allows a fast adsorption but a slow migration of the DIW. As for Objects B & C, they are characterised by a lower sorptivity translated by a slow adsorption and slow migration kinetics, thus increasing the tendency of the surface to be impermeable. A note of caution should be given concerning this conclusion, though. Indeed, the wettability test gives only a qualitative assessment of the sorptivity, as this is a function of the capillary force, the viscosity, density, and surface tension of the liquid, as well as the pore structure and surface energy of the tested solid [7]. Assessment of residual water using a protimeter BLD 2000 Moisture meter (Fig. C–Supplementary materials) revealed that there was no residual moisture present near to the surface of Object A. Conversely, tests showed that surfaces of Objects B and C were characterised by a low level of dampness.

Subsequent to the condition assessment, Object A was conditioned using the steam cleaning and UAH techniques (Fig. D, a-d – Supplementary materials). It was decided that Object B would not be conditioned because of the residual water content and the PEG present in the porous matrix. Due to the impermeability of its surface, Object C was conditioned with steam cleaning only (Fig. D, f-h – Supplementary materials), as the use of UAH for 30 mins would have saturated the surface with moisture.

After the conditioning, the consolidation with alcoholic nanolime was carried out. It was decided that Object A, affected by superficial damage, would be consolidated with CaLoSiL® E5 brushed over a Japanese tissue layer (Fig. D, i – Supplementary materials). Based on the wettability results and due to the slow adsorption kinetic characterising the surface, the first application was carried out with CaLoSiL® E5 diluted at 10% V/V in isopropanol. Butanol or propanol, characterised by slower *EvR*, should have been used, however, because of the shortage of these solvents during the treatment of Object A, isopropanol was used instead. Water was also discarded to avoid affecting too much the kinetic stability of CaLoSiL® E5 and preventing the solubilisation of the archaeological materials (i.e. dirt and soil) covering the surface. Areas #1 & #2 of Object A were quickly saturated following the first application, possibly because of the ingrained materials

making the surface more impermeable. Therefore, it was decided that the number of applications would be reduced to less than 5 to avoid an accumulation of the nanolime over the surface. Treatment of Object A showed that the surface was not able to absorb nanolime after the third application anymore. To prevent any detrimental accumulation of nanolime, it was decided that the second and third applications would be carried out with CaLoSiL® E5 diluted at 50% V/V in isopropanol. As a result, 10 ml of nanolime was used to treat Object A, 6 ml of CaLoSiL® E5 (10% V/V in isopropanol) was applied for the first application, then, the second and the third applications were carried out each with 2 ml of CaLoSiL® E5 (50% V/V in isopropanol). Due to its more deteriorated surface, Object B was treated with a higher number of applications. Upon completion of the treatment, Areas #1 and #2 quickly became saturated at the 10th application and could not absorb nanolime afterwards. Therefore, 10 applications were deemed sufficient to consolidate Object B, as more applications would have entailed an over-accumulation of nanolime. Five applications were carried out with CaLoSiL® E5 diluted at 50% V/V in butanol and the other 5, with Nanorestore Plus® E10 diluted at 50% V/V in butanol. Each application was carried out using a two-step strategy. First, one millilitre of Nanorestore Plus® E10 (50% V/V in butanol) was injected through the cracks and the contours scaling with a 25 G (0.5 mm) hypodermic syringe. Then, the same quantity of CaLoSiL® E5 (50% V/V in butanol) was brushed over a Japanese tissue layer applied on the crumbly surface (Fig. D, j & k – Supplementary materials). As a result, 2 ml of nanolime was used for each application, thus making a total of 10 ml of nanolime for the consolidation of each area. It will be noted that because of the higher impermeability and residual moisture content characterising the surface of Object B, it was decided to use highly diluted (i.e. 50% V/V) alcoholic nanolime dispersion, with the view of limiting the accumulation of nanolime throughout the applications. Due to its lower evaporation rate, butanol, was used for diluting both CaLoSiL® E5 and Nanorestore Plus® E10, this, with the purpose of giving the nanolime enough time to penetrate the surface. Water was naturally discarded to avoid increasing the moisture content already present in the porous matrix. Object C, also characterised by an impermeable surface but deteriorated to a lesser extent, was treated with CaLoSiL® E5 diluted at 50% V/V in butanol. Ten applications were required to consolidate Object C and 2 ml of nanolime was used for each application, thus making a total of 10 ml of nanolime for the consolidation of Areas #1 & #2. First, one millilitre of CaLoSiL® E5 (50% V/V in butanol) was injected along the peeling and flaking surface with a 25 G (0.5 mm) hypodermic syringe. Then, the same quantity of CaLoSiL® E5 (50% V/V in butanol) was brushed over a Japanese tissue layer applied on the powdering surface (Fig. D, l & m – Supplementary materials). After each application carried out on Objects A-C, the excess nanolime was wiped. Areas #1 were humidified by spraying water and covered with humidification pads for 24 h, whereas Areas #2 were sprayed with water only (Fig. E, a-g – Supplementary materials).

Subsequent to the final application of nanolime, the final step of the *En-NCT* was carried out. Treated areas were cured for five weeks at the required environmental conditions for ensuring a proper carbonation (Fig. E, h-s – Supplementary materials). Upon completion of the curing process and before doing the assessment tests, the curing chambers were gradually dismantled over a week in order to acclimatise the objects to ambient environmental conditions, thus preventing the crystallisation and efflorescence of potential solubilised salts.

Assessment of the *En-NCT* performance

Assessing the performance of a consolidation treatment in a museum context is a challenge, as to date, there is no specific

conservation standard dedicated to assessing the treatment performance on priceless and unique collections. However, conservators can benefit from the various Non/Minor Destructive Techniques (N/MDT) for assessing the consolidation efficiency. N/MDT generally involve the use of sclerometric, acoustic, and pull-off methods. Laboratory techniques such as the use of X-rays coupled with 3D Computed Tomography, or Micro-spatially offset Raman spectroscopy (micro-SORS) [99], could also be used to determine the penetration depth of the product applied during the treatment. However, the techniques aforementioned can cause (micro) damage to the surface and, often, require the use of expensive equipment, the access to research facilities, and to work on samples with specific size. For this project, it was decided that after discussions with curators and conservators, the performance of the *En-NCT* would be assessed qualitatively by means of (i) spectrophotometry for aesthetical purposes and (ii) surface hardness testing, for establishing changes to strength characteristics to eliminate the risk of further damage to these priceless objects.

Spectrophotometry

The Spectrophotometry was used to assess the chromatic variations induced by the nanolime-based treatment. A Konica Minolta® CM-2600d spectrophotometer with the CIELAB system was used to carry out the tests before and after treatment. Following the method described in the literature [7], a total of 10 measurements were taken on each area consolidated. The total colour variation (ΔE_{ab}^*) was calculated as following (1):

$$\Delta E_{ab}^* = \sqrt{(\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2} \quad (1)$$

Where ΔL^* , Δa^* and Δb^* are the changes in luminosity for white-black, red-green and blue-yellow parameters, respectively. The ΔL^* , Δa^* and Δb^* were calculated as the difference after (Δ_1) and before (Δ_0) the treatment (i.e. $\Delta = \Delta_1 - \Delta_0$). It will be recalled that the main aesthetical issue with the application of the nanolime is the formation of a white haze left over the treated surface. Therefore, an increase of ΔL^* would translate into a paler coloration caused by the whitening formed by the deposits of the nanolime over the surface. As proven by previous works [45], it will be noted that ΔL^* significantly increases if the surface is not wiped (with a solvent dampened gauze swab) to absorb the excess of nanolime straight after its application. Some studies [100,101], mentioned that the chromatic alteration of the treated surface can be classified by three aesthetic risk levels based on the ΔE_{ab}^* values, these are:

- 1) $\Delta E_{ab}^* > 5$ (CIELAB units) = High risk
- 2) $3 < \Delta E_{ab}^* < 5$ (CIELAB units) = medium risk
- 3) $\Delta E_{ab}^* < 3$ (CIELAB units) = low risk

However, previous stone conservation works [80,102,103], proved that for a ΔE_{ab}^* less than 5 (CIELAB units), any chromatic variations potentially caused by the treatment would be visually imperceptible. Therefore, for this research project, to validate the efficiency of the *En-NCT* in a museum context, $\Delta E_{ab}^* < 5$ will be considered.

Surface hardness test

To assess the superficial consolidation efficiency with a non-destructive technique, an Equotip® 550 Leeb Portable Hardness Tester was used. This technique measures the hardness of the (sub)surface layers using the dynamic rebound testing method described in the literature [51,104]. During the test, an impact body with a hard metal test tip (D Leeb impact probe in this research) is propelled by spring force against the surface of the stone object. Surface (micro)deformation takes place when the impact body hits

the test surface, which results in the loss of kinetic energy. This energy loss is detected by a comparison of velocities v_i (impact velocity) and v_r (rebound velocity) when the impact body is at a precise distance from the surface for both the impact and rebound phase of the test, respectively. The Hardness Leeb calculated as shown in Eq. (2) [105], was measured using the probe D (HLD units) following an average of 15 rebound testing points taken over the area consolidated.

$$HLD = \frac{v_r}{v_i} * 1000 \quad (2)$$

Results & discussion

Condition assessment

Selection of Area #1 & #2 of Objects A-C, as well as pictures of damage and surface condition obtained with digital microscopy and UV fluorescence are shown in Fig. 4.

Spectrophotometry

The spectrophotometry results described in Table 1 show that the *En-NCT* did not impair the aesthetical appearance of Objects B and C. Indeed, for both Objects, the area treated by the *En-NCT* (i.e. Area 1) is characterised by a reduced colour alteration ($\Delta E_{ab}^* < 5$ CIELAB units). It is noticed that in comparison with the control treatment (i.e. treatment applied on Area 2), the *En-NCT* induced a far less significant chromatic variation and surface whitening. For the three objects, the ΔE_{ab}^* and ΔL^* values are lower for Area 1 than for Area 2, thus providing a very acceptable *En-NCT* performance. It is also noted that only one area (i.e. Area 2 of the limestone head) is affected by marginal perceptible colour change ($\Delta E_{ab}^* = 5.95$ CIELAB units). After the application of the control treatment, Area 2 showed a paler surface, this is because the area treated by the control treatment was not properly wiped subsequent to the application of nanolime. As a result, it cannot be concluded that the *En-NCT* induced a less significant chromatic variation on Object A. However, it can be said that based on the results obtained for Objects B & C, the application of the *En-NCT* in a museum context is deemed aesthetically safe for the object given the fact that the proposed treatment does not induce any perceptible chromatic variations and obvious surface whitening subsequently to ten applications of nanolime.

Surface hardness

Details of surface hardness tests show that all the treated objects are characterised by an increase in the surface hardness. In addition, the comparison between the areas treated with the *En-NCT* and the control treatment illustrates the higher efficiency of the former treatment. Indeed, from the data presented in Table 2 and Fig. 5 (Fig. F– Supplementary materials), it can be seen that after the application of the *En-NCT*, surfaces of Objects, A, B, and C, see their hardness increased by ~35%, ~57%, and ~49%,

Table 1

Chromatic data obtained after spectrophotometry tests carried out on Objects A – C with a Konica Minolta® CM-2600d spectrophotometer.

| Object vs Areas treated | Δa^* | Δb^* | ΔL^* | ΔE_{ab}^* |
|----------------------------|--------------|--------------|--------------|-------------------|
| Object A (Head) - Area 1 | −2.43 | −3.42 | 0.09 | 4.20 |
| Object A (Head) - Area 2 | −1.07 | −3.79 | 4.46 | 5.95 |
| Object B (Statue) -Area 1 | 0.76 | 2.32 | 1.67 | 2.96 |
| Object B (Statue) - Area 2 | 0.17 | 2.77 | 2.47 | 3.71 |
| Object C (Sphinx) - Area 1 | −0.79 | −2.72 | 0.73 | 2.92 |
| Object C (Sphinx) - Area 2 | −0.21 | 1.68 | 4.05 | 4.39 |

Table 2

Surface hardness data (expresses in HLD unit) obtained for Objects A – C after testing with an Equotip® 550 Leeb Portable Hardness Tester, (1.5-column fitting image).

| Object vs Areas treated | HLD before treatment | HLD after treatment | HLD Change | HLD Change (%) |
|----------------------------|-------------------------|------------------------|------------|----------------|
| Object A (Head) - Area 1 | 245.40 (± 26.55) | 331.87 (± 27.34) | 86.47 | 35.2 |
| Object A (Head) - Area 2 | 290.40 (± 24.21) | 341.67 (± 9.34) | 51.27 | 17.7 |
| Object B (Statue) - Area 1 | 244.13 (± 35.53) | 382.80 (± 13.40) | 138.67 | 56.8 |
| Object B (Statue) - Area 2 | 265.27 (± 50.57) | 275.00 (± 44.35) | 9.73 | 3.7 |
| Object C (Sphinx) - Area 1 | 247.13 (± 34.85) | 368.53 (± 4.76) | 121.40 | 49.1 |
| Object C (Sphinx) - Area 2 | 277.87 (± 34.87) | 339.07 (± 41.63) | 61.20 | 22.0 |

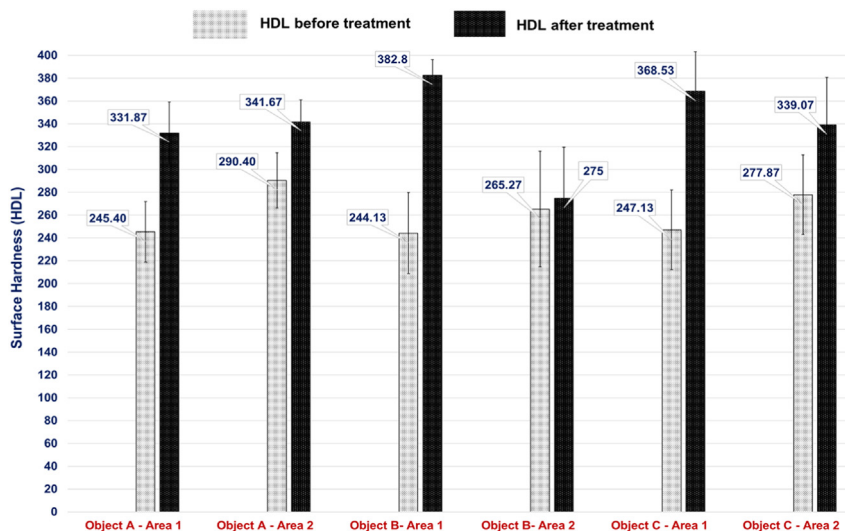


Fig. 5. Bar chart showing the surface hardness before and after treatments for Objects A-C

respectively. Conversely, the areas treated with the control treatment show a reduced surface hardness. Δ HLD gained is only about ~18%, ~4%, and ~22%, for Objects, A, B, and C, respectively. Therefore, it can be asserted that the *En – NCT* greatly restores the mineral cohesion of the near-to-the surface layers.

Conclusions

This project revealed that the introduction of the nanolime in a museum context by means of a tailored and enhanced consolidation technique is a realistic and promising conservation approach. An enhanced nanolime consolidation technique named *En – NCT* and developed in the laboratory was tested for the first time in a museum context on three limestone objects characterised by distinctive superficial damage. The experiments showed that the proposed *En – NCT* does not impair the aesthetical appearance of the objects and restores the mineral cohesion of the treated surface by increasing its hardness. Although this project validated the efficiency of the nanolime for the superficial consolidation of limestone museum objects, the *En – NCT* needs to be optimised to increase its efficiency and reliability in the case of the treatment of advanced deterioration patterns and for the consolidation of large-scale objects. Further research needs to be conducted to assess the effectiveness and the limits of the *En – NCT* for outdoor conservation work entailing the consolidation architectural and decorative elements, for instance.

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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.2023.04.007.

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