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Nanostructured lime-based materials for the conservation of calcareous substrates

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Nanostructured lime-based materials for the conservation of calcareous substrates

Giovanni Borsoi

Nanostructured lime-based materials for the conservation of calcareous substrates

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Delft University of Technology, Faculty of Architecture and the Built Environment,
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TOC

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Nanostructured lime-based materials for the conservation of calcareous substrates

Proefschrift

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus prof. ir. K.C.A.M. Luyben,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen op 27 September 2017 om 12:30 uur

door

Giovanni BORSOI
Laurea Magistrale in Scienze Chimiche per la Conservazione e il Restauro, Cá Foscari
universiteit van Venetië, Venetië, Italië
geboren te Treviso, Italië

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This dissertation has been approved by the

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To my mother, Pia, my father, Loris, and my brother, Alessandro

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Da minha aldeia vejo quanto da terra
se pode ver do Universo…
Por isso a minha aldeia é tão grande
como outra terra qualquer,
Porque eu sou do tamanho do que vejo
e não do tamanho da minha altura…
Alberto Caeiro (Fernando Pessoa), Guardador de Rebanhos, Poemas Completos, VII.

Dal mio villaggio io vedo quanto dalla terra
si può vedere dell´Universo…
Per questo il mio villaggio è grande
quanto qualsiasi altro luogo,
Perché io sono della dimensione di quello che vedo
e non della dimensione della mia altezza…
Alberto Caeiro (Fernando Pessoa), Il pastore di greggi, Poemi Completi, VII.

Vanuit mijn dorp zie ik zoveel van het heelal
als men vanaf de aarde zien kan...
Daarom is mijn dorp zo groot
als ieder ander,
Want ik ben zo groot als wat ik zie
En niet zo groot als ik lang ben...
Alberto Caeiro (Fernando Pessoa), Veehoeder, De volledige Gedichten, VII.

From my village I see as much of the universe
as can be seen from the earth…
And so my village is as large
as any town,
Because I am the size of what I see
and not the size of my height…
Alberto Caeiro (Fernando Pessoa), The Herdsman, The Complete Poems, VII.

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Grazie, Dank u wel, Obrigado!

Giovanni

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Summary

Nanolimes, i.e. dispersions of lime ($Ca(OH)_2$)nanoparticles in alcohol, have been extensively investigated over the last two decades as consolidation products for calcareous substrates.

The use of nanolimes for consolidation of mural paintings arises from the lack of effective and compatible consolidants for this type of substrates; the use of nanolimes was later extended also to limestone and lime-based mortars, as an alternative for silica-precursor consolidants (e.g. tetraethoxysilan - TEOS), which had shown to have a limited effectiveness and compatibility with calcareous substrates.

Nanolime dispersions are characterized by a very small size of the lime particles, which should provide a proper penetration within the porous network of most building materials. In fact, a homogeneous and in-depth penetration of the consolidant is a crucial requirement when dealing with decayed stones and plasters/renders.

The effectiveness of nanolime dispersions reported in literature appears controversial. Some authors observed a proper penetration and moderate consolidating action, whereas others report poor penetration, poor consolidation action and sometimes the formation of a white haze on the treated surface. There is no agreement concerning the factors affecting the transport and deposition of the lime nanoparticles within a porous network, and the causes of the observed drawbacks are not well understood.

Therefore, the main research question is:

Is nanolime a suitable alternative to silica-precursor consolidants (e.g. TEOS) for the consolidation of calcareous substrates?

More specifically, the following research questions can be formulated:

- How and up to which extent can the effectiveness and compatibility of nanolime be improved? How can deposition of nanolime in depth be improved and the appearance of a white haze on the surface avoided?
- How can nanolime properties be fine-tuned to improve the effectiveness and compatibility of the treatment?
- What is the effect of different application methods on the effectiveness of nanolime consolidation?

This research investigates and elucidates the behaviour of nanolime products for consolidation of calcareous substrates. Based on the developed knowledge, it proposes and validates a methodology (including solvent modification and application protocol) for improving the consolidation effectiveness of nanolime dispersions, making these a suitable alternative for TEOS products.

Firstly, an experimental campaign was carried out in order to understand the penetration and deposition of commercial nanolimes on coarse porous calcareous substrates (Maastricht limestone). The main cause of the poor nanolime deposition in-depth was identified in the back-transport of the nanoparticles towards the drying surface, as a consequence of the high volatility and low kinetic stability of the dispersions.

The modification of the nanolime properties, through the optimization of the solvent, appears thus a feasible strategy to improve the in-depth deposition of the lime nanoparticles. New nanolimes were synthetized and dispersed in a selection of solvents conferring different stability and drying rate to the obtained nanolime dispersions. A conceptual model, correlating the properties (i.e. drying rate and kinetic stability) of nanolimes dispersed in different solvents, to the moisture transport behaviour of the substrates to be treated, was conceived. The model was experimentally validated on coarse porous (Maastricht) and fine-porous (Migné) limestones.

Experimental results confirmed the predictions of the model that nanolimes dispersed in solvent with lower volatility and stability (e.g. water or butanol) have a good in-depth deposition within coarse porous networks. On the other hand, solvents with higher volatility and guaranteeing higher kinetic stability (e.g. ethanol or isopropanol) to the relative dispersions, should be preferred for substrates with fine porous networks. Fine-tuning the properties of the nanolime dispersion (by modification of the solvent) to the moisture transport behaviour of the substrate, is shown to be a successful strategy for improving in-depth deposition of lime nanoparticles.

On the basis of the obtained results, the solvent mixture was further fine-tuned using ethanol-water mixtures. Results proved that ethanol-based nanolime, mixed with a minor amount of water (5%), can provide better nanoparticles in-depth deposition within coarse porous substrates (e.g. Maastricht limestone), when compared to dispersions in pure ethanol.

The application procedure of nanolime dispersions was also studied and optimized, this step being a crucial aspect for a successful consolidation; nanolimes were applied both by capillary absorption (method commonly used for laboratory tests) or by nebulization (method widely used *in situ*) on a coarse porous limestone and a mortar.

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The research showed that results obtained by application through capillary absorption do not always correspond to those obtained by nebulization.

The effectiveness and compatibility of nanolimes with improved properties and a fine-tuned application protocol were finally verified. Fresh and weathered Maastricht limestone, as well as lime-based mortars, were treated. Results showed that nanolime dispersions can guarantee an in-depth consolidation both in laboratory mortar specimens and weathered limestone, with only a moderate alteration of the total porosity and of the moisture transport properties of the investigated substrates.

Therefore, nanolime dispersions, provided that they are properly formulated and applied, can be a suitable and compatible alternative to TEOS for the consolidation of coarse porous substrates.

This dissertation contributes to define guidelines to support restorers and professionals in the choice and application of nanolime dispersions for consolidation of calcareous substrates.

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Samenvatting

Nanokalk, d.w.z. dispersie van kalk ($Ca(OH)_2$) nanodeeltjes in alcohol, is de laatste twee decennia uitgebreid onderzocht als verstevigingsproduct voor kalkhoudende ondergronden.

Het gebruik van nanokalk voor de versteviging van muurschilderingen komt voort uit het gebrek aan effectieve en compatibele verstevigingsproducten voor dit type ondergrond; het toepassen van nanokalk is later uitgebreid naar kalksteen en kalkhoudende mortels, als een alternatief voor op silica gebaseerde verstevigingsproducten (b.v. TEOS), welke een slechte effectiviteit en compatibiliteit vertoonden met kalkhoudende ondergronden.

Nanokalk kenmerkt zich door een zeer kleine deeltjesgrootte van de kalk, dit zou moeten leiden tot een goede indringing in het poreuze netwerk van de meeste bouwmaterialen. Een homogene en diepe indringing van het verstevigingsproduct is een cruciale voorwaarde voor de toepassing op verweerde stenen en buiten en binnen pleisterwerk.

De effectiviteit van nanokalk dispersies is in de literatuur omstreden. Sommige auteurs rapporteren voldoende indringing en redelijke versteviging, terwijl anderen slechte indringing en nauwelijks versteviging melden en daarnaast soms een witte waas op het behandelde oppervlakte zien. Er is geen overeenstemming over welke factoren het transport en afzetting van de kalk nanodeeltjes in een poreus netwerk beïnvloeden. Daarnaast worden de oorzaken van de geconstateerde nadelen nog niet goed begrepen.

Op grond hiervan is de hoofdvraag van dit onderzoek:

Is nanokalk een geschikt alternatief voor op silica gebaseerde verstevigers (b.v. TEOS) voor de versteviging van kalkhoudende ondergronden?

Vervolgens kunnen de volgende onderzoeksvragen geformuleerd worden:

- Hoe en in welke mate kan de effectiviteit en compatibiliteit van nanokalk worden verbeterd? Hoe kan de diepte van afzetting van de nanokalk verbeterd en het verschijnen van een witte laag op het oppervlakte voorkomen worden?
- Hoe kunnen de eigenschappen van de nanokalk nauwkeurig worden afgestemd zodat de effectiviteit en compatibiliteit van de behandeling wordt verbeterd?

- Wat is het effect van verschillende applicatie procedures op de effectiviteit van nanokalk versteviging?

Dit proefschrift onderzoekt en verheldert het gedrag van nanokalk producten voor de versteviging van kalkhoudende ondergronden. Op basis van de opgedane kennis wordt er een methodologie opgesteld en gevalideerd (inclusief aanpassingen aan het oplosmiddel en de applicatie procedure) voor het verbeteren van de verstevigingseffectiviteit van nanokalk dispersies, resulterende in een geschikt alternatief voor de TEOS producten.

Allereerst is er uitgebreid experimenteel onderzoek uitgevoerd om de indringing en afzetting van commerciële nanokalk producten op grof poreuze ondergronden (Maastrichter kalksteen) te begrijpen. Als hoofdoorzaak voor de slechte diepe afzetting van de nanokalk werd transport van de dispersie terug naar het drogingsoppervlakte geïdentificeerd. Dit wordt veroorzaakt door de hoge vluchtigheid en kinetische stabiliteit van de dispersies.

Het aanpassen van de nanokalk eigenschappen, door optimalisatie van het oplosmiddel, vormt dus een goede strategie om de diepe afzetting van de kalk nanodeeltjes te verbeteren. Nieuwe nanokalk is gesynthetiseerd en vervolgens in dispersie gebracht met een selectie aan oplosmiddelen, resulterend in nanokalk dispersies met verschillen in stabiliteit en drogingssnelheid. Daarna is er een conceptueel model opgesteld waarin de eigenschappen (d.w.z. drogingssnelheid en de kinetische stabiliteit) van de nanokalk gedispergeerd in verschillende oplosmiddelen gecorreleerd worden aan het vloeistof transport gedrag van de te behandelen ondergronden. Het model is gevalideerd op grof poreuze (Maastrichter) en fijn poreuze (Migné) kalkstenen.

De resultaten valideerden de voorspelling van het model dat nanokalk gedispergeerd in oplosmiddelen met een lagere vluchtigheid en stabiliteit (b.v. water of butanol) een goede diepe afzetting heeft in grof poreuze netwerken. Daarentegen worden oplosmiddelen met een hogere vluchtigheid en garantie van hogere kinetische stabiliteit (b.v. ethanol of isopropanol) van de dispersies geprefereerd voor ondergronden met fijn poreuze netwerken. Het afstemmen van de eigenschappen van de nanokalk dispersie (door aanpassingen aan het oplosmiddel) op het vloeistof transport gedrag van de ondergrond, bleek een succesvolle strategie voor het verbeteren van de diepe afzetting van kalk nanodeeltjes.

Aan de hand van de verkregen resultaten is het oplosmiddel verder geoptimaliseerd voor ethanol-water mengsels. De resultaten toonden aan dat op ethanol gebaseerde nanokalk, gemengd met een kleine hoeveelheid water (5%), leidde tot een betere

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diepe afzetting van nano kalkeeltjes in grof poreuze ondergronden (b.v. Maastrichter kalksteen), in vergelijking met dispersies in pure ethanol.

Tevens is de applicatie procedure van de nanokalk dispersies onderzocht en geoptimaliseerd, aangezien dit een cruciaal aspect is voor een succesvolle versteviging; nano kalk werd aangebracht via capillaire absorptie (gebruikelijke methode in laboratorium testen) of via verneveling (veelgebruikte methode *in situ*) op een grof poreuze kalksteen en een mortel.

Het onderzoek toonde aan dat de resultaten verkregen door applicatie via capillaire absorptie of verneveling niet altijd gelijk zijn.

De effectiviteit en compatibiliteit van nanokalk met verbeterde eigenschappen en geoptimaliseerd applicatie protocol zijn eindelijk bevestigd. Verse en verweerde Maastrichter kalksteen en op kalk gebaseerde mortels zijn behandeld. De resultaten toonden aan dat nanokalk dispersies zorgen voor een grondige versteviging van zowel mortelmonsters gemaakt in het laboratorium als voor verweerde kalksteen. Dit alles met slechts kleine veranderingen van de totale porositeit en van de vochttransporteigenschappen van de onderzochte ondergronden.

Nanokalk dispersies vormen daarom, mits correct gekozen en toegepast, een geschikt alternatief voor TEOS voor de versteviging van kalkhouden grof poreuze ondergronden.

Deze thesis draagt bij aan het definiëren van richtlijnen ter ondersteuning van restaurateurs en vakmensen bij hun keuze voor en toepassing van nanokalk dispersies voor het verstevigen van kalkhoudende ondergronden.

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Riassunto

Le nanocalci, ossia nanoparticelle di calce ($Ca(OH)_2$) disperse in alcol, sono state ampiamente studiate nell'ultimo ventennio come prodotti consolidanti per materiali calcarei.

L'utilizzo delle nanocalci per il consolidamento di pitture murali è stato inizialmente promosso dalla mancanza di consolidanti efficienti e compatibili per questi tipi di substrati; in un secondo momento le nanocalci sono state usate anche su pietre calcaree e intonaci a base di calce, come alternativa a consolidanti generanti silice (per esempio prodotti TEOS - tetraetossilano), che hanno dimostrato scarsa efficacia e compatibilità con substrati calcarei.

Le nanocalci sono caratterizzate da una ridotta dimensione delle particelle, tale da permetterne la penetrazione nei sistemi porosi della maggior parte dei materiali da costruzione. Una penetrazione omogenea e in profondità è infatti un requisito fondamentale nel consolidamento di rivestimenti lapidei o murali con perdita di coesione.

L'efficienza delle nanocalci è d'altronde controversa, come riportato in letteratura scientifica. Alcuni autori hanno infatti osservato una adeguata penetrazione e una moderata azione consolidante, mentre altri riportano una scarsa penetrazione e azione consolidante, e in alcuni casi la formazione di una patina bianca sulla superficie trattata. I fattori che influenzano il trasporto e deposizione delle nanoparticelle dentro sistemi porosi non sono pertanto unanimemente identificati, e le cause degli effetti collaterali osservati non sono ancora completamente compresi.

Il tema principale della ricerca è dunque:

Le nanocalci posso essere una alternativa ai consolidanti generanti silica (per esempio, prodotti TEOS) per la consolidazione di substrati calcarei?

E più nello specifico, sono proposti i seguenti temi di ricerca:

- Come e fino a che limite l'efficienza e la compatibilità delle nanocalci può essere migliorata? Come si può migliorare la deposizione in profondità delle nanocalci ed evitare la formazione di patine bianche sulla superficie trattata?
- Come si possono ottimizzare le proprietà delle nanocalci al fine di migliorarne l'efficienza e la compatibilità?

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- Quale è l'impatto di differenti metodologie di applicazione sull'efficacia di un trattamento consolidante con nanocalce?

Questa tesi intende studiare le nanocalci come prodotti consolidanti per substrati calcarei. Sulla base dei dati ottenuti, una metodologia (che include la modifica del solvente e del protocollo di applicazione) è proposta e validata per migliorare l'efficienza consolidante delle nanocalci, rendendole un'alternativa adequata ai prodotti TEOS.

Una campagna sperimentale è stata quindi avviata per studiare e comprendere la penetrazione e deposizione di nanocalci commerciali, quando applicate su substrati calcarei molto porosi (nel caso, pietra calcarea 'Maastricht'). La causa principale della scarsa deposizione in profondità delle nanoparticelle è stata individuata nel ritorno della nanoparticelle verso la superficie di evaporazione, a causa della elevata volatilità e stabilità cinetica delle dispersioni.

Una strategia adeguata per aumentare la deposizione in profondità delle nanoparticelle di calce è stata individuata nella modifica delle proprietà delle nanocalci, attraverso un'ottimizzazione del solvente. Nuove nanocalci sono state quindi sintetizzate e disperse in solventi selezionati, conferenti differenti stabilità e velocità di evaporazione alle relative nanocalci.
È stato elaborato un modello concettuale che correla le proprietà delle nanocalci (ossia, velocità di evaporazione e stabilità cinetica) disperse in differenti solventi alla proprietà di trasporto di liquidi dei materiali da trattare. Il modello è stato poi validato su pietre calcaree con porosità sia elevata che ridotta, rispettivamente pietra calcarea Maastricht e pietra calcarea Migné.

Come suggerito dal modello, i risultati confermano che le nanocalci disperse in solventi con bassa volatilità e stabilità (come nel caso di acqua o butanolo) presentano una buona penetrazione in profondità in sistemi particolarmente porosi. Solventi con elevata volatilità, e che garantiscono elevata stabilità cinetica (come nel caso di etanolo o isopropanolo) alle relative dispersioni, sono d'altro canto consigliati nel caso di sistemi porosi più compatti. L'ottimizzazione delle proprietà delle nanocalci (attraverso la modifica del solvente), sulla base delle proprietá di trasporto del substrato, si è dimostrata una strategia efficiente per aumentare la deposizione in profondità delle nanoparticelle di calce.

Sulla base dei risultati ottenuti, il solvente è stato ulteriormente messo a punto usando miscele di etanolo e acqua. Le evidenze sperimentali provano che nanocalci a base di etanolo, mescolate a percentuali ridotte di acqua (5%), possono assicurare una migliore deposizione in profondità in substrati molto porosi (ossia, nella pietra calcarea Maastricht), se comparati a nanocalci disperse in puro etanolo.

La procedura di applicazione, passaggio fondamentale per ottenere un trattamento efficace, è stata inoltre analizzata e ottimizzata; le nanocalci sono state applicate per assorbimento capillare (metodo comunemente usato in test laboratoriali) o nebulizzazione (metodo spesso usato *in situ*) su pietre calcaree ed intonaci molto porosi.

La ricerca mostra che i risultati ottenuti con assorbimento capillare non sempre corrispondono a quelli ottenuti con nebulizzazione.

Sono stati infine verificate l'efficacia e la compatibilità delle nanocalci con proprietà migliorate e procedura di applicazione ottimizzata. Sono state trattate pietre calcaree *Maastricht* sia sane che degradate, e intonaci a base di calce. I risultati provano che le nanocalci possono garantire un consolidamento in profondità sia sui campioni di intonaco che sulla pietra sana e degradata, con una moderata alterazione delle porosità totale e delle proprietà di trasporto delle superfici prese in esame.

Se adeguatamente selezionate ed applicate, le nanocalci possono essere una adeguata e compatibile alternativa ai prodotti TEOS per il consolidamento di substrati calcarei molto porosi.

Questa ricerca ha l'obiettivo di stabilire delle linee guida per restauratori e professionisti del campo nella selezione ed applicazione di nanocalci per il consolidamento di materiali calcarei.

1 Introduction: definition and relevance of the problem

The safeguarding of our historical built heritage requires the conservation of its original materials.

A large part of this heritage consists of calcareous materials, such as limestone and lime-based renders and plasters. These substrates are vulnerable to several weathering processes, including specific degradation mechanisms as salt damage or acid attack due to environmental pollution. Loss of coherence (in the form of sanding, powdering, crumbling, chalking) is a common form of decay of calcareous materials and it includes the loss, either by dissolution or by physical and/or mechanical stresses, of the original clastic grains of the limestone or of sand in the mortars [van Hees et al., 2016; van Hees et al. 2017].

Loss of cohesion at the surface of porous material can be recovered by surface consolidation. Surface consolidation consists in the application of a liquid with specific strengthening characteristics (consolidant product) on the substrate to be treated; after reaction/hardening, this product should re-establish the coherence in the material.

In the field of cultural heritage, and above all in the conservation of objects of great artistic, cultural and historical value, surface consolidation should be, whenever possible, preferred to the replacement of the original material, in order to preserve the historical and/or artistic value.

Nowadays, the most used products for consolidation are silica-precursor consolidants, e.g. TEOS or tetraethoxysilane, commonly known as ethyl silicate. These products are in use since the 19th century, thanks to their ease of application and good penetration in the substrate. Although positive results are generally reported for application on sandstone, silica-precursor products have their limitations when applied on calcareous substrates, due to their low chemical compatibility and significant shrinkage. However, silica precursor consolidants, sometimes modified to obtain a better compatibility (and flexibility), are still the most widely used products for calcareous substrates, because of the lack of effective alternatives.

Inorganic, and more specifically lime-based consolidants, might offer an alternative for the consolidation of calcareous materials. Recent research in the field of nanotechnology has resulted in nanostructured products with improved properties

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for applications in the field of cultural heritage conservation. Among nanomaterials, calcium hydroxide nanoparticles dispersed in alcohols, the so-called *nanolime dispersions*, have attracted the interest of conservators for their promising properties as consolidant products.

Nanolimes have been shown to be effective for superficial consolidation of e.g. mural paintings, limestone and renders. However, although lime particles with nano to submicron dimensions can potentially penetrate the pores of most building materials, generally lime nanoparticles barely achieve an in-depth homogenous deposition in the material. This low penetration limits their application in those cases , such as severely decohesioned mortars and limestones, where an in-depth consolidation is required. Accumulation of nanoparticles at the treated surface, with white haze formation and poor consolidation in depth, are problems often reported by conservators and researchers.

Literature shows a tendency to tackle these problems by a trial-and-error approach; very little systematic research has been carried out to elucidate the mechanisms (e.g. substrate and nanolime properties, environmental conditions, etc.) influencing the penetration and deposition of the lime nanoparticles in the treated material, and thus the consolidation action of the nanolime treatment.

§ 1.1 Aim of the research

This PhD research proposes a systematic investigation of the mechanisms governing the transport and deposition of nanolime dispersions, with the final scope of improving the consolidation effectiveness and compatibility of nanolime consolidants and making them a suitable alternative to commonly used silica-precursor products (e.g. TEOS).

In order to reach this goal, first the different factors possibly influencing nanolime transport and deposition need to be identified. The relevance and role of each of these factors should be then assessed experimentally. Based on the results, proposals for improvement of the consolidant product and application methodology can be defined.

For a better effectiveness and compatibility of the consolidation, a homogeneous deposition of nanolime particles in-depth is necessary. It is expected that this can be obtained by fine-tuning the nanolime properties to the moisture transport characteristics of the material to be treated. New nanolime dispersions with improved

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performance will be thus synthetized and their effectiveness and compatibility assessed in the laboratory.

Special attention will be given to the translation of the laboratory results to the practice of conservation: different application methods will be compared and a draft protocol for the application of nanolime dispersions on calcareous substrates in the field will be formulated.

§ 1.2 Outline of the thesis

This thesis is composed of five peer-reviewed papers (Chapter 4 to 8), which summarize the development and results of the research. A literature review (Chapter 2) precedes these papers and a last chapter summarizes the main conclusions, points out the still unsolved issues, and provides an outlook for future research. In the appendix, a draft protocol for the application of nanolime dispersions in practice is given (Appendix A).

The review of previous research, next to providing the state of the art in the field of nanolime for consolidation of calcareous substrate, points out the limitation of the available consolidant products for calcareous substrates and identifies important research questions, which have been addressed in this study (Chapter 2, 3).

At first, the transport of nanolime dispersions in a substrate during absorption and drying was investigated in order to elucidate the cause of the often observed deposition or concentration of consolidant on and near the treated surface. The results definitively show that in coarse substrates (such as Maastricht limestone) accumulation of nanoparticles directly beneath the surface mainly occurs during drying, due to the partial back-migration of the lime nanoparticles with the solvent towards the drying surface. Carbonation was shown to not significantly affect the deposition of nanolime within the Maastricht limestone (Chapter 4, [Borsoi et al. 2016a]).

Based on the results of these first series of experiments, the stability of the dispersion and the moisture transport properties of the substrate have been identified to be the crucial factors influencing the penetration and deposition of nanoparticles in-depth. The effectiveness of nanolime consolidation can thus be improved by tuning the stability of the nanolime dispersion to the moisture transport properties of the material to be treated. A conceptual model, correlating the drying rate and the kinetic stability of nanolimes dispersed in different solvents, to the porosity of the limestone to be treated, has been proposed and validated (Chapter 5, [Borsoi et al. 2016b]). A coarse and a fine porous limestone (Maastricht and Migné limestone, respectively) have been used in the validation. This model can help to select a suitable nanolime solvent depending on the moisture transport properties of the substrate.

The effect of the solvent on nanolime stability has been further investigated in Chapter 6 [Borsoi et al. 2016c]. The effect of the addition of low percentages of water to the alcoholic solvent on the kinetic stability of the obtained nanolime dispersion has been studied. The results validate the model and confirm that knowledge on moisture transport properties of the substrate is required for a successful in-depth consolidation treatment.

Another important aspect of any consolidation action, the application procedure, has been addressed in Chapter 7 [Borsoi et al. 2017a]. As the application procedure used in laboratory studies often differs from that applied in the field, it is important to link the results obtained in laboratory research to conservation practice. This has been done in this research by comparing the effect of different application methods on the final deposition of nanoparticles in the substrate. This part of the research contributed to the definition of a draft application protocol for restorers and professionals in the field (Appendix A).

Finally, the effectiveness and compatibility of the newly synthetized nanolime dispersions with improved properties, applied according to the developed application protocol, have been verified (chapter 8, [Borsoi et al. 2017b]) by application on fresh and weathered substrates (both Maastricht limestone and lime mortar). The treatment has shown to be able to considerably improve the strength and coherence of the substrates up to a depth of 10 to 16 mm (depending on the substrate), without any whitening of the surface. Besides, the treatment did not significantly alter the total porosity and the moisture transport properties of the investigated substrates. These results confirm that a careful tuning of the nanolime properties to the moisture transport properties of the substrate to be treated, together with a suitable application procedure, can make nanolime dispersion a good alternative to silica-precursor products for the consolidation of calcareous substrates.

The main results of the PhD research are summarized and discussed in the conclusion chapter (Chapter 9); still unsolved issues are pointed out and an outlook for future research is sketched.

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2 Consolidation of calcareous substrates: state of the art review

§ 2.1 Introduction

The cohesion within inorganic materials is made up by mineral bridges, whose strength is given by the adhesive forces across the mineral surfaces (e.g. electrostatic, water film, Van der Waals forces and/or hydrogen bonds) and to mechanical interlocking effect of indentation [Toniolo et al. 2010].

The surface cohesion of a material can be generally recovered by a consolidation intervention, provided damage occurs in the form of loss of cohesion (e.g. sanding, powdering) and not as scaling, delamination or other forms of loss of adhesion of different layers of the material.

The main objective of a consolidation action is to restore the granular disintegration of the material.

A consolidation intervention usually consists in the application of a low viscosity substance containing a binding agent, that impregnates the pore network of the substrate. After the impregnation with the consolidant, the solvent evaporates and a chemical reaction (e.g. polymerization, carbonation) and solidification occur [Matteini & Moles 2003; Matteini et al. 2008; van Hees et al. 2017]. The consolidant forms mineral or organic bridges within the grains structure of the porous material recovering the cohesion of the material.

Cleaning and desalination (e.g. by poultice) are preliminary actions commonly performed on surfaces to be treated with a consolidant [Ferreira Pinto & Delgado Rodrigues 2008a; Lubelli & van Hees 2010]. When the surface is very fragile, the consolidation action, that normally would be executed after the cleaning, should be applied before it (i.e. pre-consolidation) [Torraca 2009]. In fact, it may be very risky to apply a consolidant on salt laden objects [Delgado Rodrigues 2010]. As an example, TEOS-based (tetraethoxysilan) consolidants do not lose their initial water repellency when applied on salt loaded substrates; this, apart from making future desalination impossible, adds the risk of damage due to the low compatibility of water repellent treatments with salt loaded substrates [van Hees & Lubelli 2013]. Besides, the partial filling of the pores with the consolidant, as well as the development of small cracks (due to shrinkage of the TEOS), might create fine porosity in the material and increase thereby the risk of salt damage [Scherer 2004].

It has to be considered that a consolidation action is generally an irreversible treatment, regardless the supposed reversibility of the used agent [Matteini et al. 2011]. This operation can thus be risky when using procedures and products that are not compatible with the treated materials. In practice, harmful side effects and short- and long-term consequences, including the possible loss of the surface that was supposed to be preserved, are frequent [Delgado Rodrigues 2001; Ferreira Pinto & Delgado Rodrigues 2008a].

Despite the extensive research carried out over the last decades, consolidation is still often carried out following a trial-error approach in the selection and application of consolidants [Delgado Rodrigues 2010]. This is also due to the lack of (internationally) recognized norms, protocols or recommendations for the application of consolidants.

Many factors should thus be taken in account when dealing with a consolidation action: intrinsic material properties (e.g. chemical mineralogical composition, total porosity and pore size distribution, moisture transport properties, etc.), state of conservation (e.g. water and salt content), the degradation mechanisms and decay types, the characteristics of the consolidant product (e.g. chemical composition, concentration and strengthening capacity, penetration capacity, particle size, viscosity, setting time, type of solvent or medium, ect.) and environmental factors (e.g. relative humidity, temperature, air speed, etc.) [Ferreira Pinto & Delgado Rodrigues 2008a; van Hees et al. 2017]. A preliminary characterization of the materials to be treated and a suitable monitoring of the environmental conditions are thus essential for a successful consolidation action. Besides, the application protocol, which includes the amount of product applied, the application method and the number of applications and time interval between applications are crucial in determining the effectiveness of a consolidation action.

The products can be applied to the surface using different methods (coating, spraying/nebulization, immersion, pouring, poulticing or injection) and tools (brush, sprayer, syringe, pipette etc.). Generally, in situ applications are performed by spraying or brushing, whereas in laboratory studies often immersion and capillary absorption are used. In all cases, the consolidants are absorbed by the stone by capillary action. For movable objects and ashlars, low-pressure application techniques and vacuum systems are adopted in some cases [Doehne & Price 2010].

Although it is not possible to provide a single standard procedure for all situations, once the main factors influencing the effectiveness of the treatment are identified, recommendations for the choice of the product and the application method can be formulated. In this PhD research, this approach has been followed in order to define guidelines for an effective consolidation of calcareous materials by the use of nanolime dispersions.

§ 2.2 Requirements

A consolidation intervention should be effective (i.e. should be able to recover the cohesion of the decayed material), compatible with the substrate, (i.e. should not cause any damage to the substrate or adjacent material) and, at the same time, be durable.

As discussed in the previous sections, the achievement of these requirements depends not only on the product and on the substrate characteristics, but also on the application procedure and on the ambient conditions during and after the product application.

Another relevant requirement concerns the toxicity and eco-compatibility of the consolidant products: consolidant products (especially the solvents concerned) should be unharmful to both operator and environment, and thus have a near-zero toxicity, amongst others.

§ 2.2.1 Effectiveness

A consolidant should be able to recover the cohesion and the strength of the decayed stone, optimally up to the level of the sound stone as existing before degradation [Delgado Rodrigues 2001].

The consolidant product should be homogenously distributed in-depth in the substrate (i.e. in the full thickness of the decayed layer) and thus guarantee mass consolidation. Therefore, the achievement of a successful consolidation action is also related to the ability of the product of penetrating in the material; this ability, is, on its turn, affected by e.g. the viscosity, the surface tension and, in the case of a dispersion, by the size of

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the suspended particles. In addition, after penetration and solvent evaporation, the consolidant product should be capable to deposit in a homogenous way and react within the strengthened layer [Doehne & Price 2010].

§ 2.2.2 Compatibility

The concept of reversibility has been conceived with the idea that each restoration treatment should be reversible [Brandi 1963; ICOMOS 1966; Plenderleith 1976; Siegesmund & Snethlage 2014]. However, as practice demonstrated that many intervention actions, including consolidation, are intrinsically irreversible, this concept has been later substituted by those of compatibility and retreatability [Petzet 1993; Teutonico et al. 1997]. These two concepts provide the framework for a scientific approach to conservation, being the basis of conservation science. Compatibility means that an intervention should not cause any damage to the substrate or adjacent material. Retreatability implies that the present conservation treatment will not preclude or impede future treatments.

In the last decades, several interdisciplinary teams have tried to define, through laboratory and in-situ observations, the parameters and tolerance limits to evaluate to what extent a conservation treatment can be defined compatible. A consolidation treatment can be considered compatible if it ''does not lead to technical (material) or aesthetic damage to the existing materials, while at the same time being as durable as possible'' [van Hees 1999; van Hees et al. 2002; Delgado Rodrigues & Grossi 2007; van Hees et al. 2017]. Thus, several compatibility requirements must be taken into account, in order to avoid to initiate or enhance any damage or decay patterns related e.g. to the transport of water and/or soluble salts within the treated surface, or to the over-strengthening of the consolidated part with respect to the sound, original material [van Hees et al. 2017]. These compatibility requirements can be further subdivided as follows [van Hees 1999; Delgado Rodrigues & Grossi 2007, van Hees et al. 2017]:

- *Physical requirements:* the consolidant should not significantly alter the physical properties of a material, e.g. its porosity and pore size distribution, moisture transport properties (e.g. water absorption, drying rate, vapour permeability), thermal dilatation and hygric swelling;
- *Chemical requirements:* the consolidant should preferably have a chemical composition similar to the material to be treated, thus e.g. the use of calcium-based products is recommended for calcareous substrates and the use of silica-based materials for

sandstones; a good chemical compatibility, apart from favouring chemical interaction between the consolidant and the substrate, limits also differences in the solubility of treated and untreated areas, which can lead to differential degradation between the consolidated and not consolidated areas of the substrate. In addition, the consolidant should not form by-products or harmful chemical compounds (e.g. salts);

- *Mechanical requirements*: the treatment should guarantee to the treated material hardness, cohesion and deformability values as much as possible similar to those of the sound, untreated material. For example, the mechanical properties of the decayed, treated material should not be as much as possible in the range of those of the sound material.
- *Aesthetic requirements*: after treatment, no discolouration or chromatic alteration (such as whitening, in the case of inorganic materials) or surface gloss should be macroscopically visible.

In general, it can be recommended that the physical, chemical, and mechanical properties of a weathered material should be, after consolidation, as much as possible similar to those of the untreated sound substrate. It should be avoided that the treatment initiates new damage processes or worsen those already existing.

The definition of tolerance limits for the definition of a compatible consolidation has been attempted by some authors in the case of limestone and mortar [van Hees 1999; Delgado Rodrigues & Grossi 2007; Snethlage 2013; Siegesmund & Snethlage 2014; van Hees et al. 2017]. However, the definition of these limits remains a difficult task: laboratory tests can provide some guidelines and indicative limits to the operators, which should match the necessities of the case through preliminary trials on the substrate to be treated.

§ 2.2.3 Durability

The durability of a consolidation intervention is determined not only by the stability of the consolidant material (e.g. its resistance to chemical alteration, UV light etc.), but also by the resistance of the treated material to future environmental or stress-induced deterioration. The consolidation treatment should improve the resistance of the decayed material to weathering due to e.g. salt crystallization, freeze-thaw, biological attack, decay processes induced by atmospheric pollutants, photo-degradation by UV and sunlight. A consolidated material should have a better durability towards damage processes (e.g. salt crystallization) than the decayed, untreated material.

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§ 2.3 Consolidant products for calcareous materials

A wide variety of both mineral and organic products has been used in the past for consolidation of calcareous materials.

Lime is one of the oldest consolidant materials for calcareous substrates. Used since ancient Greeks and more extensively in Roman times [Vitruvius Pollio, ed. 1970], lime (calcium hydroxide, $Ca(OH)_2$) is obtained by the thermal decomposition of calcium carbonate ($CaCO_3$) from limestone or shells at high temperature (800-900 °C). The obtained porous lumps of calcium oxide (quicklime, CaO) are then hydrated to form calcium hydroxide (the so-called slaking process), in the form of dry lime powder, lime putty or lime slurry (depending on the amount of water involved in the process). The hydration of CaO to $Ca(OH)_2$ is a heterogeneous phase precipitation process [Rodriguez-Navarro et al. 2005].

When lime is used for consolidation, a saturated solution of calcium hydroxide (*limewater*) is allowed to penetrate into a porous network; subsequent evaporation of the solvent will lead to the deposition of calcium hydroxide within the material and thus, after carbonation, the formation of interlocking calcium carbonate crystals [Van Balen 2005; Doehne & Price 2010]:

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

The occurrence and rate of carbonation is influenced by several parameters, e.g. environmental conditions (temperature, RH, moisture content in the substrate), size and shape of the portlandite crystals, and properties of the substrate material [Van Balen & Van Gemert 1994]. For a successful consolidation effect, the type of $CaCO_3$ polymorph formed during carbonation is very important, some being more stable (e.g. calcite, aragonite), and thus more effective for consolidation, than others (e.g. vaterite, amorphous calcium carbonate or monohydrocalcite) [Hansen et al. 2003; Lópe-Arcé 2010; Gomez-Villalba et al. 2012; Rodriguez-Navarro & Elert 2016a].

Limewater is chemically fully compatible with lime-based substrates and has low costs. Furthermore, lime has initially (i.e. before carbonation occurs) also a biocide effect due to its high alkalinity. However, depending also on the application procedure, limewater effectiveness is often scarce, due to low consolidation action and poor in-depth penetration.

In fact, due to the low solubility of calcium hydroxide in water (1,17 g/l at T=20ºC), many applications are necessary to achieve some strengthening effect [Slížková et al. 2015]. Besides, carbonation (and thus strengthening effect) is usually quite slow [Daniele et al. 2008]. In addition, a considerable amount of water is introduced in the treated materials, posing a risk to the substrate through the mobilization of soluble salts, biological colonization or freeze-thaw effects, and an additional stress due the weight of the water [Hansen et al. 2003].

Limewater has been the only (lime-based) consolidant used until the 19th century, when the developments of chemistry introduced other (synthetic) products. New artificial silica-based materials were synthetized and proposed for the conservation of stone, limestones included [Barff 1860; Egleston 1886].

Among alkoxysilanes, *tetraethoxysilanes* (or TEOS), firstly conceived by Ebelmen in 1846 and by Regnaulg in 1853 and commonly known also as ethyl silicate, were proposed as stone consolidant by A.W. Von Hoffman in 1860, and later optimized by Ladenburg in 1872 [Wheeler 2008; Siegesmund & Snethlage 2014].

These products were later re-proposed in the field of conservation by Laurie in the 1920s, and commercialized on a wider scale in the 1970s with the invention of Wacker OH, a tetraethoxysilane in acetone and other ketones [Wheeler 2008]. The chemical composition of ethyl silicate has been modified throughout the years (e.g. Wacker OH100 is now solventless), and nowadays different TEOS-based formulations and products are commercialized (e.g. Tegovakon V100® by BASF, Conservare® line by Prosoco, Funcosil® line by Remmers, CPX309® by Evonik, etc.) [Wheeler 2008; Tavares et al. 2008].

TEOS-based products, with formula $Si(OCH_2CH_3)_4$, are by far the most used consolidants, also for the consolidation of calcareous substrates [Siegesmund & Snethlage 2014]. These consolidants are absorbed within the stone and, after silanol formation through hydrolyzation, polymerise through a condensation reaction and form nanometrical spherical particles of tetra-coordinated silica, that produces the required strength increase [Zendri et al. 2007; Wheeler 2008; Ferreira Pinto & Delgado Rodrigues 2008a]. The simplified reaction of tetraethoxysilane is as follows:

$$[Si(OCH_2CH_3)_4]_n + 2\ nH_2O \rightarrow nSiO_2 + 4\ nCH_2CH_3OH \qquad (2)$$

These products can penetrate deeply into porous materials. No deleterious by-products are formed in the reaction, since ethanol formed in the reaction evaporates completely. De Clercq [De Clercq 2007; De Clercq 2008] showed that the application of ethyl silicate on Maastricht limestone with an optimized protocol (e.g. number and interval between applications) can induce a strong in-depth increase of the mechanical resistance. Nevertheless, TEOS-based products have low chemical and mechanical compatibility with calcareous substrates and in some cases low effectiveness and durability [Hansen et al. 2003; Ferreira Pinto & Delgado Rodrigues 2012a; van Hees et al. 2014]. In fact, the Si-OH groups have poor chemical bonding to calcitic substrates and a tendency to shrink and crack during condensation and drying [Ferreira Pinto & Delgado Rodrigues 2012a]. A lack of moisture in the pores of the treated material can create an additional problem, due to the necessity of water in the reaction.

The introduction of elastified, nanostructured and hybrid silanes has minimize the tendency to shrinkage. Modified products can include surfactants (as primary amine) [Mosquera et al. 2008], or silane components and/or silica nanoparticles [Kim et al. 2009]), which can influence the sol-gel transition and thus provide a crack-free material. Additionally, pretreatments with coupling agents can enhance the chemical bondings to calcareous substrates [Ferreira Pinto & Delgado Rodrigues 2008b; Lubelli et al. 2012].

However, important problems may still occur in the presence of excessive moisture or salts in the substrate [Doehne & Price 2010].

At present, the use of TEOS-based products for the consolidation of carbonated stones results from the lack of more adequate alternatives [Ferreira Pinto & Delgado Rodrigues 2008a].

Sodium and potassium silicates (or *waterglass*), invented in the first half of 19th century and later used for stone consolidation [Siegesmund & Snethlage 2014], constitute another class of compounds which is still commercially available. Lithium silicates were introduced in recent years and attracted some interest due to the lower solubility of the relative carbonate (formed by reaction in air), when compared to sodium and potassium carbonate. This would limit the risk of salt damage due to the formation of soluble carbonate salts, often observed in the case of the sodium and, in a lower extent, potassium silicates.

In fact, these compounds react in presence of CO_2 and moisture to form the relative carbonate and silica, e.g.:

$$Na_2SiO_3 + CO_2 + nH_2O \rightarrow SiO_2 \cdot nH_2O + Na_2CO_3 \qquad (3)$$

A limitation of, these silicates is their low reactivity in air and the formation of silica gel (Si-O-Si siloxane bonds), which can hardly penetrate in depth in the substrate (the penetration depth is limited generally to 1-2mm) and cause the formation of a brittle surface layer [Siegesmund & Snethlage 2014].

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Fluosilicates (or fluates) were synthetized and introduced in 1883 by Kessler, and they have been used for consolidation and as water repellent products since the last decades of the 19th century [Siegesmund & Snethlage 2014; Nijland 2016]. These salts of the fluosilicic acid H_2SiF_6, generally functionalized with metal ions as Mg ($MgSiF_6$) or Zn ($ZnSiF_6$) (and more rarely with Pb or Al), were used also in the form of double-fluosilicates (such as $MgSiF_6$-$ZnSiF_6$ or $Al_2(SiF_6)_3$-$ZnSiF_6$) [Nijland 2016].

These compounds react in presence of calcium (as in limestone) or other alkalis to produce amorphous silica gel and insoluble fluorite:

$$2CaCO_3 + MgSiF_6 \rightarrow 2CaF_2 + MgF_2 + SiO_2\,\text{gel} + 2CO_2 \quad (4)$$

These treatments induce a high strength increase, but this is confined to the first millimetres of the surface (generally 1 to 6mm). These treatments can therefore be harmful, as they induce a differential behaviour between the very strong, superficial consolidated layer and the inner part of the substrate [Siegesmund & Snethlage 2014; Nijland 2016]. The presence of water in the substrate at the moment of the application of this consolidant product can furthermore produce hydrofluoric acid, which is highly aggressive for the treated substrate and highly toxic for the operator. Besides, iron-containing stone can be discoloured due to the high acidity of the fluosilicate solutions.

Acrylates are an important class of organic compounds, which were used mostly as adhesive for the conservation of calcareous substrates such as limestone and mural paintings. These materials are formed by esters of acrylic acid (CH_2=CH−COOH) and alcohols (general formula $C_nH_{2n+1}OH$) [Siegesmund & Snethlage 2014]. Polymethyl methacrylate (PMMA, commonly known as Plexiglas), synthetized in 1932 by Rohm and Bauer, is the most known product among acrylates.

These products are easy to be used, widely available and have good adhesive properties. In addition, these materials were thought to be highly resistant to aging and easily removable [Baglioni et al. 2013].

However, the penetration depth of meta-acrylates is limited. They are mainly adopted for coarse porous materials or strongly weathered stone, or they are applied under vacuum (mainly in the case of movable objects) [van Hees & Larbi 2000].

In fact, these compounds can undergo long-term physico-chemical degradation at the surface [Favaro et al, 2007], and can alter significantly the visual aspect of the treated substrate (yellowing, due to the presence of amines and peroxides, and glossy surface); moreover, these synthetic adhesives can drastically alter the physico-chemical properties of the original substrates, such as porosity, water capillarity, water vapor

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permeability and surface wettability [Baglioni et al. 2015a]; finally, acrylates are usually diluted before application in highly toxic solvent as toluene, acetone or ethyl acetate.

Acrylate products, such as Paraloid B72 (copolymer of methyl and ethyl metacrylates), became sadly famous for their dramatic effects on the treated material, with an increase of surface degradation [Baglioni & Giorgi 2006a]. A significant example is the restoration of the external limestone and marble façade of the San Petronio Cathedral in Bologna, performed in the 1970s' using a mixture of acrylic resin and silane (the so-called Bologna Cocktail) [Gnudi et al. 1979]. The treatment resulted in a rather good conservation of the treated surface for almost 50 years. However, this architectonical surface recently underwent a new restoration due also to the long-term degradation of the polymers, which implied a strong content reduction of the silane and alteration (photo-oxidation) of the acrylic component [Favaro et al. 2007].

Epoxy resins are another class of synthetic compounds, which were used for stone consolidation. These polymers are generally obtained by mixing a bi-phenol agent resin to an amine-based hardener. These compounds have a strong adhesive force, which however make them mechanically incompatible with stone and lime-based mortars. Besides, the two components of the epoxy can separate during absorption in the substrate, causing an incomplete hardening [Siegesmund & Snethlage 2014]. In addition, the degradation of the amine induces yellowing of the treated surface.

In recent times, the drawbacks observed with polymers and organic consolidants has made conservation scientists reconsider traditional inorganic consolidants [Baglioni et al. 2013, van Hees et al. 2017], mostly calcium- and barium-based treatments. These treatments develop a structure of neo-formed products (e.g. $CaCO_3$ or $BaCO_3$), inducing the consolidating effect [Hansen et al. 2003].

Amongst the lime-containing consolidation treatments, *biomineralization* has been a method experimented by many researchers [Adolphe et al. 1990]. It involves the application on the surface of calcite-forming bacteria. Calcite growth appears, however, to be confined to larger pores due to the size of the bacteria [Hansen et al. 2003], with a limited in-depth penetration and thus consolidation action.

Barium hydroxide is another consolidant considered already in the 19th century [Church 1862] for its durability and compatibility with calcareous substrates. When applied on a calcareous material, barium hydroxide can form a coating of barium carbonate, which is more resistant than calcium carbonate to acid rain [Bracci et al. 2008; Doehne & Price 2010; Delgado Rodrigues & Ferreira Pinto 2016a]. In addition, barium hydroxide is much more soluble in water (56 g/l) compared to calcium hydroxide (1,8 g/l)

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[Hansen et al. 2003], allowing for a higher amount of binding agent and a fairly in-depth consolidation action [Delgado Rodrigues & Ferreira Pinto 2016a].

Since the late 1960s', barium hydroxide was used in the so-called Ferroni-Dini method [Matteini 1991], mainly for conservation of mural paintings. This method allows the conversion of gypsum to carbonates and the consolidation of surfaces affected by sulfates [Hansen et al. 2003; Baglioni & Giorgi 2006a]. At first, an application of ammonium carbonate converts gypsum (selenite) into ammonium sulfate and calcium carbonate:

$$(NH_4)_2CO_3 + CaSO_4{\cdot}2H_2O \rightarrow (NH_4)_2SO_4 + CaCO_3 + 2H_2O \tag{5}$$

Secondly, a solution of barium hydroxide is applied, which reacts with ammonium sulfate to form barium sulfate (baryte). Barium sulfate is much less soluble than gypsum and thus consolidates the surface:

$$(NH_4)_2SO_4 + Ba(OH)_2 \rightarrow BaSO_4 + 2NH_3 + 2H_2O \tag{6}$$

The volatile ammonia and water resulting from the reaction evaporate, while the excess of $Ba(OH)_2$ is subjected to carbonation:

$$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O \tag{7}$$

Barium carbonate crystals act as 'filler' for the empty spots created by the reconversion of gypsum into calcite, thus sensibly reducing the porosity of the treated surface and recovering the superficial cohesion. This method is reported to give a durable improvement of the mechanical resistance.

Calcium oxalate is another compound, which has been recently reproposed for consolidation [Hansen et al. 2003]. Oxalates, used since the 19th century in the form of oxalic acid [Schwab & Koehl 1984], can be considered chemically compatible with calcareous materials [Hansen et al. 2003; Matteini et al. 2008]. The method implies the application by poultice of a solution of ammonium oxalate, which reacts with carbonates in the substrate to form calcium oxalate as final product.

$$CaCO_3 + (NH_4)_2C_2O_4 \rightarrow CaC_2O_4 + (NH_4)_2CO_3 \tag{8}$$

Ammonium carbonate formed in the reaction promotes the conversion and removal of gypsum [Matteini et al. 2008], or spontaneously decomposes in volatile ammonia, water and carbon dioxide.

The formation of an acid resistant calcium oxalate layer can be beneficial in a highly aggressive environment. However, this treatment has a very limited penetration depth and is therefore suitable only for very superficial damage in marble and low-porous limestones [Matteini et al. 2008]. In some cases, it can create a compact crust and a slight whitening on the treated surface. Additionally, repetitive oxalate exposure can be toxic to human health.

Calcium phosphate, mostly in the form of the hydroxyapatite (HAP) with formula $Ca_5(PO_4)_3(OH)$, has been considered as consolidant product in the last two decades [Matteini et al. 2011; Sassoni et al. 2011]. HAP is less soluble than calcite, assuring both a good compatibility with calcareous substrates and good durability [Sassoni et al. 2011]. The most suitable method for in situ stone strengthening involves the reaction of diammonium hydrogen phosphate (which has good solubility in water, 10g/l) with calcite in the substrate to form carbonate-containing HAP [Sassoni et al. 2011]:

$$10CaCO_3+6(NH_4)\cdot H_2PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 +6NH_3 + 10CO_2 + 8H_2O \tag{9}$$

This method is reported to confer a good in-depth consolidation action in limestone and a rather good durability to wetting/drying cycles [Matteini et al. 2011; Sassoni et al. 2011]. Compared to calcium oxalate, HAP can guarantee a more uniform consolidation action, without the formation of an external crust [Matteini et al. 2011]. The consolidating effectiveness, near-zero toxicity, the absence of significant colour variations and the minor reduction of the water absorption capacity make ammonium phosphates a promising consolidation agent [Matteini et al. 2011]. However, to the author best knowledge, no applications in practice are documented yet for this product.

§ 2.3.1 Colloidal dispersions and nanomaterials

In the last two decades, the progress in colloid and surface science provided new possibilities in the field of conservation. Colloidal dispersions, which consist of nano- to submicron-particles dispersed in a medium, demonstrated to overcome some of the limits of more traditional restoration methodologies (as seen in the previous section). In fact, the high area/volume ratio of the nanoparticles affects the physical-chemical properties and confers a potentially high reactivity, stability and performance [Baglioni & Giorgi 2006a; Baglioni et al. 2009; Baglioni et al. 2013].

As seen in the previous section, alkoxysilanes are at present the most used products in the conservation of calcareous materials [Baglioni et al. 2013]. Nanosilica, consisting of an aqueous dispersion of nanostructured colloidal silica (10-20 nm), can be considered a bi-phase evolution of these silane-based materials. After water evaporation, nanosilica particles aggregate and induce the formation of a silica gel matrix [De Ferri et al. 2011]. One of the main advantages of nanosilica dispersions is that they, differently from TEOS-based consolidants, can be applied under wet conditions; besides, their drying (and thus reaction) time is short (3-4 days). However, nanosilica products are chemically incompatible with calcareous substrates and may have a limited penetration depth. Additionally, they can lead to the formation of a compact colloidal silica layer on the treated surface, which shows significant shrinkage [Borsoi et al. 2013; Zornoza et al. 2016].

Nano-particulate inorganic sols (nanosols) based on alkaline earth metal hydroxides (e.g. calcium, barium and magnesium hydroxide) are a promising alternative to the use of silicon-based coatings [Baglioni et al. 2012]. In particular, calcium-based nanosols can be considered chemically compatible and potentially highly durable products for the consolidation of calcareous substrates [Chelazzi et al. 2013].

Calcium alkoxides constitute another class of compounds which have been proposed also for the consolidation of calcareous substrates. The generic alkoxide formula is $Ca(OR)_2$, where R is an alkyl or aryl group. Calcium alkoxides, e.g. calcium ethoxide $Ca(OCH_2CH_3)_2$, can be obtained with several synthesis methods (e.g. direct reaction of metallic calcium in alcohol, alcoholysis, using tetrahydrofuran (THF) suspensions or ammonia-activated calcium [Favaro et al. 2008; Ossola et al. 2012; Favaro et al. 2013].

There are several similarities between calcium hydroxide (which has a crystalline structure, in the case of portlandite) and alkoxides (which have mostly an amorphous structure), as they both lead to the formation of calcium carbonate. Depending mainly on the used dispersant and on the environmental conditions, alkoxides act as intermediate (after hydrolysis) for the formation of calcium hydroxide, and ultimately form calcium carbonate (vaterite or calcite) after carbonation.

Highly concentrated (> 40 g/l) nanosized dispersions of calcium alkoxides with low polydispersity can be obtained, thanks to the high solubility of alkoxides in water [Ossola et al. 2012]. In addition, no further purification of the synthetized product is necessary, the dispersion being ready to be applied after synthesis.

The possible limit of this method can be related to the instability and high reactivity of the dispersions. In addition, alkoxides can lead to the formation of metastable vaterite as well as of amorphous calcium carbonate and aragonite, which have a lower consolidation effect than calcite [Rodriguez-Navarro & Elert 2016a]. However, since the high reactivity of alkoxides speeds up the carbonation process and increases the $CaCO_3$ yield, alkoxides can be advantageous for consolidation interventions when fast carbonation is required (e.g. for pre-consolidation treatment) [Campbell et al. 2011; Rodriguez-Navarro et al. 2013].

Nanolimes, i.e. calcium hydroxide nanoparticles dispersed in alcohols, are extensively described in the next section.

§ 2.4 Nanolime

§ 2.4.1 Definition and history

The so-called nanolimes are amongst the most innovative consolidation products delivered by colloidal science for conservation purposes. Nanolimes are opal fluids consisting of nanosize particles dispersed in an alcoholic medium (mostly isopropanol or ethanol) [Giorgi et al. 2000; Ambrosi et al. 2001a]. They can be considered a modern evolution of limewater [Ambrosi et al. 2001b; Baglioni et al. 2013]. The first attempt to synthesize $Ca(OH)_2$ nanoparticles was performed in 1996 by the group of Baglioni at the CSGI in Florence [Baglioni et al. 2015b]. An innovative bottom-up synthesis method was developed, following the way suggested by Matijević in the field of colloid syntheses [Matijević & Cimaš 1987; Chelazzi et al. 2013].

The high lime content and the stability of the dispersions are the most important advantages of nanolimes. Thanks to the nanosize of the particles and to the use of an alcoholic dispersant, nanolimes overcome the limitations imposed by the low solubility and stability of calcium hydroxide in water (section 1.3).

Nanolimes have proven to be able to recover the superficial cohesion of different materials, such as frescos and plasters[Giorgi et al. 2000; Giorgi et al. 2005; Dei & Salvadori 2006; Ziegenbalg et al. 2010]., as well as in the pre-consolidation and deacidification of paper and wood [Poggi et al. 2014]. They have been successful in the consolidation of e.g. lime-based lifted paint layers and in the substitution of previous treatments [Baglioni & Giorgi 2006a]. For instance, a combination of the Ferroni-Dini method and of lime nanoparticles demonstrated to be effective in the conversion of sulfate salts to carbonate within painted layers, later consolidated with lime nanoparticles [Baglioni et al. 2013].

However, nanolimes show a poor effectiveness when mass consolidation is required, like for example in the case of decayed mortars or limestones [Campbell et al. 2011; Costa & Delgado Rodrigues 2012]. The scarce consolidation effect in-depth has limited until now a wider diffusion of these nanomaterials.

The literature review shows that the effectiveness of nanolime as consolidant is still doubtful in some cases, as seen above. Further research is thus necessary in order to understand if nanolime is an effective alternative to silica-precursor consolidants (e.g. TEOS) for the consolidation of lime-based and calcareous substrates (i.e. mortars and limestone).

§ 2.4.2 Synthesis methodologies and evolution

Nanometric (≤ 100nm) and submicrometric particles (<1 µm) of calcium hydroxide can be obtained through two different methodologies.

The first is the *breakdown process*, a top-down strategy, which consists in the grinding of bulk solids into nanosize particles. This process is usually obtained by mechanical grinding and/or thermal decomposition, which produce particles with an average size of 300 nm [Baglioni & Giorgi 2006a; Baglioni et al. 2013; Baglioni et al. 2014]. However, these processes are generally subjected to contamination during the process and by exposure in air.

The second methodology is a *bottom-up strategy*, which is based on the reactions of different precursors in solution to obtain freshly synthetized nanoparticles. Nanoparticles can be built up by deposition and growth of crystals from a liquid or vapour phase, or by solid-state sintering and reaction among nanoparticles [Baglioni & Giorgi 2006a]. The main problem of nanoparticles synthesis is related to their self-aggregation, mainly due to electrostatic, dipolar and Van der Waals forces.

As illustrated in the next sections, different bottom-up synthesis methodologies have been developed for the production of calcium hydroxide nanoparticles dispersed in ethanol. Several pathways have been optimized for controlling the size and shape of the particles, their crystallinity and purity, and ultimately their reactivity and penetration depth [Baglioni & Giorgi 2006a; Baglioni et al. 2009; Baglioni et al. 2013].

The review presented in the next sub-sections aims at evaluating the cutting-edge technologies available for the production of nanolime dispersions, considering the stability, size and purity of the obtained nanolime particles and the production costs. Besides, the possibility of up-scaling the process, the evaluation of the eco-toxicity and possible impact of the production process on the operators are also considered. Based on these considerations, the choice for the most suitable method for nanolime production is made.

§ 2.4.2.1 Homogeneous phase reaction

Calcium hydroxide can be synthesized via either heterogeneous (e.g. lime slaking) or homogeneous phase precipitation. The latter methodology consists in a precipitation reaction, which involves the formation of calcium nanoparticles from the reaction of precursors in solution.

Precipitation reaction of solid particles from the liquid phase is probably the simplest and cheapest method to obtain nanoparticles with monodispersity and similar morphology [Baglioni & Giorgi 2006a]. The control of the reaction conditions (e.g. temperature, concentration of reacting species, aging time) is crucial to achieve a high supersaturation degree, necessary for nucleation and for controlling the size, shape and structure of the nanoparticles [Salvadori 2001; Baglioni & Giorgi 2006a; Daniele & Taglieri 2010].

The most used precursors are calcium chloride and sodium hydroxide, two soluble salts which are solubilized in super-saturating conditions and at high temperature in water (60-90°C) [Baglioni & Giorgi 2006a; Daniele & Taglieri 2010] or diols (e.g. ethylene glycol, up to 190°C) [Salvadori 2001]:

$$CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl \qquad (10)$$

This process can produce very fine calcium hydroxide nanoparticles (50 to 300 nm in aqueous phase, 30-80 nm in diols) with a significant yield; the morphology and symmetry vary from plate-like shaped particles to cauliflower-like agglomerates [Salvadori 2001; Ambrosi et al. 2001a; Baglioni & Giorgi 2006a]. Ultrahomogenizer systems and ultrasonic baths are usually used to obtain reasonably stable dispersions [Chelazzi et al. 2013] and minimize aggregation phenomena. The use of a nitrogen atmosphere guarantees nanoparticles with more defined and homogeneous morphology [Girginova et al. 2016].

The hexagonal plate-like shape is considered to be an advantageous morphology, since these crystals tend to be oriented in parallel layers, that can retain water and thus enhance the plasticity of the nanolime [Rodriguez-Navarro et al. 1998].

The main limitation of this process is the formation during the reaction of a by-product, sodium chloride, which needs then to be removed by washing (peptization). After cooling down to room temperature and under N2 atmosphere to avoid carbonation, the mixture of calcium hydroxide and sodium chloride is centrifuged and the supernatant solvent (excess of solvent) is substituted by distilled water; this process is repeated several times in order to wash out soluble NaCl. Finally, water is replaced by an alcoholic solvent, such as isopropanol or ethanol [Giorgi et al. 2001; Ambrosi et al. 2001a; Daniele et al. 2008]. When using diols, a higher number of peptizations is necessary to remove the diols, as these tend to be strongly adsorbed within the nanoparticles, enhancing micro-size agglomeration [Ambrosi et al. 2001a].

§ 2.4.2.2 Micelle-assisted synthesis

The method described in 2.4.2.1 was modified by Daniele and Taglieri [Daniele & Taglieri 2012; Taglieri et al. 2013] by adding a non-ionic surfactant within the solution (Triton X100, a phenol- functionalized glycol); this addition catalyses the precipitation reaction and allows to obtain small particle sizes (20 to 200nm); however, also in this case the removal of the organic surfactant from the solution is complex. In addition, the phenol-based surfactant is toxic and, if not properly removed, can affect the durability of the consolidation treatment.

A modification of this method was proposed by Taglieri [Taglieri et al. 2014]. This method consists in synthetizing calcium hydroxide nanoparticles directly in a hydro-alcoholic suspension. This method can drastically reduce the time of synthesis while still maintaining a good yield (nanoparticles of 40-300nm), thus scaling-up the production of nanolime. However, this is again a surfactant-assisted (or micelle-assisted) synthesis, which implies the use of Triton X100; repeated washing is therefore necessary to remove the produced NaCl and the surfactant.

Another modification of the method is proposed again by Taglieri in [Taglieri et al. 2015]: this method is based on a ion exchange process between an anionic resin and a calcium chloride aqueous solution, operating at room temperature. A dispersion of pure $Ca(OH)_2$ nanoparticles can be obtained after separating the resin from the suspension, without a purification step being necessary. This synthesis guarantees

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a good yield, reduces the time of synthesis and ensures hexagonal plate-like nanoparticles with sizes of 50 to 200 nm.

§ 2.4.2.3 Water/oil microemulsions

Another bottom-up method consists in the use of *water/oil microemulsions*, commonly used for the synthesis of nanoparticles of inorganic materials [Baglioni 2006a]. This method consists of two microemulsions (one containing the metallic salt and the other the precipitating agent), which react within nanocompartments or inverted micelles (water droplets in oil). The surface-active agent (oil) constitutes the drops of the microemulsions and controls a possible further crystal growth, guaranteeing a high monodispersity.

Delftort [Delftort 1997] used a surfactant-assisted (or micelle-assisted) synthesis but with a water in oil microemulsion. The author, by dispersing calcium hydroxide ($Ca(OH)_2$) in aqueous solution additivated with a sulfonate, obtained very thin nanoparticles (10 to 30nm). This method has however a low yield and is time-consuming.

Nanni [Nanni 2004] obtained quasi-spherical lime nanoparticles of 6-10 nm, by the use of NaOH and $CaCl_2 \cdot H_2O$ as precursors and an ester- functionalized glycol as non-ionic surfactant and cyclohexane as dispersant. However, the removal of the surface-active agent is a complex process, since this is partially absorbed within the nanoparticles. In addition, the yield of this reaction is very low [Baglioni 2006a; Chelazzi 2013].

Other similar synthesis methods by means of a template are reported in literature, including e.g. the use of hydrosoluble polymers [Xu 2004] to form calcium hydroxide nanoparticles of 50–100 nm.

§ 2.4.2.4 Sol-gel synthesis

Another very recent synthesis method involves the synthesis of nanoparticles of calcium hydroxide using the sol–gel citrate method [Darčanova 2015]. In this case, calcium nitrate $CaNO_3$ is used as precursor and dissolved in water and citric acid (organic additive used as emulsifier), to obtain nanostructured calcium hydroxide, which is immediately hydrated and forms calcium hydroxide. This method allows to produce particles with about 100 nm size and it does not need any purification or washing (the by-product, ammonia, evaporates from the solution).

§ 2.4.2.5 Insolubilisation-precipitation method

This method involves the preparation of a saturated aqueous solution of calcium hydroxide, to which a certain amount of 2-propanol is added, causing the formation of nanostructured calcium hydroxide [Nasillo et al. 2011; Bastone et al. 2016]. This method appears promising, since it is easy and forms nanoparticles directly into the solvent to be used for applications [Nasillo et al. 2011]. However, the yield is very low, due to the low solubility of calcium hydroxide in water (1,27-1,81 g/l).

§ 2.4.2.6 Solvothermal reaction of metallic calcium

A different method to obtain nanostructured $Ca(OH)_2$ crystals consists in the use of bulk (metallic) calcium. This method, performed by vaporizing metallic calcium at high temperature (70 to 130ºC) in a nitrogen/hydrogen atmosphere, allows high nanoparticle purity and yield. Starting from metallic calcium and by the use of the hydrogen plasma-metal reaction method (a vapor deposition process), Liu [Liu et al. 2010] obtained nanoparticles of about 100 nm size, with hexagonal nanocrystalline structure and quasi-spherical shape.

High-pressure thermal reaction of metallic calcium is another method to form calcium hydroxide nanoparticles [Ziegenbalg et al. 2010; Poggi et al. 2014]. This procedure consists of a two-step reaction: at first calcium metal is oxidized by short chain alcohol at a pressure of around 350 bars, leading to the production of the corresponding alkoxides $Ca(OR)_2$; in a later stage, the compound is hydrated and undergoes hydrolysis leading to a colloidal calcium hydroxide, already dispersed in an appropriate solvent for the application. This method allows to produce high crystallinity nanoparticles with a bimodal particle size distribution (80 and 200 nm) with high yield and no by-products (e.g. harmful sodium chloride) [Poggi et al. 2014; Poggi et al. 2016]. This method can be relatively easily setup and a reasonable amount of nanolime dispersion (1-2 litres at a laboratorial scale) can be produced within few hours.

For the reasons given above, the solvothermal method was considered suitable for the production of nanolime dispersions during this PhD research. The synthesis method used is described in detail in chapter 5.

§ 2.4.3 Mechanism of consolidation

The consolidation action induced by nanolime consists of a two-step process. Firstly, after the application of nanolime, the alcoholic solvent evaporates, followed by the carbonation of lime nanoparticles in air and formation of water (as seen in equation 1, section 1.3).

A first advantage of nanolimes is its carbonation rate. The carbonation process is faster in the case of nanoparticles than in the case of the traditionally used micro-size calcium hydroxide (e.g. slaked lime), leading to a quick consolidation effect. In fact, due to the high surface area of the nanoparticles, complete carbonation can be achieved in a time span of 24 hours to a maximum of 3-4 weeks [Campbell et al. 2011; Daniele & Taglieri 2012; Rodriguez-Navarro et al. 2013], depending on environmental conditions, on the penetration depth and on the properties of the nanolime and on those of the treated substrate.

Environmental conditions especially influence the carbonation process, both in terms of morphology and type of calcium carbonate polymorphs (calcite, aragonite or vaterite). Among calcium carbonate polymorphs, calcite is the most effective for the scope of consolidation, because of its stability. Research by López-Arcé [Lópe-Arcé 2010; López-Arcé 2011] and Daniele [Daniele et al. 2008] showed that high relative humidity conditions (RH ≥ 75%) can lead to large and high crystallinity nanoparticles (a mixture of $CaCO_3{\cdot}H2O$ - monohydrocalcite - and $CaCO_3$ polymorphs such as, calcite, aragonite, vaterite or amorphous calcium carbonate) which fill the pores of the treated substrate homogeneously, thus ensuring a potentially high consolidation action [Lópe-Arcé 2010]. Besides, fast carbonation is observed. Differently, at low RH (RH ≤ 54%) the carbonation is slow, and smaller and less crystalline particles (mostly vaterite) are formed.

Therefore, the presence of moisture in the carbonation process is critical to convert the instable and more soluble amorphous calcium carbonate (ACC) into the more stable and less soluble calcite, and to minimize the formation of vaterite (deleterious for the strengthening effect if present in large percentages).

The alcoholic solvent plays also a relevant role in the carbonation of nanolime. In fact, the formation and stability of the calcium carbonate polymorphs is influenced by the alcohol/water ratio (including water present in the solvent, substrate and air) [Gomez-Villalba et al. 2011].

Rodriguez-Navarro [Rodriguez-Navarro & Elert 2016a] showed that the alcoholic solvent physisorbed onto the $Ca(OH)_2$ nanoparticles favours the formation of metastable precursor phases of calcite (amorphous calcium carbonate - ACC, vaterite and aragonite). At first, ACC is formed, followed by the transformation into vaterite (and minor aragonite). These polymorphs are finally dissolved in the presence of water and converted into stable calcite precipitates within some days through a water-mediated (dissolution–precipitation) mechanism. This underlines the importance of high RH conditions in order to achieve stable calcite, which can guarantee an effective consolidation.

Not only the environmental conditions but also the material properties and the moisture content in the substrate can influence the carbonation rate and the formation of calcium carbonate polymorphs. This aspect has to be considered since a considerable amount of moisture is generally present in masonry.

In some cases, the carbonation of the lime nanoparticles can be slowed down due to the lack of CO_2 or moisture (for example in a very compact porous network) or due to the possible dense packing of the nanoparticles [Ghaffari et al. 2012]; in this case, the use of water or carbonation accelerators (consisting of e.g. mixture of diethyl carbonate and water) has been proposed to speed up the carbonation [Adolfs 2007; Campbell et al. 2011]. However, the high volatility of diethyl carbonate can also speed up the drying rate of the dispersion and this has to be considered in the application.

The addition of yeast fermentation (through a simple yeast–sugar aqueous solution) can also enhance the carbonation [López-Arce & Zornoza-Indart 2015], thanks to the formation of a microclimate with high humidity and CO_2. However, this method can enhance the growth of biological colonization on a treated substrate. The presence of sugar will likely also influence the precipitation of any remaining dissolved calcium hydroxide or the recrystallization of amorphous $CaCO_3$ (e.g. vaterite) into calcite.

It has to be considered that the carbonation of nanolime can be partially inhibited within salt loaded substrates. In this case, the carbonation process is affected especially at low RH, when the conversion into carbonate is slower. Under these conditions and in presence of sodium sulfate, lime carbonation is slowed down due to the very similar solubility of gypsum and calcium hydroxide. Di Gregorio [Di Gregorio 2010] showed that the introduction of alcoholic dispersions of strontium hydroxide seems to be beneficial to compensate the effect of the sodium sulphate, due to an exchange reaction of the strontium hydroxide with the calcium sulfate. On the other hand, being many salts highly hygroscopic, at high relative humidity conditions (85% RH) the water that is adsorbed due to the hygroscopic behaviour of the salts seems to have a positive influence on the process of carbonation of the involved particles [Di Gregorio 2010]

Concluding, high RH conditions are positive to speed up the carbonation and form stable polymorphs of $CaCO_3$, i.e. calcite. However, the presence of moisture or water in the treated substrate should be not excessive, in order to allow the penetration of CO_2 which is fundamental in the carbonation process.

§ 2.4.4 Nanosize

Calcium hydroxide nanoparticles obtained from the synthesis methodologies discussed in the previous section have a spherical to hexagonal plate-like shape and a size ranging from 5 to 600 nm [Giorgi et al. 2000; Dei & Salvadori 2006; Ziegenbalg et al. 2010; Chelazzi et al. 2013], depending on the synthesis procedure and conditions. Due to their small dimensions, nanoparticles can potentially penetrate within smaller pores, which are generally bigger than 500 nm in most calcareous materials.

Another important feature of nanoparticles is their higher surface area (and thus reactivity) in comparison to traditional micro-limes, i.e. limewater, which results in faster carbonation [Daniele & Taglieri et al. 2012]. Furthermore, submicrometric and nanometric particles have a higher kinetic stability than micro-sized particles.

In particular, nanoparticles (size $<$100 nm) have properties (e.g. surface and mechanical properties) that can differ from those of bulk materials [Baglioni & Giorgi 2006a]. For this reason, lime nanoparticles do not obey to Stokes law for sedimentation (that states a dependence of the settling rate on the square of the particle radius), commonly applied for aqueous dispersions of microparticles. At constant temperature and pH, nanoparticles deposition is related to the concentration and thus kinetic stability of the dispersion [Ambrosi et al. 2001a].

An important issue when dealing with nanotechnologies concerns the possible harmfulness of the nanoparticles. Although the long-term effect of nanoparticles on the human body and environment is unknown, a recent study [Tedesco et al. 2015] demonstrated the low toxic effect of the lime nanoparticles, when compared for example to silica-based nanomaterials.

§ 2.4.5 Alcoholic solvent: colloidal stability

As seen in the previous sections, the effectiveness of aqueous lime solutions, like limewater, is limited due to the low solubility and the low kinetic stability of lime particles in water. The use of alcoholic solvents, such as ethanol or isopropanol, can guarantee a much higher lime content (up to 80 g/l), in the form of dispersed nanoparticles, if compared to limewater solutions (1,17 g/l). In addition, short-chain aliphatic alcohols provide a higher kinetic stability to the dispersion and thus a slower particle sedimentation rate than water. The enhanced stability of alcoholic dispersions is due to the combination of electrostatic and hydrophobic (steric) interactions [Giorgi et al. 2000; Salvadori 2001; Rodriguez-Navarro et al. 2005]. The length of the hydrophilic tail of the alcohol influences the stability, being thus the stability order: 1-propanol > ethanol > 2-propanol [Ambrosi et al. 2001b].

The alcohols physisorbed onto $Ca(OH)_2$ surface prevent particle agglomeration, which usually happens for nanoparticles in water by hydrogen bonding [Ambrosi et al. 2001b; Fratini et al. 2007]. In addition, hexagonal plate-like nanoparticles in aqueous dispersions have a partially irreversible colloidal behaviuor, as a result of the crystallographically oriented aggregation mechanism along their hexagonal plate-like surface [Rodriguez-Navarro et al. 2005]. Although the same preferential orientation of the nano-crystals is observed also in alcohols, with piling of the crystals and formation of mass-fractal superstructures [Salvadori 2001; Fratini et al. 2007; Daniele & Taglieri 2010], nanoparticles aggregation phenomena are completely reversible in alcoholic dispersions [Ziegenbalg & Piaszczynski 2012], through e.g. sonication. In order to prevent or minimize the formation of nanoparticles aggregates, which can reduce the penetration depth of nanolime, a proper sonication of the nanolime dispersions is thus highly recommended prior to application.

Another important feature of nanolimes is the small dielectric constant and low surface tension given by the short chain aliphatic alcohols, which guarantees a low viscosity and high wettability to the nanolimes. Nanoparticles can thus penetrate easily in depth within a porous network.

Besides, the use of alcohol instead of water as dispersant limits the carbonation of the nanoparticles during storage and thus increases their shelf-life [Doehne & Price 2010]. In absence of humidity, the sols are stable for 3-6 months [Ziegenbalg & Piaszczynski 2012; D'Armata & Hirst 2012], whereas the addition of water results in coagulation and flocculation phenomena, which considerably reduce the shelf-life of the nanolimes [Ziegenbalg & Piaszczynski 2012].

However, also storage in alcohol may have some limitations. In fact, lime nanoparticles can be subjected to chemical transformation during storage in alcohols. Recent research by Rodriguez-Navarro [Rodriguez-Navarro & Elert 2016a] showed that, even if maintaining the same hexagonal morphology, calcium hydroxide nanoparticles stored in alcohols can be converted into amorphous calcium alkoxides within a few weeks [Rodriguez-Navarro et al. 2005; Rodriguez-Navarro et al. 2013; Rodriguez-Navarro & Elert 2016a]. This is due to the pseudomorphic replacement of $Ca(OH)_2$ particles by calcium alkoxides $Ca(OR)_2$, upon reaction with ethanol or 2-propanol:

$$Ca(OH)_2 + 2ROH \rightleftarrows Ca(OR)_2 + 2H_2O \qquad (11)$$

Thus, when using ethanol as solvent, the formation of calcium ethoxide $Ca(OCH_2CH_3)_2$ is expected. This reaction is reversible, and thus alkoxides are converted back to hydroxide by hydrolysis (e.g. an addition of water or high RH).

Alkoxides are highly-reactive and can lead to the formation of metastable vaterite (as well as ACC and aragonite), which has lower crystallinity compared to calcite and can thus be detrimental for the consolidation effect. For this reason, in order to avoid the conversion of the calcium hydroxide into alkoxides, freshly prepared alcoholic dispersions should be preferred. In addition, dispersions should be kept at low temperature, because their conversion into Ca-alkoxides is temperature-dependent [Rodriguez-Navarro et al. 2016b].

The hydroxide-to-alkoxide conversion might, however, be beneficial in some cases. In fact, the high reactivity of alkoxides can speed up the carbonation process (complete carbonation within 24 h) and increases the $CaCO_3$ yield, being an advantage for in-situ consolidation when fast carbonation is required (e.g. for preconsolidation treatment) [Campbell et al. 2011; Rodriguez-Navarro et al. 2013].

Regarding the environmental issues related to the use of alcoholic dispersants, ethanol and isopropanol are environmentally friendly and have a lower impact and toxicity for the operator than other solvents used in conservation [Baglioni & Giorgi 2006a; Baglioni et al. 2015a]. In addition, the alcoholic dispersions have a biocidal effect, with destruction of biological colonization e.g. mildew and algal growth [Ziegenbalg & Piaszczynski 2012].

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§ 2.4.6 Requirements

§ 2.4.6.1 Compatibility

Nanolimes have full chemical compatibility with calcareous substrates, after conversion of calcium hydroxide into calcium carbonate [Drdácký & Slížková 2008]. Based on laboratory and in-situ measurements performed on treated substrates, it was found that nanolime treatments tend to not excessively alter the structural (porosity and micro-roughness), mechanical (superficial hardness) and hydric properties of the original material [Giorgi et al. 2000]. When compared to untreated substrates, nanolime treatments appear to show a limited effect on the moisture transport properties (sorptivity, water vapour permeability and drying) of surfaces such as wall paintings, limestone and mortars [Giorgi et al. 2000; Campbell et al. 2011; Daniele & Taglieri 2011; Borsoi et al. 2012; Slížková & Frankeová 2012; Baglioni et al. 2014; Musacchi & Gonçalves 2014].

Most research reported in literature consists in the application of nanolime on sound materials. However, in order to assess the physical and mechanical compatibility of a consolidation treatment, the properties (e.g. water absorption and drying rate, mechanical strength) of the decayed, consolidated layer should preferably be evaluated in comparison with that of the sound, underlying material. These concepts are further described in chapters 5 and 8.

Concerning the aesthetical compatibility, contrasting results are reported in literature; some authors [Giorgi et al. 2000; Borsoi et al. 2012; Slížková & Frankeová 2012] report no significant colour variations (e.g. whitening) of the treated surface, whereas others describe the formation of white hazing on the treated surface, especially when dealing with low porosity limestone [Campbell et al. 2011; Costa & Delgado Rodrigues 2012].

However, until now no research has specifically addressed the process(es) of the formation of white haze on the surface (see also chapter 2 and 4). It is not clear whether nanoparticles deposit at the surface during absorption or drying, what is the role played by nanoparticle aggregation phenomena, carbonation etc. and, above all, what is the relation between the nanolime behaviour and the moisture transport properties of the substrate. Understanding these factors is of crucial importance for the achievement of an effective and compatible treatment. The investigation of these issues has been therefore one of the main aims of this PhD research.

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§ 2.4.6.2 Effectiveness

As seen in the previous sections, there are several factors that influence the consolidation effectiveness of nanolimes such as porosity and pore size distribution of the substrate, environmental conditions, particle size, nature of the solvent, etc.

The pre-consolidation and consolidation of wall paintings with nanolimes is generally reported to give good results, i.e. a partial or complete recovery of the robustness of the surface [Baglioni et al. 2013; Natali et al. 2014]. Several authors [Giorgi et al. 2000; Ambrosi et al. 2001b] report an increase of the surface cohesion in frescos and mural paintings (e.g. assessed by durometer or Scotch Tape Test).

Interestingly, nanolime treatment demonstrated to successfully consolidate wall paintings or stone previously treated with acrylate polymers (e.g. Paraloid B72). Even if the carbonation rate of the lime nanoparticles is lower in these cases, nanolime treatments are reported to increase the mechanical strength and to limit the decay due to the polymeric treatment [Carretti et al. 2013].

Different and not conclusive results are reported in literature about the effectiveness of nanolimes for consolidation of different calcareous lithotypes.

In the case of low-porosity limestones, such as Tivoli travertine (a whitish organogenic limestone from the Lazio region, Italy) or Poggio Picenze limestone (a white-beige organogenic limestone from the Abruzzo region, Italy), nanolime treatments ensured a partial pore filling and the recovery of cohesion between the stone grains [Daniele & Taglieri 2011]. However, the consolidation effect was mostly superficial, due to the poor penetration depth (0.3-1 mm) of the nanoparticles. Also Ruffolo [Ruffolo et al. 2013; Ruffolo et al. 2017] reports that nanolime treatment can provide a good surface strength and re-establish the cohesion of decayed stone, but only at the surface. Similar results are reported by Macchia [Macchia et al. 2014], who describes that the application of nanolime on lithotypes in hypogeum conditions (95% RH, T = 16ºC, high CO_2 content) is able to recover the cohesion only at the surface of the stone.

In many cases the formation of a white deposit, described as a “haze” or “patina” is observed [Campbell et al. 2011; Costa & Delgado Rodrigues 2012; Ziegenbalg & Piaszczynski 2012, Ghaffari et al. 2012, Daehne & Herm 2013]. Different hypotheses are proposed to explain this phenomenon: selective migration of the solvent and of the nanoparticle during absorption [Costa & Delgado Rodrigues 2012]; back migration of nanoparticles towards the surface during drying [Ghaffari et al. 2012]; quick evaporation of the solvent [Daehne & Herm 2013]. It has been observed that the use of highly concentrated nanolime dispersion [> 25 g/l] usually leads to low penetration

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and deposition of nanoparticles at the surface [Campbell et al. 2011; Costa & Delgado Rodrigues 2012; Ziegenbalg & Piaszczynski 2012].

A more adequate in-depth consolidation is reported for coarse porous limestone or for lime-based mortars; however often a heterogeneous in-depth distribution of the lime nanoparticles is observed [Ghaffari et al. 2012, Slížková & Frankeová 2012].

Positive results of nanolime treatment of weak mortars are reported by Drdácký and Slížková. Different treatments with different concentrations and applied by syringe dripping resulted in a good consolidation effect [Drdácký et al. 2009, Slížková & Frankeová 2012]. When dealing with mortar and in general with substrates with multimodal pore size distribution, it is reported that the use of nanolimes with a wide range of nanoparticle sizes (nano to submicrometric) improves the effectiveness of the consolidation [Baglioni et al. 2014]. In this case, smaller pores are filled with very small nanoparticles (20-100 nm), whereas bigger pores are consolidated with larger particles (100-600 nm).

Combination of nanolime with other consolidation products, e.g. silicic acid esters, can have a positive consolidation effect [Ziegenbalg et al. 2010; Borsoi et al. 2012]; however, the mutual chemical compatibility remains doubtful.

Summarizing, the literature on the effectiveness of nanolimes generally reports good results when the aim is to recover the superficial cohesion of e.g. wall paintings. However, when a mass consolidation is required, like in the case of limestone and mortars, different results are reported, and (especially in the case of limestone) nanolime treatments often resulted in a poor consolidation effect and/or in an uneven distribution of the nanoparticles in depth. It is thus necessary to understand how in-depth deposition of nanoparticles can be improved, avoiding the appearance of a white haze on the surface.

It is important to observe that the transport of nanolime within calcareous substrates is not fully understood. It seems that the effectiveness of nanolimes has limitations, which can be overcome only by a better understanding of transport and deposition of nanolime in the substrates. Further research is necessary to clarify these aspects and define how the properties of the nanolime dispersions can be adapted to the moisture transport characteristics of the substrate to be treated.

§ 2.4.6.3 Durability

Data from literature show that nanolime treatment can lead to an improved resistance to degradation mechanisms caused by the development of crystallization pressure in the pores of the material, like salt crystallization [Dunajská 2012; Ruffolo et al. 2013; Matos et al. 2014; Zornoza-Indart et al. 2017] and freeze-thaw [Dunajská 2012; Matos et al. 2014; Ball et al. 2016]. The treatment is reported to increase the mechanical strength of the material, while only slightly reducing the size of its pores [Giorgi et al. 2000] (this is positive, as higher crystallization pressures can be developed in smaller pores) [Scherer 2004].

However, some risks exist, mainly in the case of a not homogenous distribution of the nanoparticles in the materials. For example, an accumulation of nanoparticles at the very surface of the material can lead to significant reduction of the superficial porosity and thus of the moisture transport properties of the treated material; in this case the severity of decay processes like salt crystallization or frost action (see section 2.5.3) may increase. As a matter of fact, an unevenly distributed nanolime layer on salt loaded substrates can jeopardize the long-term durability of the treated substrate [Zornoza-Indart et al. 2012]. Consequenly, an even distribution of the nanolime in the decayed part of the substrate as well as avoiding accumulation near the surface should be strived for as otherwise durability may be impaired.

§ 2.4.7 Application

Nanolimes are generally applied by brushing or spraying, but other techniques (e.g. injection, capillary absorption, immersion, poulticing, vacuum impregnation, drop-by-drop by syringe) are also possible [Adolfs 2007; D'Armata & Hirst 2012]. Some authors [D'Armata & Hirst 2012] report that application by brushing is not as effective as the other methods and that poulticing appears to be generally ineffective, particularly when nanolime has a greater affinity with the poultice material (e.g. cellulose) than with the minerals in the substrates.

Due to the aggregation phenomena that usually affect nanoparticles (phenomena which are, however, partially reversible by using e.g. an ultrasonic bath), preparation of the nanolime dispersion shortly before application is a recommended step to achieve a successful in-depth consolidation. Manual or mechanical stirring and especially sonication (i.e. ultrasonic bath of the nanolime dispersion) are strongly recommended in order to get nano- to submicron-size (nano)particles.

Some authors recommend also a preliminary application of ethanol on the treated surface, in order to remove residual moisture from the surface and thus improve the penetration and in-depth deposition of the nanoparticles [Adolfs 2007]. In fact, moisture-filled substrates are detrimental for nanolime in-depth penetration and thus consolidation effectiveness.

The pre-consolidation and consolidation of mural paintings is generally performed using a low concentration of lime nanoparticles (0,5 to 5g/l) [Chelazzi et al. 2013]; in this case, a sheet of japanese paper in contact with the painted surface is often used in order to protect the decayed surface. When dealing with mortar or limestone, nanolime concentration can be higher (1 to 25 g/l), depending on the properties and state of conservation of the surface. Many researchers report that several applications at low concentration (or use of a dispersion with increasing concentration, starting from very diluted dispersions) allow a more effective and in depth consolidation, if compared with one application at higher concentration [D'Armata & Hirst 2012; Daehne & Herm 2013; Baglioni et al. 2014]. It can be expected that the pore size distribution and total porosity of the substrate will be key factors when choosing the concentration of the nanolime dispersion to be applied.

The total amount of nanolime dispersion to be applied should be preferably defined by preliminary trials (complete saturation of the surface is not always necessary). In general, an amount of nanolime dispersion ranging from 0.1 to 1 l/m^2 (depending on the porosity of the substrate and its state of conservation) per application is considered sufficient. If necessary, several applications need to be performed (e.g. 3 to 10x).

Some authors [Daehne & Herm 2013] suggest the use of covering (e.g. hydroxypropylcellulose gel) on the treated surface, in order to slow down the evaporation of the solvent and the carbonation of the nanoparticles, favouring thereby the in-depth deposition of the nanoparticles. Alcoholic hydroxypropyl cellulose gel solvent, cellulose poultice soaked with water or even damp cloths [Adolfs 2007; Ghaffari et al. 2012; Daehne & Herm 2013], applied in the first 24h after nanolime application, are reported to reduce the evaporation and contribute to achieve a more even distribution of the nanoparticles. The nebulization of water immediately after nanolime application is another method used to favour a more homogeneous in-depth distribution of calcium hydroxide nanoparticles [Niedoba et al. 2017].

The use of small percentages of acetone or cyclohexane within the nanolime dispersion is also advised [Ziegenbalg et al. 2010; Daehne & Herm 2013], with the aim of destabilizing the colloidal kinetics of the dispersion, and thus favouring the in depth deposition of the nanoparticles. Also the addition of a certain percentage of water to the nanolime is expected to have a destabilizing effect that might contribute to in-depth deposition. However, this option has not been explored yet, and will be considered in this work (chapter 6).

When dealing with very compact surfaces, the eventual excess of nanolime accumulated at the surface can be removed with a sponge or with soft washing with water [Dei & Salvadori 2006], to avoid the formation of a strong white deposition and to prevent the formation of a harmful over-consolidated subsurface layer.

Summarizing, a protocol for the application of nanolime dispersion is not provided by the producers and in most of the results reported in literature, application seems to be based on a trial-and-error approach. One of the main aims of this PhD research is to provide a theoretic basis, which can support the user in the choice of nanolime product and application method.

§ 2.4.8 Commercial products

Nowadays two different lines of nanolimes are commercially available:

- The Nanorestore® line: commercialized by CTS (Altavilla Vicentina, Italy) and CSGI (Sesto Fiorentino, Italy), under the name *Nanorestore* and *Nanorestore Plus*, these nanolimes have a concentration of 5 or 10 g/l and are dispersed in ethanol or isopropanol; this line includes also products for cleaning and deacidification of other types of substrates (e.g. paintings, paper, wood).
- The CaloSil® line: commercialized by IBZ (Freiburg, Germany), these nanolimes have a concentration of 5, 15, 25 or 50 g/l and are dispersed in ethanol, isopropanol or propanol; these products are commercialized under acronyms that represent their solvent (ethanol – E; isopropanol IP; n-propanol NP) and concentration (5, 15, 25, 50 g/l). This product line includes also paste-like products and micro-structured sols, for example for injections or removal of biological growth.

§ 2.4.9 Case studies reported in literature

Tables 2.1 and 2.2 report study cases from literature in which nanolime dispersions were applied on different calcareous materials, with the purpose of pre-consolidation (mostly in the case of wall paintings, tab. 2.1) and/or surface or mass consolidation (as in the case of lithotypes, mortars and other building materials, tab. 2.2). The effectiveness of nanolime dispersions was considered satisfactory and successful in the case of pre-consolidation actions or surface consolidation. More ambiguous and sometimes unsatisfactory results are reported in cases when a mass consolidation was needed. In addition, no monitoring over time of the durability of the treatment is reported in most of the cases, leaving unresolved questions with respect to the long-term effects of the treatments. Although the cases, mentioned, are not further used in this thesis, the overview is considered useful for possibible future research on durability of these treatments.

TABLE 2.1 Study cases of nanolime application on frescos and mural paintings

LOCATION	TREATED ELEMENT	REFERENCE
Santa Maria del Fiore Cathedral, Florence, Italy	Santi di Tito's wall paintings	Ambrosi et al. 2001a
Santa Maria Novella Church, Florence, Italy	Wall paintings of Cappellone degli Spagnoli and Chiostro Verde	Dei 2004, Giorgi et al. 2010
San Marco Church, Florence, Italy	Wall paintings of Beato Angelico	Baglioni et al. 2015a
San Marco Church, Florence, Italy	Frescos of Sogliano	Baglioni et al. 2015a
Prato Cathedral, Italy	Wall paintings of Filippo Lippi	Baglioni et al. 2009
San Cristoforo Church, Milan, Italy	Frescos	Baglioni et al. 2015a
Bargello museum, Florence	Frescos of the chapel	Dei et al. 2005
Santa Croce Church, Florence	Frescos of Agnolo Gaddi	Dei et al. 2007
San Zeno Crypt, Verona, Italy	Medieval mural paintings	Dei et al. 2006
Villa del Bene, Verona, Italy	Mural paintings	2007
S. Maria delle Grazie a Gravedona, Como, Italy	Mural painting of the clauster	Napoli et al. 2005
Herculaneum excavation, Naples, Italy	Ancient Roman frescoes of the Casa dei Cervi	Daehne & Herm, 2013
Steri's prison, Palermo, Italy	XV century graffiti	Saladino 2009, Natali et al. 2014
SS. Giuda e Simone Cloister, Corniola, Italy	XVIII century lunettes	Natali et al. 2014
Domus Aurea, Rome, Italy	Roman mural painting	Bartoli 2013
Calakmul, Campeche, Mexico	Mesoamerican mural paintings	Baglioni et al. 2006b, Giorgi et al. 2010, Baglioni et al. 2012
Cholula, Mexico	Aztec mural paintings	Alvarez & Nadal 2016
Mexico city, Mexico	Aztec mural paintings	Alvarez & Nadal 2016
Annunciation Basilica in Nazareth, Israel	Wall paintings	Baglioni et al. 2015a
Avnso Church, Copenhaghen, Denmark	Mural paintings	Dei 2004
Vendel Church, Sweden	Mural paintings	Garreau 2007
State Exhibit Building Museum, Shreveport, USA	Murales of Conrad Albrizio (1938)	Dei 2004
Mersch, Luxemburg	Wall paintings	Piaszczynski 2010
All Saints' Church, Buckinghamshire, UK	Wall paintings	D'Armata & Hirst 2012
Hakka residential building, Hong Kong	Mural paintings	Leung et al. 2016

TABLE 2.2 Study cases of nanolime application on lithotypes, plasters and renders

LOCATION	TREATED ELEMENT/SUBSTRATE MATERIAL	REFERENCE
S. Margherita Abbey, Vigonza (Padua), Italy	External walls, Nanto limestone	Ambrosi et al. 2001b
Impruneta Church, Florence, Italy	Bell tower, Alberese limestone	Dei & Salvadori 2004
Mantova, Italy	Façade of an historical building, Gallina sandstone	Dei 2006
Santa Prisca in Aventino Church, Rome, Italy	External wall of the apse, brick surface	Ambrosi et al. 2001b
Cá Grande University, Milan, Italy	Bas-relief, Angera dolostone	Pigozzi 2008
Ghislieri collegium Pavia, Italy	Bas-relief, Angera dolostone	Chelazzi et al. 2013
Catacombs of St. Callixtus, Rome, Italy	Funerary inscriptions, Limestone	Macchia et al. 2014
Saint Peter rectory, Aachen, Germany	Injection grout on marlstone	Piazszczynski & Ziegenbalg 2010
Bartra Martello Tower, Dalkey, Ireland	Interior of tower, mortar joints	Bolton 2016
Cathedral of Mainz, France	Amor and Psyche statue, Carrara marble	Piazszczynski & Ziegenbalg 2010
Malbork, Poland	Medieval plasters	STONECORE 2013
Church of St. Josef, Warsaw Poland	Architectonical elements, limestone	STONECORE 2013
Capilla de Ánimas, Santiago de Compostela, Spain	High relief, limestone	STONECORE 2013
Saint Trigham, UK	Element, Limestone	STONECORE 2013
Xanthen Cathedral, Germany	Element, Limestone	STONECORE 2013
Private house, Freiburg, Germany	Ceiling, Adobe	STONECORE 2013
Lichfield Cathedral, UK	Sculpture, limestone	D'Armata & Hirst 2012
Benedictine cloister, Tholey, Germany	Portal, lithotype	STONECORE 2013
Alhambra, Granada, Spain	Islamic decoration, gypsum and lime plasters	Villegas Sanchez et al. 2016
Leuben Castle, Germany	Lime plaster and lime stucco	STONECORE 2013
Dahlen Castle, Germany	Gypsum mortar and white gypsum stucco	STONECORE 2013
Salisbury Cathedral and Bath Abbey, UK	Element, Chilmark and Bath Limestone	Pesce et al. 2013
Pöide church, Saaremaa, Estonia	Element, stone and plasters	Workshop 2016
Calakmul, Campeche, Mexico	Mesoamerican mortars	Baglioni et al. 2006b
Norwich Cathedral, UK	Stone carved detail of the cloisters	Historic England 2017

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Kensal Green Cemetery, London, UK	Limestone memorial	Historic England 2017
Salisbury Cathedral, UK	Chilmark limestone capital on the Chapter House	Historic England 2017
York Minster, York, UK	Magnesian limestone on the East Front	Historic England 2017
Westminster Cathedral, London, UK	Remains of the Reigate limestone columns	Historic England 2017

3 Research questions

The review of the state of the art of nanolime dispersions provides an overview of the application methods, requirements, advantages and limitations of these products. Based on the literature research, the following research questions can be formulated:

Is nanolime a suitable alternative to silica-precursor consolidants (e.g. TEOS) for the consolidation of calcareous substrates?

The literature review shows that the effectiveness and compatibility of nanolime as consolidant is still doubtful in some cases. In this PhD work, research has been undertaken to assess the effectiveness and compatibility of nanolime.

More specifically, the following research questions have been addressed:

How and up to which extent can the effectiveness and compatibility of nanolime be improved? More specifically: how can deposition of nanolime in depth be improved and the appearance of a white haze on the surface avoided?

The literature review shows that transport and deposition of nanolime within calcareous substrates is not fully understood. This implies that the relevant factors influencing transport and deposition need to be identified and investigated.

How can nanolime properties be fine-tuned to improve the effectiveness and compatibility of the treatment?

The literature review suggests that the stability of the dispersion, particle size, moisture transport properties of the material, carbonation and the environmental conditions, are relevant factors for obtaining an effective and compatible consolidation. However, this hypothesis needs to be validated. The relation between these factors and the deposition and thus effectiveness of the nanolime dispersions needs to be assessed.

What is the effect of different application methods on the effectiveness of nanolime consolidation?

The literature review shows that in most cases the application is based on a trial-error approach. One of the main aims of this PhD research is to provide a theoretical basis, which can support the user in the choice of the correct nanolime dispersion composition and application method.

4 Understanding the transport of nanolime consolidants within Maastricht limestone

§ 4.1 Introduction to the chapter

As seen in the literature review, nanolime dispersions do not always provide a proper penetration and deposition of nanoparticle in-depth. However, it is not clear which factors affect the transport and the solvent-nanoparticle phase separation within a porous network.

This chapter, which is based on the paper published in the Journal of Cultural heritage (http://dx.doi.org/10.1016/j.culher.2015.07.014) with some minor changes to incorporate suggestions of the PhD committee members, clarifies the transport of a commercial nanolime (CaloSil E25) when applied on a coarse porous, calcareous substrate (Maastricht limestone).

Tests were set-up with the aim of understanding which are the parameters that affect the nanoparticles penetration and possibly limit the in-depth deposition and thus consolidation action of nanolime dispersions.

§ 4.2 Abstract

Novel nanomaterials, such as nanosilica or nano-titanium oxide, have been developed in the last decade for the conservation of the built heritage. Among nanomaterials, nanolimes have acquired a considerable relevance due to their potential as consolidant product. The so-called nanolimes, colloidal dispersions of calcium hydroxide nanoparticles in alcohols, have been successfully applied as pre-consolidants on frescos and paper, and their use has later been extended to plasters, renders and

stone. Nanolimes have better potentialities compared to conventional inorganic consolidants based on limewater (e.g. faster carbonation rate and higher calcium hydroxide concentration). Moreover, nanolimes are considered more compatible with $CaCO_3$-based substrates than alkoxysilanes (e.g. TEOS), the most widely used consolidant products. Nanolimes can guarantee the recovery of the superficial cohesion of degraded materials. However, when mass consolidation is required, like in the case of decayed stone, nanolimes show some limitations. One of the problems is caused by nanolime accumulation at or just beneath the surface of the treated material. In order to solve this problem, the transport mechanism of nanolime within porous materials, as stone or renders, should first be better understood. Commercial nanolimes were applied on Maastricht limestone, a high-porosity yellowish limestone, used in the Netherlands and Belgium as traditional building material. The absorption and drying behaviour of nanolime in this limestone were measured and nanolime deposition in the stone was studied by optical and scanning electron microscopy. The results show that nanolime transport is strictly related to the properties of the solvent. The alcoholic solvent guarantees a stable dispersion that penetrates in depth in the material, but is partially back-transported to surface. The high volatility of the solvent and the high stability of the dispersion favour the partial back-migration of lime nanoparticles to the surface during drying.

§ 4.3 Introduction of the paper

Calcareous materials such as limestone have demonstrated over the centuries to be durable building materials. However, if exposed to the action of atmospheric agents, these materials may suffer several degradation processes (e.g. salt crystallization, frost action, biological growth) leading to surface decay. Decay patterns showing in the form of loss of cohesion (e.g. powdering, sanding, chalking) can be recovered through the application of consolidant products.

A consolidation treatment should fulfil three main requirements: effectiveness (i.e. improvement of the mechanical strength), compatibility (with the treated substrate) and durability (resistance to different damage mechanisms) [Hansen et al. 2003; Toniolo et al. 2010; van Hees et al. 2014b]. In fact, the concept of compatibility and retreatability of an intervention has nowadays replaced that of reversibility. Products used for conservation issues should be compatible, from the chemical, mechanical, physical and aesthetical point of view, with the substrate on which they are applied [van Hees et al. 2014b].

Organic consolidants such as acrylic and epoxy resins generally have a low durability and compatibility when applied on calcareous substrates [Hansen et al. 2003; Toniolo et al. 2010; Doehne & Price 2010]. Tetraethyl orthosilicate (TEOS), often referred to as ethyl silicate or silicic acid ester, is at present the most widely used consolidants for limestone, mainly because of the lack of more adequate alternatives [Ferreira Pinto & Delgado Rodrigues 2012a]. These silica-based products can penetrate deeply into porous materials, but have low chemical compatibility with calcareous substrates and in some cases low effectiveness and durability.

Inorganic lime-based consolidants are more recommended for limestone, because of their better chemical compatibility [Ferreira Pinto & Delgado Rodrigues 2012a]. The most known inorganic lime-based consolidant product is limewater, a $Ca(OH)_2$ aqueous solution. Limewater, however, has a low calcium hydroxide concentration, resulting in limited consolidation effectiveness. Alternatives to limewater have been looked for in the last decade, as the use of alcoholic dispersions of calcium hydroxide nanoparticles, commonly known as nanolimes [Giorgi et al. 2000; Dei & Salvadori 2006]. Nanolimes are colloidal alcoholic dispersions with high stability and high lime concentration, facts that can improve the consolidating action [Ziegenbalg et al. 2010; Chelazzi et al.2013]. Calcium hydroxide nanoparticles have spherical to hexagonal shape and a size ranging from 50 to 600 nm.

Nanolimes have been applied for the conservation of many different materials (e.g. frescos and mural paintings, wood, paper), showing to work properly for the pre-consolidation and recovery of the superficial cohesion [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Borsoi et al. 2012; Baglioni et al. 2013]. However, when mass consolidation is required, as in the case of render or stone, nanolimes often have poor effectiveness [Campbell et al. 2011; Costa & Delgado Rodrigues 2012]. One of the reasons of their limited effectiveness is the accumulation of nanolime at or just beneath the surface [Costa & Delgado Rodrigues 2012; Ghaffari et al. 2012], resulting in a poor consolidating effect in depth.

Nanolime transport mechanism within porous materials, as stone or renders, is poorly described and should be better understood to solve this problem. From the literature it is not clear if nanolime simply accumulates at the absorption surface or if it penetrates in depth in the material, and afterwards migrates back towards the surface.

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§ 4.4 Research aims

In this research, the transport of a commercial nanolime product on Maastricht limestone was studied. The absorption and drying kinetics of nanolime was measured according to two different protocols and compared to that of pure ethanol and water (Section 4.5.2.1). The effect of carbonation on nanolime deposition was assessed by carrying out the experiments both in air and in a nitrogen-rich environment (Section 4.5.2.2). Microscopy observations were performed by means of optical microscopy and scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM-EDS) in order to investigate nanolime deposition within the material as a result of the transport mechanism (Section 4.5.2.3).

§ 4.5 Materials and methods

§ 4.5.1 Materials

§ 4.5.1.1 Substrate

The Maastricht limestone has been selected as substrate.It is a soft (1.3 to 5 MPa), yellowish limestone (over 95% $CaCO_3$) [Dreesen & Dusar 2004; Nijland et al. 2006], quarried and used in the Belgian and Dutch provinces of Limburg. The Maastricht limestone has a high-porosity (ca. 50%) and a unimodal pore distribution (30–50 µm) [Lubelli et al. 2015], and thus uniform physico-chemical properties. Due to the low mechanical strength, this substrate is prone to weathering and it may need consolidation. All the above mentioned properties make this substrate ideal for the study of the transport of the nanolime dispersion.

Despite its low mechanical strength, Maastricht limestone has generally shown a good durability, probably linked to skin formation by dissolution and re-precipitation of carbonates within the limestone pore network, when exposed to atmospheric agents [Dreesen & Dusar 2004; Dubelaar et al. 2006]. This process was in the past enhanced

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by the application of limewater, which forms a sort of protective layer. Despite its good durability, Maastricht limestone may in some cases show decay in the form of loss of cohesion and loss of material [van Hees & Nijland 2009].

§ 4.5.1.2 Nanolime and sample preparation

The transport and deposition of the commercial nanolime CaloSil E25 (by IBZ, Germany) in Maastricht limestone has been measured. This colloidal dispersion has a calcium hydroxide nanoparticle concentration of 25 g/L (which was considered suitable for the in-depth consolidation of Maastricht limestone) and is dispersed in ethanol. Nanoparticles have hexagonal plate-like shape and size ranges between 50 and 250 nm [Ambrosi et al. 2001a].

Before use, E25 was placed in an ultrasonic bath (60Hz) for 30minutes, to minimize nanoparticle aggregation phenomena. Ethanol (p.a.>99.5%, by Sigma Aldrich) and distilled water (conductivity < 2 µs/cm) were used for comparison.

§ 4.5.2 Methods

Maastricht limestone core specimens (4×4cm) were drilled from sound blocks, with orientation perpendicular to limestone bedding, in order to exclude possible minor lithological variations and anisotropy influencing the results [Baxevanis et al. 2006]. Different specimens were used for the different tests, as summarized in Table 4.1.

TABLE 4.1 Overview on the tests performed on different specimen types (SEM-EDS: Scanning electron microscopy coupled with energy dispersive X-ray spectroscopy)

TEST PROCEDURE	SPECIMEN TYPES IDENTIFICATION						
	A1	D1	P1	P2	P3	TA	TB
Absorption test	✓						
Drying test		✓					
Phenolphthalein test			✓	✓	✓		
Macroscopical observation			✓	✓	✓		
Optical microscopy				✓	✓	✓	✓
SEM-EDS						✓	✓

§ 4.5.2.1 Absorption and drying measurements

The core specimens (A1) were sealed on the lateral side with Parafilm M (by Bemis NA, USA) in order to prevent nanolime evaporation on these sides.

The capillary absorption of nanolime E25 through one circular base of the core specimens was measured; the specimens, sealed on the sides, were partially immersed in a petri dish, filled with nanolime and with a grid on the bottom; the absorption of ethanol and water was measured for comparison (Fig. 1.4).

During the absorption process, the weight of the core specimens was measured till saturation was reached. The height of the wetting front, which corresponds to the height of the level of the nanolime in the treated specimen, was visually identified through the (transparent) parafilm and photographically recorded. Water, ethanol and nanolime absorption were carried out in sequence on the same specimens, in order to minimize the effect of the stone variability. The absorption test was carried out in threefold under controlled conditions (50% RH, T = 20° C, air speed < 0.1 m/s) [CEN 2008].

The drying kinetics of specimens (D1) saturated with nanolime, ethanol and water were evaluated by measuring the weight loss over time. The test was performed in threefold under controlled conditions (50% RH, T = 20° C, air speed < 0.1 m/s) on specimens sealed on the lateral sides and on the surface across the drying surface.

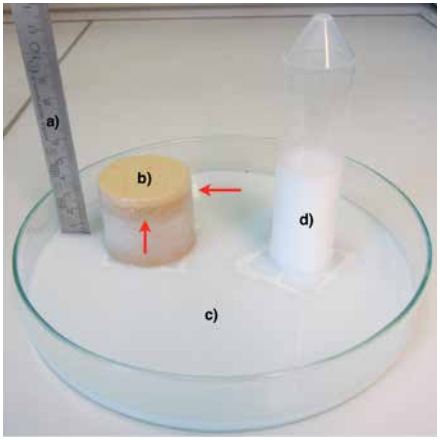

FIGURE 4.1 Setup used for capillary absorption of nanolime on Maastricht limestone: a: yardstick; b: Maastricht core specimen sealed with parafilm on the lateral side; it is possible to observe the homogeneous capillary rising of the E25 (arrows); c: Petri dish; d: reservoir of nanolime.

Additionally, in order to clarify if any nanolime accumulation at the absorption surface occurs during absorption, some specimens were tested in two different setups, as shown on Fig. 4.2 Nanolime absorption was performed as previously described in this section. Afterwards, drying was performed in one case (specimen TA) on the same side of the absorption (as normally in the practice), and in the other case (specimen TB) through the surface opposite to the absorption surface.

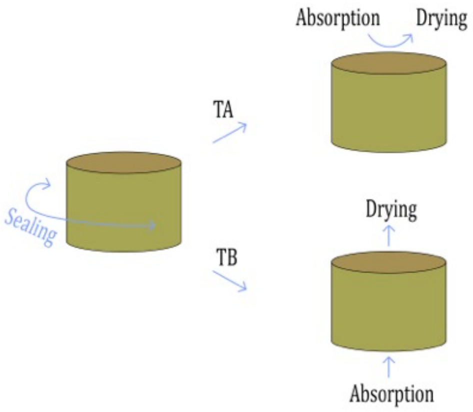

FIGURE 4.2 Specimens setup for the drying models (corresponding to specimen TA and TB).

§ 4.5.2.2 Assessment of the penetration depth of nanolime

The penetration of the lime nanoparticles immediately after absorption was assessed by the phenolphthalein test (P1). After complete saturation, the specimens cross section was nebulized under controlled conditions (50% RH, T = 20° C, air speed < 0.1 m/s) with a 1% phenolphthalein solution (60% ethanol - 40% water). Phenolphthalein is a pH indicator: it remains uncoloured for pH < 8.2, while pH conditions higher than 9.8 lead to a purple colour change. In this case, a purple colour of the substrate indicates the presence of nanolime [$Ca(OH)_2$, $pH_{E25} > 11$]. Nanolime is not soluble in ethanol and thus the purple colour indicates the presence of nanolime particles and not of the solvent.

By comparing the results of the phenolphthalein test with the photographical observations of the wetting front, conclusions can be drawn on deposition of nanolime particles during absorption.

The phenolphthalein test was performed also during the drying process on specimens (P2) saturated with nanolime; the test was performed at different stages of drying (1, 4, 8, 24 and 48 h) in order to understand nanolime migration within the material. The cross section of each treated specimens was observed, by breaking the specimen with hammer and chisel at the given time. Additional tests were carried out on specimens (P3) saturated with E25 and dried in a nitrogen atmosphere (using a N2 Boy nitrogen gas-supplying device, by Taitec; 45 ± 5% RH, T = 20° C). In this way, the fast carbonation of nanolime was avoided and it was possible to clarify the possible effect of carbonation on the transport of nanolime within the treated material.

§ 4.5.2.3 Assessment of nanolime deposition by microscopic observation

In order to assess the deposition of nanolime in the stone, the drying surface and the cross section of the specimens treated with nanolime (P2, P3, TA, TB) were observed with a stereomicroscope Zeiss Stemi SV 11 (with up to 66x magnification). Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera and with the AxioVision 4.8 software.

The observations and findings of the specimens' cross section were complemented by SEM-EDS. SEM-EDS observations were carried out after 3 months from the application of the nanolime dispersions (during this period treated specimens were stored at 50% RH, T = 20° C, air speed < 0.1 m/s), when full carbonation of the nanolime particles has already taken place. The equipment used (Nova NanoSEM 650, by FEI) has a SE/BSE (Secondary Electrons/Backscattered Electrons) in-lens detector and is coupled with a low vacuum solid-state detector BSED (GAD), as well as an EDS detector by Oxford Instrument. This equipment allows high resolution imaging (up to 1.4 nm). In this work, a voltage of 4 to 5 kV was used for SEM-EDS observations.

§ 4.6 Results

§ 4.6.1 Absorption and drying behaviour

Fig. 4.3a and b show the capillary absorption curves of water, ethanol and E25 (A1). Water, ethanol and nanolime quickly saturate the sample (less than 5 minutes), due to the coarse porosity of Maastricht limestone. When comparing the capillary wetting curves of the different liquids, water absorption is faster than that of ethanol and nanolime. The trend of the capillarity curves can be related to the sorptivity (S), a measure of the capacity of the porous material to absorb and transmit liquid by capillarity; when comparing different liquids and when the treated specimen is completely wetted, as in this case, the sorptivity is related to the liquid surface tension (σ) and to the viscosity (η) [Taylor et al. 2000], being:

$$S = (\sigma/\eta)^{1/2} \qquad (12)$$

Water has lower viscosity than ethanol and its surface tension is more than three times that of ethanol (Table 4.2), explaining the higher sorptivity values and the capillarity wetting curves observed for water (Figs. 4.3a and b). The trend of the capillarity wetting curves of EtOH and H_2O agrees with what is predicted theoretically from thermodynamic principles [Hall & Hoff 2012] (Table 4.2).

TABLE 4.2 Solvent surface superficial tension [Fu et al. 2000], dynamic viscosity [Aminabhavi et al. 1993] and sorptivity of water and ethanol at T = 20° C.

SOLVENT	SURFACE TENSION σ (N/m)	DYNAMIC VISCOSITY η (mPa s)	SORPTIVITY S (m/s)
H_2O	0.073	1.002	0.245
EtOH	0.022	1.216	0.147

E25 instead has a slower absorption compared to ethanol. In fact, lime nanoparticles slightly modify the density (and therefore viscosity) and possibly affect the surface tension of the alcoholic solvent. As pointed out by Duan et al. [Duan et al. 2011], nanoparticle agglomeration, that easily takes place in colloidal dispersions, can affect the viscosity of the dispersion. The small difference in weight between EtOH and E25 (Fig. 4.3b) corresponds to the presence of nanoparticles in the E25 (25 g/L).

When considering the drying behaviour (Fig. 4.3c and d), the evaporation rate of water is much slower (up to 7 days for complete drying) than that of ethanol (complete drying in 48–72 h) and E25 (up to 72h). The faster evaporation of ethanol is mainly due to its lower boiling point (78.37 º C at T = 20 º C) compared to that of water. Moreover, the surface tension of water is almost 3 times higher than that of ethanol (Table 4.2), explaining the higher water retention within the Maastricht pore network.

In the drying curves, two stages can be observed. In the 1st stage of drying, called the constant drying period, the drying front is at the surface and the drying rate is constant and controlled by the external conditions [Hall & Hoff 2012; Gonçalves et al. 2014]. This first phase ends after 24 h in the case of EtOH and E25, while for water it ends after approximately 96 h.

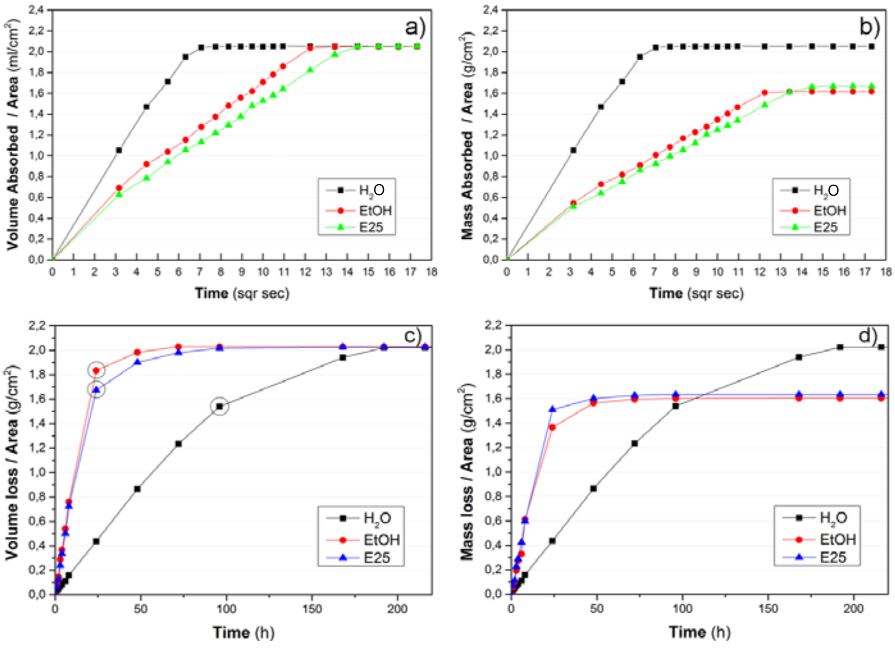

FIGURE 4.3 Comparison of the capillarity wetting curves of water, ethanol and E25, a) volume b) mass. Capillarity drying curves, in c) volume and d) mass, of H_2O, EtOH and E25. The red circles indicate the critical liquid content and the end of the first step of drying.

In the 2nd stage of drying, identified by the change in the slope of the drying curve, the liquid content can no longer support the demands of the evaporation flux. The drying front recedes progressively into the material and the properties of the liquid and of the substrate control the rate of drying [Hall & Hoff 2012]. In this 2nd stage of drying, where drying occurs in the vapor phase, lime nanoparticles cannot physically take part in the process and are deposited in the material. It is thus important to observe the deposition of nanolime at 24 h, which corresponds to the end of the 1st stage.

By comparing the drying curves of pure ethanol and E25, a slight delay in the drying of the material is observed in the case of nanolime.

§ 4.6.2 Penetration depth of nanolime

§ 4.6.2.1 Wetting front

The movement of the wetting front in the stone during absorption was visually observed; all liquids (H_2O, EtOH and E25) completely wetted the limestone specimens within a few minutes, confirming the features observed on Fig. 4.4a.

§ 4.6.2.2 Phenolphthalein test

Phenolphthalein test was performed as described in Section 4.5.2.2, immediately after complete saturation of the P1 specimens with nanolime. Nanolime has penetrated to the full depth of the specimen (40 mm), as shown on Fig. 4.4a. No accumulation of nanolime at the absorption surface can be observed at the end of the imbibition.

Phenolphthalein test was performed on P2 specimens (dried in air) at different times during the drying process. Specimen P2 shows that nanolime is stable and homogeneously distributed within the porous network for at least 8 h after nanolime application (Fig. 4.4b). At 24 h no nanolime is detected beneath the drying surface (0.5 mm in depth), while it is visually detected deeper in the specimen; nanolime is however less visible in the outer 6 to 7 mm of specimen (Fig. 4.4d). This distribution might be due to the possible partial back-migration of nanolime in the direction of the drying surface and/or to the fast carbonation in air of nanolime.

In order to check the relevance of nanolime carbonation during the drying period, phenolphthalein test was performed also on specimens dried in nitrogen atmosphere (P3). At 8 h, nanolime distribution in specimens dried in air and in nitrogen atmosphere is similar, showing no accumulation of nanolime nearby the absorption surface (Fig. 4.4c). At 24 h, no nanolime is detected in the first 0.5–1 mm beneath the drying surface; this evidence can be justified by the formation of an internal drying front. However, nanolime forms a thin layer beneath the drying front (0.5mm in depth), showing that it has partially migrated towards the drying surface (Fig. 4.4e). No substantial differences are observed between specimens P2 and P3 at 24 h, confirming that carbonation is not significantly influencing the deposition of nanolime within Maastricht limestone.

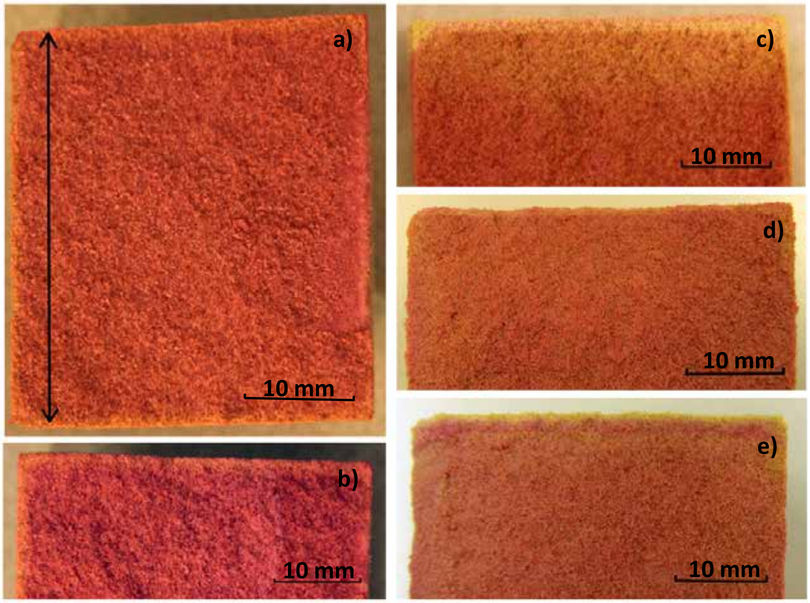

FIGURE 4.4 Pictures of the phenolphthalein test performed on the cross sections of specimens treated with E25 and observed a) immediately after saturation (P1); specimens (P2) treated and stored in a air and observed at b) 8 h and c) 24 h during drying; specimens (P3) treated and stored in N_2 chamber and observed at d) 8 h and e) 24 h during drying. The drying surface is on the top of the specimen.

§ 4.6.2.3 Microscopic observations

Observations by stereomicroscope of the P2 and P3 cross sections (Fig. 4.5a and b) were carried out after 48 h of drying (at 50% RH, T = 20º C, air speed < 0.1 m/s), which corresponds to the almost complete evaporation of ethanol; the microphotographs confirm a thin layer and a deposition of nanolime beneath the drying surface (0.5mm depth), but no white deposition was macroscopically identified on the dying surface. Nanolime accumulation under the drying surface suggests that lime nanoparticles are partially moving back to the surface with its solvent during drying.

In order to definitely assess whether deposition near the surface occurs during the absorption or drying phase, cross sections of the specimens TA and TB (Fig. 4.2) were investigated by optical microscopy.

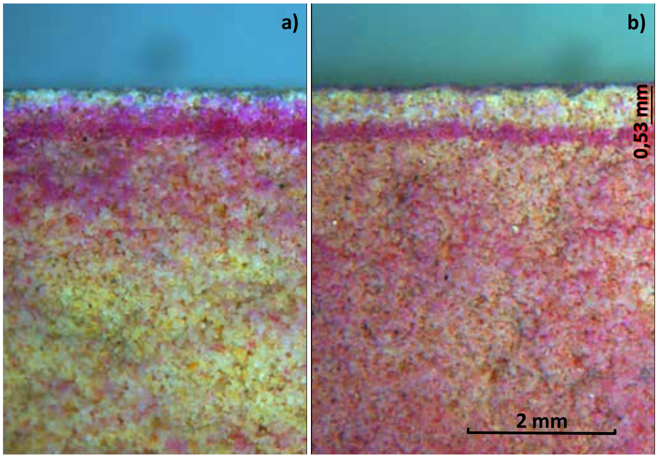

FIGURE 4.5 Microphotographs of specimens a) P2 and b) P3 observed at 48 h; in both cases, an accumulation of nanolime is visible beneath the drying surface.

Stereomicroscope microphotographs of the cross sections of specimens TA and TB, observed after complete drying, are shown on Fig. 4.6a and b. In both cases, nanolime accumulates at 0.5–0.7 mm beneath the drying surface. Once more, no deposition of nanolime was identified at the absorption surface of TB. Observations on specimen TB definitively clarify that nano- lime penetrates in the material without any accumulation at the absorption surface during the absorption phase. No phase separation between the nanoparticles and the solvent is observed during the absorption process. Deposition just beneath the drying surface occurs during the drying phase, due to the partial back-migration of the nanoparticles.

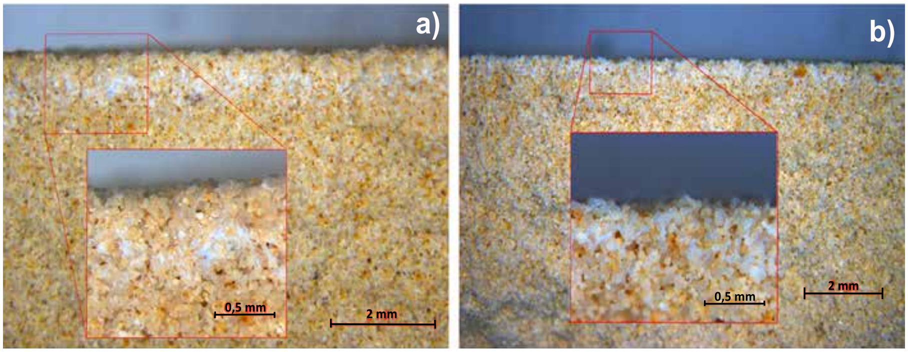

FIGURE 4.6 Microphotographs of the cross section of specimen a) TA and b) TB (proximity of the drying surface). In both cases nanolime is partially accumulated in a thin layer nearby of the drying surface.

§ 4.6.2.4 SEM-EDS

Microstructural observations and microanalyses were per- formed by SEM-EDS in order to further study the deposition of nanolime within limestone.

The cross sections of specimens TA and TB (Fig. 4.2) were observed after complete drying of the solvent and complete carbonation of nanolime. In both cases, samples were collected from the middle of the specimen, and at the absorption/drying surface. The microstructural analysis of TA confirms a large deposition of Ca-carbonate nanoparticles at 0.5 mm from the drying surface (Fig. 4.7a and b); nanoparticles deposited at this location have dimension between 30 to 100 nm and have mainly agglomerated in clusters (Fig. 4.7b and c). Some deposition of nanoparticles is visible up to 10 mm in depth from the drying surface (Fig. 4.7d).

Next to the accumulation of nanoparticle clusters near the drying surface, local depositions of isolated nanolime particles are visible deeper in the cross section: at 20mm from the drying surface, sporadic and heterogeneously distributed deposits of nanolime particles are visible (Fig. 4.7e); at 35 mm in depth, the presence of nanoparticles is very limited (Fig. 4.7f).

When considering the particle size of the nanolime deposits in the cross section, it can be observed that nanoparticle size is smaller (30 to 100 nm) at the drying surface, than that in depth in the material (100 to 300 nm). This suggests that smaller lime nanoparticle are probably back-transported more easily to the drying surface, whereas bigger nanoparticles deposit preferentially in depth.

The SEM-EDS analysis of TB (drying through the surface across the absorption side) shows significant nanolime deposition at 0.5mm from the drying surface (Fig. 4.8a). Nanolime is visible as well at 10 mm in depth (Fig. 4.8b); nanolime deposition is decreasing gradually in depth, with local clusters at 20–25 mm (Fig. 4.8c and d). At 35 to 40 mm, sporadic accumulations of nanoparticles are locally visible (Fig. 4.8e and f). As observed in TA, the size of nanoparticle is smaller (30 to 60 nm) at the drying surface and considerably larger (70 to 200 nm) in depth. These observations confirm the results obtained by phenolphthalein test and optical microscopy and definitively show that nanoparticles partially accumulate beneath the drying surface during drying.

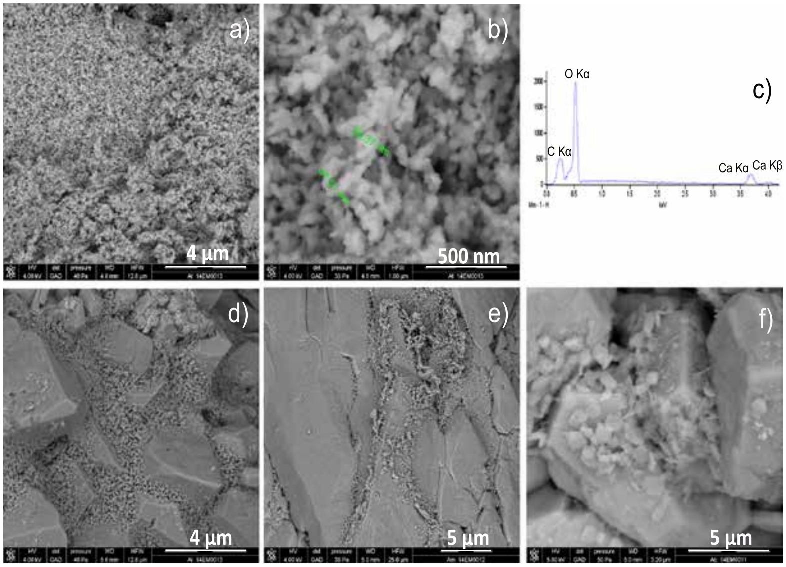

FIGURE 4.7 Scanning electron microscopy microphotographs of specimen TA: a, b) 0.5 mm in depth in the cross section (from the drying surface) and c) its energy dispersive X-ray spectroscopy spectra, showing an abundant presence of carbonated nanolime ($CaCO_3$); lime nanoparticles at d) 10 mm, e) 20 mm and f) 35 mm in the cross section, where hexagonal plate-like nanolime particles can be identified.

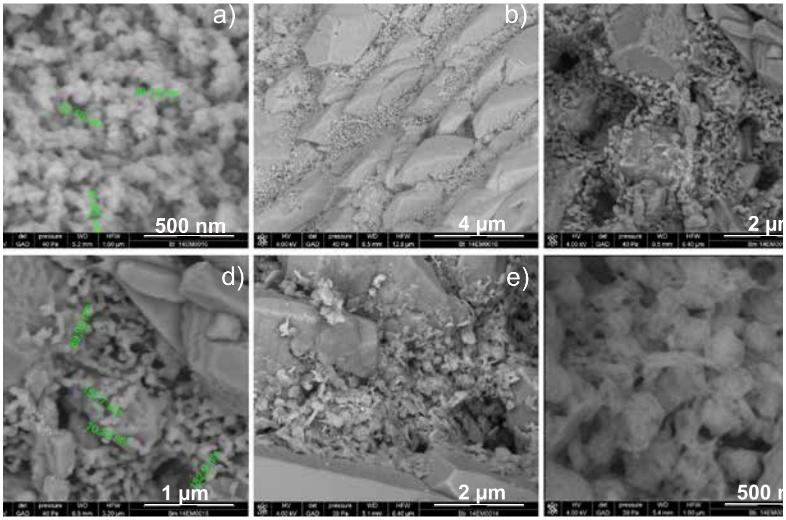

FIGURE 4.8 Scanning electron microscopy microphotographs of TB at different depths in the cross section (from the drying surface): a: 0.5 mm; b: 10 mm; c: 20 mm; d: 25 mm; e: 35 mm; f: 38 mm in depth in the cross section.

§ 4.7 Conclusions

This paper clarifies the transport of nanolime within a coarse porous calcareous material (Maastricht limestone). The results show that nanolime E25 can easily penetrate in depth in this material without any accumulation at the absorption surface during the absorption phase.

Accumulation beneath the surface occurs during drying, due to the partial back-migration of the lime nanoparticles with the solvent towards the drying surface. Carbonation do not affect significantly the deposition of nanolime within the Maastricht limestone in the studied times (up to 48 h).

The dense nanolime layer accumulated beneath the drying surface may impair the quality of consolidation and also limit the penetration of successive consolidant applications, hindering effective consolidation. These results suggest that, in order to improve nanolime precipitation in depth, the transport and deposition mechanism of nanolime should be modified. This might be obtained by slowing down the drying rate (e.g. by applying a covering, as a water-filled cellulose compress, on the treatment

[Baglioni et al. 2009]) and/or altering the kinetic stability of the dispersion (e.g. by modifying the solvent of the dispersion). Both these facts are expected to avoid the nanolime back-migration and favour nanoparticle deposition in depth in the substrate. Furthermore, a protocol for the application of nanolime, based on the physical-chemical characteristics of the material to be treated, should be developed in order to optimize the in depth deposition of the nanolime dispersion.

Research is on going to improve the consolidating effectiveness of nanolime both by optimizing the application procedure and by modifying the solvent of the nanolime dispersions.

TOC

5 Effect of solvent on nanolime transport within limestone: how to improve in-depth deposition

§ 5.1 Introduction to the chapter

In this chapter, the effect of solvent modification on the in-depth deposition of the lime nanoparticles is experimentally investigated. New nanolime dispersions were synthetized by a cutting-edge method (solvothermal reaction in water) and dispersed in different solvents. A model, which correlates the properties of the nanolime dispersions, to the properties of substrate to be treated (fine or coarse porous substrate), is proposed in order to predict which type of solvent can be used to enhance the in-depth deposition of the nanoparticles. This chapter is based on the paper published in Colloids and Surfaces A: Physicochemical and Engineering Aspects (http://dx.doi.org/10.1016/j.colsurfa.2016.03.007) with minor changes, in order to incorporate the suggestions of the PhD committee members.

§ 5.2 Abstract

Consolidation treatment is a common practice in the field of conservation. However, when considering calcareous materials, there is a lack of efficient and durable consolidants.

Colloidal dispersions of $Ca(OH)_2$ nanoparticles, commonly known as nanolimes, can effectively recover the superficial loss of cohesion. However, they do not always guarantee in-depth mass consolidation.

The aim of this paper is to give directions for improving in-depth deposition of nanolime dispersions when applied on limestone. A conceptual model, correlating the

drying rate and the kinetic stability of nanolimes dispersed in different solvents to the porosity of the limestone to be treated, is conceived. This model can help to select a suitable nanolime solvent depending on the substrate.

Nanolimes were synthetized and dispersed in different solvents (ethanol, isopropanol, butanol and water). The morphology and size of the lime nanoparticles were studied by dynamic light scattering (DLS) and scanning electron microscopy (SEM-EDS). The kinetic stability of the nanolime dispersion was assessed by UV-Vis spectroscopy. The porosity of the limestones was determined by mercury intrusion porosimetry (MIP), measuring as well their moisture transport properties (absorption and drying kinetics).

The model was validated by applying the different nanolimes to two limestones with very coarse (Maastricht limestone) and very fine porosity (Migné limestone). The absorption and drying kinetics and the deposition of the nanolimes within the treated limestones were investigated by phenolphthalein test, optical microscopy and SEM-EDS analysis.

The results show that, as suggested by the model, less stable dispersions (as obtained by higher boiling point solvents e.g. butanol) are more suitable for coarse porous limestones, while for fine porous limestones, more stable nanolime dispersions (as obtained by low boiling point solvents e.g. ethanol) should be preferred. Suggestions are given for further improvement and fine tuning of the nanolimes.

§ 5.3 Introduction of the paper

Calcareous stone when exposed to atmospheric agents may suffer degradation processes that can compromise their durability. Decay patterns in the form of loss of cohesion (e.g. powdering, sanding and/or chalking) are often observed, which can lead to strength decrease.

Loss of cohesion may be recovered by the application of consolidant products. A consolidation treatment should fulfil three main requirements: effectiveness (i.e. improve the mechanical strength), compatibility (do not induce damage to the substrate) and durability (improve the resistance of the substrate to damage mechanisms for a relatively large period) [Hansen et al. 2003; Toniolo et al. 2010; van Hees et al. 2014b]. Organic consolidants have no chemical compatibility with calcareous materials, and therefore can be potentially harmful for the treated substrate

[Hansen et al. 2003]; for example, tetraethyl orthosilicate (TEOS), often referred to as ethyl silicate or silicic acid ester, can generally penetrate deeply into porous materials, but has low chemical compatibility and, in some cases, low effectiveness and durability when applied on calcareous substrates.

Lime-based consolidants are possible alternatives for application on limestone [Hansen et al. 2003, Dei & Salvadori 2006]. Due to low effectiveness of limewater (a traditionally used Ca(OH)2 aqueous solution) alternatives have been looked for over the last decade, such as the use of alcoholic dispersions of calcium hydroxide nanoparticles, commonly known as nanolimes [Giorigi 2000; Ziegenbalg et al. 2010; Chelazzi et al.2013]. Nanolimes are colloidal alcoholic dispersions of calcium hydroxide nanoparticles with high stability and high lime concentration, facts that can improve the consolidating action [Rodriguez-Navarro et al. 2013; Poggi et al. 2014]. Commercial nanolimes have nanoparticles with spherical to hexagonal shape and a size ranging from 50 to 600 nm [Giorgi et al. 2000; Dei & Salvadori 2006; Ziegenbalg et al. 2010; Chelazzi et al. 2013; Ambrosi et al. 2001a].

Nanolimes have been applied for the conservation of many different traditional materials (mural paintings, stone, renders, paper, wood, etc.) and have proven to work properly for the pre- consolidation and for the recovery of the superficial cohesion [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Borsoi et al. 2012; Baglioni et al. 2013 Rodriguez-Navarro et al. 2013; Poggi et al. 2014; Ruffolo et al. 2017]. However, when mass consolidation is required, as in the case of thick renders, or porous stones, nanolimes often have poor effectiveness [Campbell et al. 2011; Costa & Delgado Rodrigues 2012; Ruffolo et al. 2013]. An important reason for their limited effectiveness is related to the accumulation of nanolime just underneath the surface, resulting in a poor consolidating effect in depth [Ghaffari et al. 2012; Costa & Delgado Rodrigues 2012].

The aim of this paper is to give directions for improving the in-depth deposition of nanolime dispersions. The starting point of this research is given by the results of a previous study carried out by the authors on a highly and coarse porous limestone (Maastricht limestone) [Borsoi et al. 2016a]. The authors showed that nanolime deposition does not occur during the absorption phase but during the drying of the nanolime. The high kinetic stability of nanolime dispersions and the high volatility of the alcoholic solvent do not guarantee a proper phase separation of the lime nanoparticles from the alcoholic solvent in depth in the material; lime nanoparticles stay in dispersion and migrate back to the surface during drying to form a white haze on or nearby the surface [Borsoi et al. 2016a].

The results of this previous research suggest that, in order to improve in-depth deposition, the stability of the nanolime dispersion should be adapted to the moisture transport properties (and thus porosity and pore size) of the substrate.

With this in mind, a conceptual model is presented, developed and validated in this paper. Therefore, solvents with low drying rate and providing a low kinetic stability to the nanolime dispersion, are more suitable for coarse porous substrates. For fine porous substrates, solvents with higher drying rate and guarantying a high kinetic stability to the nanolime are preferable (Fig. 5.1).

The model has been validated in this research on two different limestones (coarse and fine porous) using nanolimes dispersed in different solvents (isopropanol, ethanol, butanol and water).

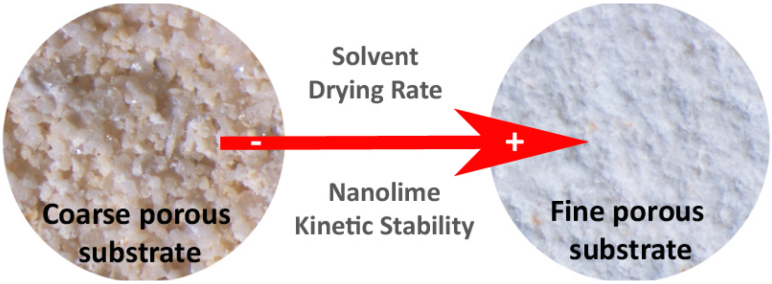

FIGURE 5.1 Graphical representation of the conceptual model developed in order to link the porosity of the substrate with the kinetic stability and drying rate of the solvents (+ = higher, – = lower).

Initially, the properties of the nanolime dispersions and of the substrates to be treated were determined. The morphology and size of the lime nanoparticles were characterized by Scanning Electron Microscopy with X-ray microanalysis (SEM-EDS, Section 5.5.1.1) and Dynamic Light Scattering (DLS) (Section 5.5.1.2); the kinetic stability of the nanolimes was studied by UV-vis spectroscopy (Section 5.5.1.2). The mineralogical composition of the limestones was determined by X-Ray Diffraction (XRD) (Section 5.5.2.1). Their porosity and pore size were measured by Mercury Intrusion Porosimetry (MIP) (Section 5.5.2.1); the moisture transport behaviour was further assessed by measuring absorption and drying (Section 5.5.2.2).

Based on physical and chemical properties of the nanolimes (size and kinetic stability) and of the two limestones (pore size distribution) to be treated, a choice of the solvents was made, based on the developed conceptual model.

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In order to validate the model, the absorption and drying kinetics of the modified nanolime applied on the two limestone were analyzed (Section 5.5.4.1). The transport and deposition of the nanolimes applied on the two limestones were studied by phenolphthalein test (Section 5.5.4.2), optical microscopy (Section 5.5.4.3) and Scanning Electron Microscopy (Section 5.5.4.4). Finally, suggestions for fine tuning of the model are proposed in Section 5.5.3.

§ 5.4 Materials and methods

§ 5.4.1 Nanolimes

§ 5.4.1.1 Synthesis

Nanolimes were synthetized by solvothermal reaction of metallic calcium in water. Metallic granular calcium (99%, by Sigma-Aldrich) and distilled water (conductivity <2 µs/cm) were used to synthetize the nanoparticles: 6.72g of metallic calcium were stirred for few hours in 100ml of distilled water, in order to obtain colloidal dispersions with an equivalent concentration of 25 g/l. The synthesis was performed in a reactor at T = 90ºC. The aqueous medium was then substituted by centrifuging the colloidal dispersions using an Eppendorf Centrifuge 5810R (rotation speed 8000 rpm, t = 10 min), maintaining the concentration at 25 g/l. The supernatant (water) was subsequently extracted through glass volumetric pipettes and substituted by short-chain aliphatic alcohol. Ethanol (p.a. 99.5% by Sigma-Aldrich), isopropanol (p.a. 99% by Sigma-Aldrich) and 1-butanol (p.a. 99.5% by Sigma-Aldrich) were used as solvents for the nanolime dispersions. The relevant properties of the selected solvents are reported in Table 1.5. The nanolimes dispersions in the different solvents are identified as E25 (dispersed in ethanol), IP25 (in isopropanol), B25 (in butanol) and H25 (in water).

TOC

TABLE 5.1 Some physical-chemical properties of the selected solvents at T = 20ºC [DDBST].

SOLVENT	DYNAMIC VISCOSITY (mPa·s)	BOILING POINT (°C)	SUPEFACE TENSION (SOLVENT/AIR) (N/m)
Ethanol	1.214	78.37	0.0221
Isopropanol	2.403	82.62	0.0230
1-Butanol	2.802	117.71	0.0247
Water	1.002	99.61	0.0728

§ 5.4.1.2 Characterization (size, mineralogical composition and colloidal stability)

The particle size was measured by Dynamic Light Scattering (DLS), using a Zetasizer Nano ZS by Malvern equipped with a 4000-channels digital autocorrelator (25 ns to 8000s) and a Nd:YAG laser (k = 633 nm, 4 mW). The particle size distribution was measured at different time intervals in order to study the variation of the mean particle size over time, due to possible aggregation phenomena. The following procedure was used: the dispersions were placed in an ultrasonic bath (Bransonic, Ultrasonic cleaner Branson 2210, output power 90 W) for 60 min, in order to reduce aggregation phenomena; afterwards, nanolimes were placed in 10 mm path length plastic cuvettes which were capped during measurements to avoid the solvent evaporation; the dispersions were then analyzed at 0, 4, 8, 24, 48, 72, 96 h from nanolime sonication.

The kinetic stability of the dispersions was determined by turbidity measurements, analyzing their absorbance at = 600 nm by a UV-Vis spectroscopy (UVmini-1240 UV-Vis Spectrophotometer, by Shimadzu). The absorbance at **λ** = 600 nm was considered as the parameter proportional to the system turbidity, and its decrease as a function of time is due to particle agglomeration and settling.

Measurements started immediately after the preparation of the dispersions (sonication of 1 h) and monitored as a function of time for up to 96 h, as in the case of DLS measurements.

The relative kinetic stability parameter (KS%) of dispersions, defined as the ratio of the optical densities of the supernatant liquid (i.e., saturated $Ca(OH)_2$ solution) and of the original dispersion determined at 600 nm, was calculated using the following formula:

$$KS\% = 1-[(A_0 - A_t)/A_0] \times 100 \qquad (13)$$

where A_0 = starting absorbance at 600 nm and A_t = absorbance at a given time at 600 nm [Giorgi 2000 et al.].

The study of the morphology and size of the lime particles was complemented by Scanning Electron Microscopy (SEM). Images were captured using a FEI Nova NanoSEM 650 with two high sensitivity retractable detectors: a Through Lens Detector (TLD), used for high resolution SE (Secondary Electrons) imaging, and a Scanning Transmission Electron Microscopy Detector (STEM II), used in Bright Field (BF) mode. The liquid samples were placed on holey carbon film TEM grids (300 mesh). A voltage of 8 kV was used for SEM observations.

The mineralogical composition of the nanolime was investigated by XRD analysis; a Philips PW3710 X-ray diffractometer, working at 35 kV and 45 mA, with Fe-filtered Co Kα radiation (λ = 1.7903 Å), was used. Diffractograms were recorded in the range 3–74º 2θ, at increment of 0.05º with a count time of 1 s for each step. A silica-based sample holder was used for the analysis.

§ 5.4.2 Limestones

Maastricht limestone is a soft, yellowish, coarse porous material (> 95 % $CaCO_3$, density = 1.25 g/cm^3), historically used as building material in Belgium and South of the Netherlands [Dreesen & Dusar 2004; van Hees & Nijland 2009]. Despite its good durability, Maastricht limestone may in some cases show decay in the form of loss of cohesion [Dubelaar et al. 2006].

Migné limestone is a whitish, fine porous material (> 98 % $CaCO_3$, density = 1.96 g/cm^3) [Walbert et al. 2015; Voronina et al. 2013]; compared to the Maastricht limestone, it is much more compact and used as building and decorative material in France.

The mineralogical composition of Maastricht and Migné limestones was investigated by XRD analysis; a Philips PW3710 X-ray diffractometer, working at 35 kV and 45 mA, with Fe-filtered Co Kα radiation (λ = 1.7903 Å), was used. As for the characterization of nanolime, diffractograms were recorded in the range 3-74° 2θ, at increment of 0.05° with a count time of 1 second for each step.

The pore size distribution was assessed by means of Mercury Intrusion Porosimetry (MIP) on one sample for each stone type. An Autopore IV9500 (Micromeritics) was used to obtain porosity data. A contact angle of 141° was assumed between mercury and the stone. An equilibration time of 30 s has been used between each pressure increase step and measurement of the intruded volume [Lubelli et al. 2015]. Pores in the range 0.01 to 1000 μm were investigated.

§ 5.4.3 Assessment of nanolime behaviour when applied on limestone

§ 5.4.3.1 Specimen preparation

Cylindrical cores of 4 cm diameter and 4 cm height, cut out of Maastricht and Migné limestone blocks and drilled with orientation perpendicular to limestone bedding,, were used for all the tests described in this section. The core specimens then were sealed on the lateral side with Parafilm M (by Bemis NA, USA) in order to prevent the evaporation of the nanolime solvent on this side during absorption and drying.

These specimens were used for assessing both the absorption and drying kinetics of both solvent and the penetration depth and deposition of nanolime.

§ 5.4.3.2 Absorption and drying kinetics

The capillary absorption of nanolimes in the limestone specimens was measured according to the following procedure: the specimens were partially immersed in a petri dish filled with nanolime and with a grid on the bottom. Before application, the nanolimes were placed in an ultrasonic bath (60 Hz, by VWR symphony Ultrasonic Cleaners) for 60 minutes, to minimize nanoparticle aggregation phenomena. The absorption of the pure solvents was measured as well for comparison. During the absorption process, the weight of the core specimens was measured till saturation was reached. The absorption test was carried out in threefold and was performed under controlled conditions (50 % RH, T=20° C, air speed <0.1 m/s). The drying rate of different specimens, saturated with the four different nanolimes and their relative solvents, was evaluated by measuring the weight loss over time. The drying kinetic test was conducted as well at 50 % RH, T=20° C, air speed <0.1 m/s.

§ 5.4.3.3 Assessment of deposition of the nanolimes in the limestones

The penetration of the lime nanoparticles immediately after absorption was assessed by phenolphthalein test. The specimens were broken with hammer and chisel and the cross section was nebulized with a 1% phenolphthalein solution (60 % ethanol – 40 % water). This pH indicator remains uncoloured for pH < 8.2, while pH conditions higher than 9.8 lead to a purple colour change. In this case a purple colour of the substrate indicates the presence of nanolime ($pH_{Ca(OH)2} > 11$).

Furthermore, in order to assess the deposition of nanolime in the stone, the drying surface and the cross section of the specimens treated with nanolime were observed with a stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to record and analyse the specimens.

Finally, the observations and findings of the specimens' cross section were complemented by SEM-EDS. Samples were collected from the top (nearby the drying surface) and middle of the specimens (approximately 20mm in depth). The equipment used (Nova NanoSEM 650, by FEI) is coupled with a low vacuum solid- state detector BSED (GAD) that allows high resolution imaging (up to 1.4nm). A voltage of 4 to 6 kV was used for SEM-EDS observations.

§ 5.5 Results

§ 5.5.1 Nanolime

§ 5.5.1.1 Morphological and mineralogical characterization of nanolime particles (SEM-EDS and XRD)

SEM-EDS analyses showed that lime nanoparticles of E25, IP25 and B25 have a rounded to hexagonal plate-like shape (Fig. 5.2a) and nano to submicrometric sizes (50 to 600 nm) (Figs. 5.2b); nanoparticles tend to aggregate into micron-sized clusters, displaying very irregular shapes; the presence of those cluster of plate-like nanoparticles can be explained by agglomeration processes [Licchelli et al. 2014] (Fig. 5.2c). The morphology and size of the nanoparticles show no significant differences when these are dispersed in different alcoholic solvents (ethanol, isopropanol, butanol); differently, lime nanoparticles dispersed in water tend to quickly agglomerate, forming clusters with dimensions up to 4-5 µm.

XRD analysis (Fig. 5.3) confirm that the newly synthetized nanolimes are pure calcium hydroxide (portlandite).

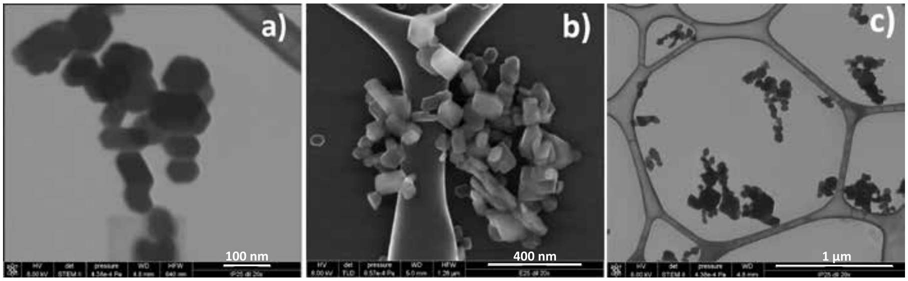

FIGURE 5.2 SEM microphotographs of two different nanolimes analyzed in the liquid phase: (a,b) E25 and (c) IP25

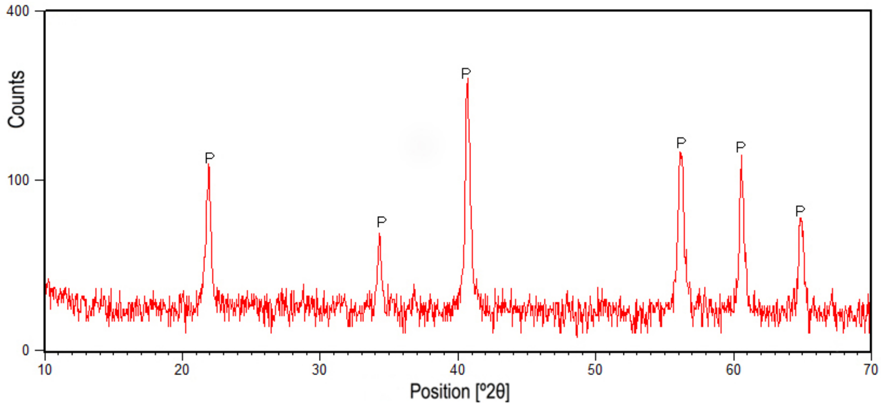

FIGURE 5.3 XRD diffraction patterns of the synthetized nanolime. The letter P stands for portlandite.

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§ 5.5.1.2 Mean particle size and colloidal stability of nanolime dispersions: evolution over time

Dynamic Light Scattering (DLS) measurements have been performed in order to investigate the particle size distribution of nanoparticles dispersions. DLS analyses are in agreement with the SEM-EDS observations, highlighting nano to submicrometric size (mostly ranging 70 to 700 nm, Fig. 5.4) of the lime particles. The analysis of H25 was not possible due to the high instability of the colloidal dispersion and very fast settling of the lime nanoparticles.

The size of the lime nanoparticles was monitored over time (0 to 96 h) (Fig. 5.4), with the procedure described in section 5.5.1.2. It can be observed that E25 and IP25 show a minimal variation of the mean particle size in the analyzed range of time (increase from 250-270 nm at 1 h, to 420 nm for E25 and 350 nm for IP25 at 96 h) (Fig. 5.4a,b); B25 shows a moderately higher increase of the size (400 to 700 nm) in the considered range of time (Fig. 5.4c), due to the formation of lime nanoparticle aggregates. This indicates that E25 and IP25, after a proper preparation and sonication, are stable dispersions up to at least 96 h. B25 has as well a moderate stability in the considered range of time (Fig. 5.4d).

In order to define the colloidal stability of the nanolimes (H25, E25, IP25 and B25) and confirm the DLS data, the kinetic stability was evaluated by UV-Vis spectroscopy, monitoring the absorbance of the dispersions at 600 nm [Dei & Salvadori 2006] (Fig. 5.5).

The aqueous dispersions (H25) showed low kinetic stability, with a rapid drop in the absorbance; the lime nanoparticles tend to agglomerate and settle rapidly, with a complete deposition in a few hours. In fact, the relative kinetic stability KS% for H25 is less than 40 % at 4 h after the preparation of the dispersion, and around 20 % at 8 h, indicating that most of the nanoparticles have settled.

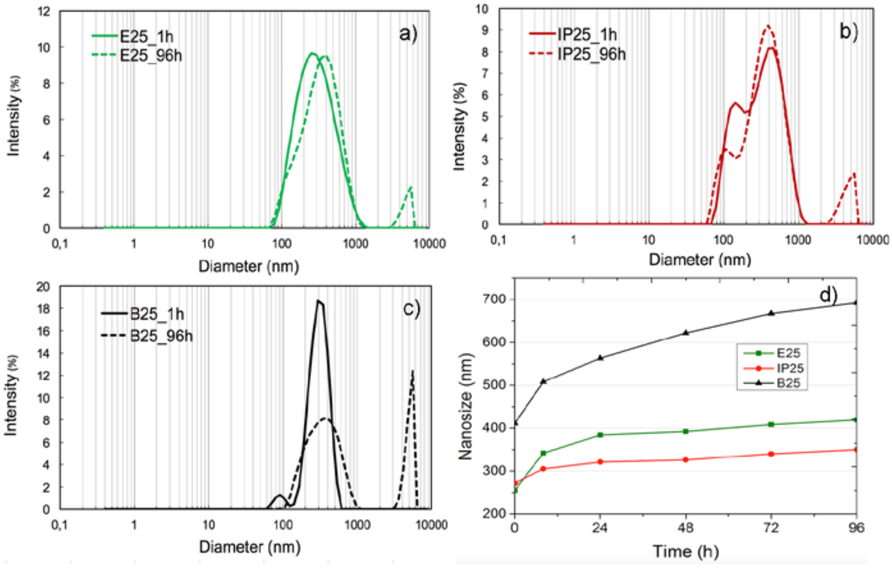

FIGURE 5.4 (a)Particle size distribution by DLS after 1 h and 96 h of nanolime a) E25, (b) IP25 and (c) B25; (d) Evolution over time (1 to 96 h) of the mean particle size of E25, IP25 and B25.

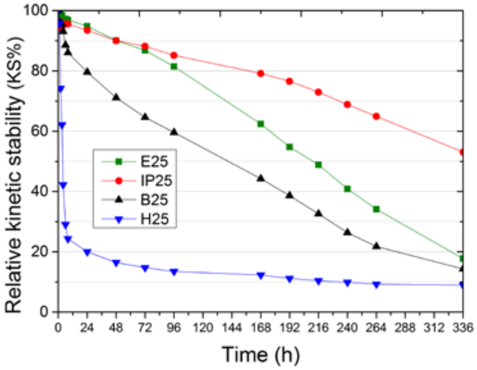

FIGURE 5.5 Relative kinetic stability (KS%) of the modified nanolimes, up to 2 weeks (336 h), in terms of the variation of the absorbance at 600 nm vs time.

Differently, IP25 and E25 show high kinetic stability, with an almost constant absorbance up to 96 h (KS% respectively 81% and 85%); B25 is less stable compared to E25, with a KS% around 60% (at 96 h). These data confirm the DLS analysis.

The high kinetic stability of nanolime dispersed in alcoholic solvents is attributed to repulsive electrostatic forces between nanoparticles. In fact, aliphatic alcohol molecules (as ethanol, isopropanol or butanol) are adsorbed onto $Ca(OH)_2$ nanoparticles, which acquire an electrical charge [Giorgi et al. 2000]. Electrostatic repulsion between the similarly charged particles decreases the frequency of "successful" collisions of particles participating in Brownian motion [Felix et al. 2014] and thus prevent both sedimentation and particle aggregation [Giorgi et al. 2000; Rodriguez-Navarro et al. 2013; Zheng et al. 2013]. When compared to water, the adsorption of ethanol, isopropanol or butanol onto lime nanoparticles guarantees a higher stabilization of the colloidal dispersion, explaining the higher kinetic stability of to E25, IP25 and B25. H25 is instead subjected to aggregation phenomena, caused as well by attractive short-range Van der Waals forces, with a consequent decreasing of absorbance [Rodriguez-Navarro et al. 2005; Lichelli 2014; Chekli 2013].

§ 5.5.2 Characterization of limestone

§ 5.5.2.1 Mineralogy and pore size distribution of the limestones

Fig. 5.6 shows the pore size distribution and the total porosity of the two limestones as measured by MIP on one sample for each stone type. Maastricht has a high porosity (50 %) and a unimodal pore size distribution (30-50 µm). Migné limestone presents a total porosity of 28% and an almost unimodal pore size distribution, but with much finer pores than Maastricht limestone (0.5-2 µm).

The XRD analysis has confirmed the high purity of both limestones. The Migné is almost pure calcite, whereas Maastricht limestone contains traces of quartz.

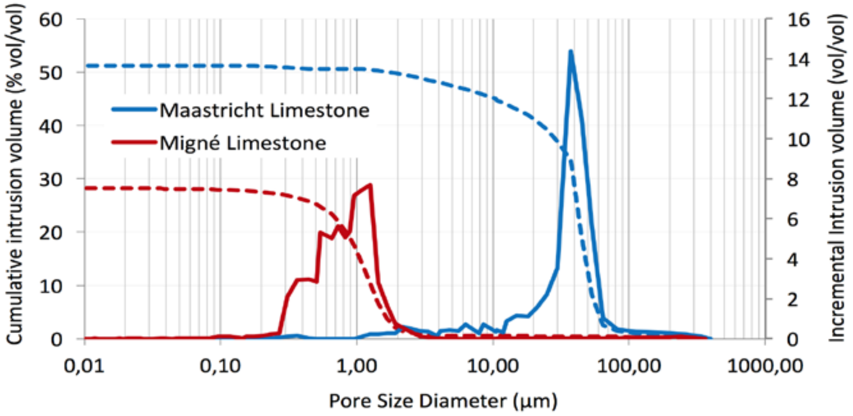

FIGURE 5.6 Pore size distribution (solid) and total porosity (dotted) by MIP of Migné limestone (red) and Maastricht limestone (blue).

§ 5.5.2.2 Moisture transport properties

Fig. 5.7a reports the absorption kinetics of the different solvents on Maastricht and on Migné limestone. For both materials, the absorption of H_2O is faster compared to alcoholic solvents, due to higher surface tension of water (about 3 times higher than EtOH, IpOH or BOH). The capillary absorption of the solvents applied on the Migné limestone takes remarkably longer time due to the higher fine porosity of this material.

When observing the drying kinetics (Figs. 5.7b), EtOH and IpOH evaporate faster compared to water, due to their lower boiling point; in addition, the higher surface tension of water enhances its retention within the pores network, delaying the drying rate. As expected, the drying rates of water and of the alcoholic solvents within Migné limestone are much lower compared to those within Maastricht limestone, due to their different porosity and pore size. Ethanol and isopropanol completely evaporate within 2-3 days in the case of Maastricht, whereas their total evaporation is completed in 5-6 days in the case of Migné limestone.

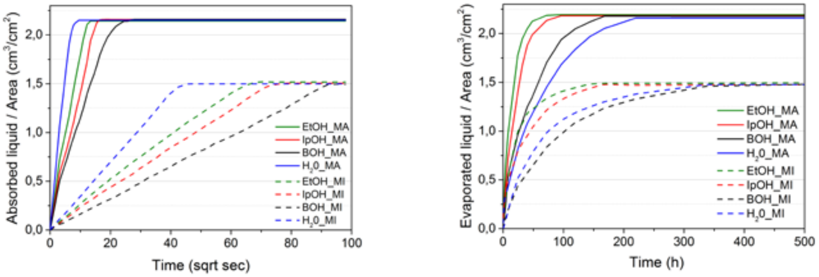

FIGURE 5.7 (a) Absorption and (b) drying kinetics of the different solvents (EtOH, IpOH, BOH, H_2O) applied on specimens of Maastricht limestone (solid line) and Migné limestone (dotted line).

§ 5.5.3 Prediction model of nanolime penetration depth: fine tuning

In the previous section, detailed data on the morphology, particle size distribution and kinetic stability of the different nanolimes were obtained. In this section, those data are related to the porosity of the limestones, which have both a unimodal pore size distribution with a different mean pore size.

Based on the conceptual model described in the introduction (Section 5.3), hypotheses on the transport, absorption and deposition of the nanolime dispersion in different solvents when applied on these limestones can be drawn:

§ 5.5.3.1 Coarse porous material

It is expected that nanolime in water (H25), in spite of its low kinetic stability (Fig. 5.5) and of the quick capillary absorption of water (Fig. 5.7a), can penetrate in this material. Similarly, nanolime in butanol (B25) is expected as well to penetrate in this material, in spite of its moderate kinetic stability (Fig. 5.5) and of the slow capillary absorption of butanol (Fig. 5.7a).

Nanolimes in ethanol (E25) and isopropanol (IP25) are expected to penetrate properly within the coarse pores of this material, due to their good kinetic stability (Fig. 5.5) and fast capillary absorption of their relative solvents (Fig. 5.7a).

However, as observed as well in a previous paper by the authors [Borsoi 2016a], the high stability of E25 and IP25 and fast drying rate of their solvents is expected to hinder a phase separation in-depth, and to facilitate the transport of the nanoparticle back towards the drying surface. Concluding, the use of a high boiling point solvent as butanol or water (Table 5.1), which provide moderate or low kinetic stability to the nanolime dispersion, is expected to guarantee at the same time sufficient nanolime absorption and limited back-migration; this would result in a deeper deposition of the lime nanoparticles.

§ 5.5.3.2 Fine-porous material

It is expected that nanolime in ethanol (E25) and isopropanol (IP25) can penetrate the fine pores of this substrate due to their high kinetic stability and relatively fast absorption of the relative solvents. Nanolimes in butanol (B25) and water (H25), due to their low kinetic stability (Fig. 5.5) and to the slow absorption of their solvent in this substrate (Fig. 5.7a), are expected to have a very limited penetration.

In addition, the drying rate of ethanol and isopropanol in this fine porous stone is slower than in the coarse porous Maastricht lime- stone (Fig. 5.7b), fact which is expected to prevent back-migration of lime nanoparticles to the drying surface.

On the basis of the previous results, the model sketched in Fig. 5.1 can be further developed as shown in Table 5.2. Nanolimes B25 and E25 have been selected for validation of the model: B25 is expected to perform properly on Maastricht and to have limited penetration on Migné. E25 is expected to lead to in-depth deposition within the Migné limestone and to show back migration in Maastricht limestone.

TABLE 5.2 Modular system correlating nanolime solvents and substrate pore network: it is possible to foresee the effectiveness (absorption and deposition) of the relative nanolimes when applied on these materials (✓= working, X= not working).

NANOLIME SOLVENTS	SUBSTRATE			
	Fine pores (0.5-2 µm)		Coarse pores (35-40 µm)	
	Absorption	Deposition in depth	Absorption	Deposition in depth
EtOH	✓	✓	✓	X
IpOH	✓	✓	✓	X
BOH	X	X	✓	✓
H_2O	X	X	✓	✓

§ 5.5.4 Validation of the model: interaction and deposition of the nanolimes in limestones

In this section, the nanolimes E25 and B25, selected on the basis of the conceptual model, were applied both on the Migné and Maastricht limestone in order to validate the hypotheses through experimental observations.

§ 5.5.4.1 Absorption and drying kinetics

Fig. 5.8a reports the absorption kinetics of nanolimes E25 and B25 applied on Maastricht and on Migné limestones.

In Maastricht limestone the absorption of E25 is completed within few minutes, whereas B25 takes around 40min to saturate the specimen; in addition, B25 barely deposit at the absorption surface, due to its lower kinetic stability, which favours nanoparticle-solvent phase separation.

In Migné limestone, the capillary absorption for both E25 and B25 nanolimes is slower than in Maastricht limestone, due to the fine pores and total porosity of this material. Complete saturation was obtained after 2 h for E25 and more than 3 h for B25. In both cases part of the lime nanoparticles was deposited at the absorption surface; this phenomenon was more evident for B25 than for E25.

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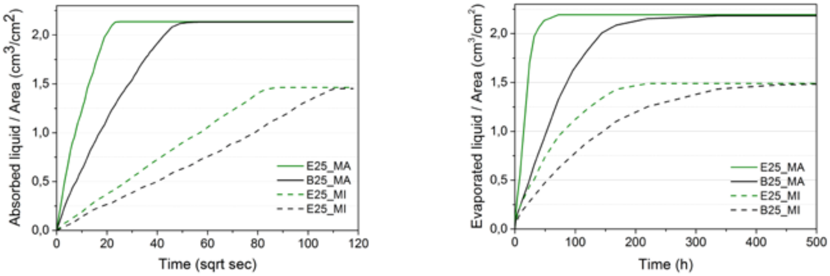

FIGURE 5.8 (a) Absorption and (b) drying kinetics of nanolimes E25 and B25 applied on specimens of Maastricht limestone (solid line) and Migné limestone (dotted line).

Fig. 5.8b reports the drying kinetics of nanolimes E25 and B25 applied on Maastricht and on Migné limestones. Maastricht limestone saturated with E25 takes around 72 h for complete drying, while B25 dries out completely in about 220 h. The drying rate of Migné limestone is much slower than of Maastricht, not only due to the fine pore network of this stone, but also to the nanolime particles which partially deposited at the surface during absorption. Drying is slower for B25 (336 h for complete drying) than for E25 (168 h).

§ 5.5.4.2 Assessment of the penetration depth of nanolimes

Phenolphthalein test was performed on the cross section of the specimens treated with E25 and B25, in order to assess the penetration depth of the nanolimes.

Nanolime E25 penetrated within Maastricht limestone (Fig. 5.9a), saturating the entire section of the specimen, and no deposition of nanolime is visible at the absorption surface; B25 penetrated for over 30 mm in depth in the specimen (Fig. 5.9b), even though a part of the nanoparticles was deposited at the absorption surface.

In the case of the Migné limestone, neither E25 nor B25 can penetrate much in depth in the material (Fig. 5.9c, d). The fine mean pore size probably enhances the nanoparticles-solvent phase separation causing deposition near the surface; this deposition, which is more evident in the case of B25 than in that of E25, can hinder further penetration of the lime nanoparticles in depth in the material.

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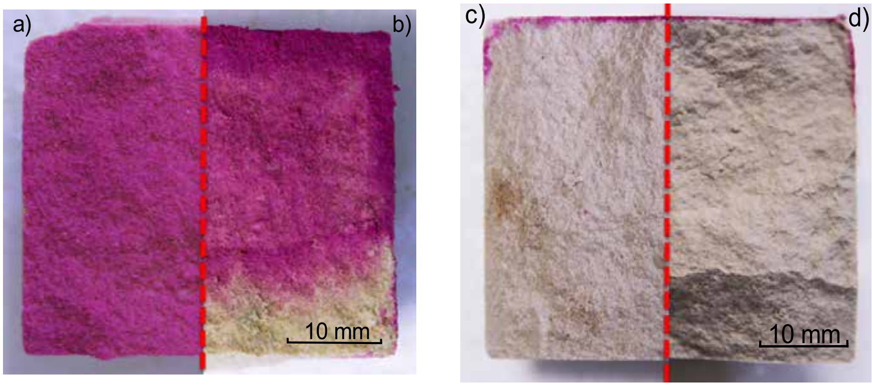

FIGURE 5.9 Pictures of the phenolphthalein test performed on the cross sections of specimens of Maastricht limestone treated with (a) E25 and (b) B25 and of Migné limestone treated with (c) E25 and d) B25. The absorption surface is on the top of the figures.

§ 5.5.4.3 Assessment of the deposition of nanolimes: optical microscopy

In order to definitely assess the location of nanolime deposition in the treated Migné and Maastricht limestones, the cross sections of the limestones treated with E25 and B25 were investigated by optical microscopy (Fig. 5.10).

In the Maastricht specimen treated with E25 (Fig. 10.5a), a thin layer of nanolime particles at 0.5-1 mm in depth in the cross section is visible. On the other hand, clusters of lime nanoparticles are barely visible in depth in the specimen. This observation confirms the back migration of the nanolime towards the drying surface, as already observed in previous research [Borsoi et al. 2016a].

The Maastricht specimens treated with B25 show clusters of lime nanoparticles, mainly present up to 20–25mm from the absorption surface. Deeper in the specimen, the presence of nanoparticles is very limited. However, some minor deposition of nanolime particles can be observed at the absorption surface (Fig. 5.10b), as observed as well in Section 4.4.1.

In the Migné specimen treated with E25 (Fig. 5.10c), nanolime deposition up to 0.5mm in depth can be observed. B25 did not penetrate at all in the specimens and only left an accumulation of nanolime particles at the absorption surface (Fig. 5.10d). In the case of B25, the excess of nanolime accumulated at the absorption surface was manually removed with a sponge before taking the microphotographs.

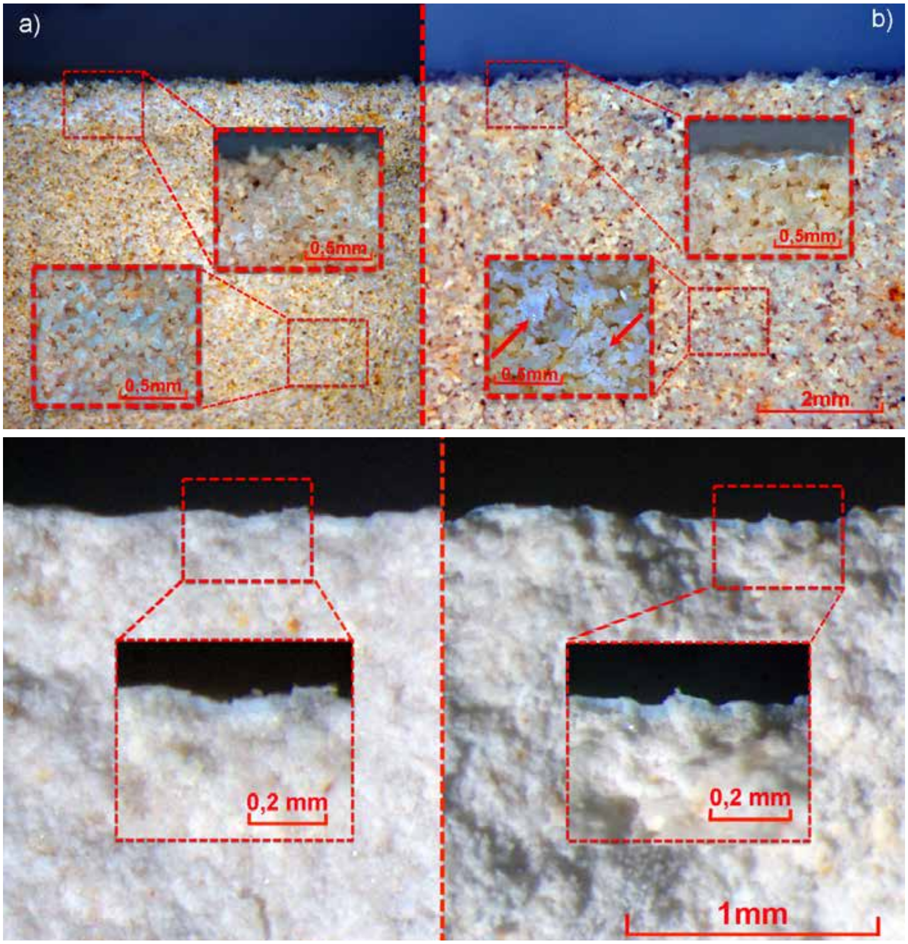

FIGURE 5.10 Microphotographs of the cross section of the specimens of Maastricht limestone, treated with (a) E25 and (b) B25 (the arrows indicate the presence of nanolime clusters), and of Migné limestone treated with c) E25 and d) B25.

§ 5.5.4.4 Assessment of the deposition of nanolimes: SEM-EDS

Microstructural observations and microanalyses were performed by SEM-EDS in order to further study the deposition of nanolime within limestone.

The cross sections of Maastricht limestone specimens treated with E25 and B25, previously investigated by optical microscopy, were observed (Fig. 5.11). Migné limestone was not analysed since either E25 and B25 did barely penetrate within the structure, as observed with the phenolphthalein test (Section 4.4.2).

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The microstructural analysis of E25 treatment confirms strong nanolime deposition nearby the drying surface, at 0.5 mm in depth (Fig. 5.11a). Nanoparticles have mainly agglomerated in clusters of 3–5 m. In addition, local depositions of lime nanoparticles are identified deeper in the cross section: at 20 mm from the drying surface, sporadic clusters of nanolime particles are visible (Fig. 5.11b).

The SEM-EDS analysis of specimen treated with B25 shows a reduced nanolime deposition at 1 mm from the drying surface (Fig. 5.11c). However, heterogeneously distributed nanolime deposition can be identified at least up to 20–25 mm in depth (Fig. 5.11d). Clusters formed of crystalline and regularly shaped nanoparticles, with dimensions mostly ranging between 50 and 800 nm, are observed and tend to fill the pores between the grains of Maastricht limestone. These observations confirm the results obtained by phenolphthalein test and optical microscopy.

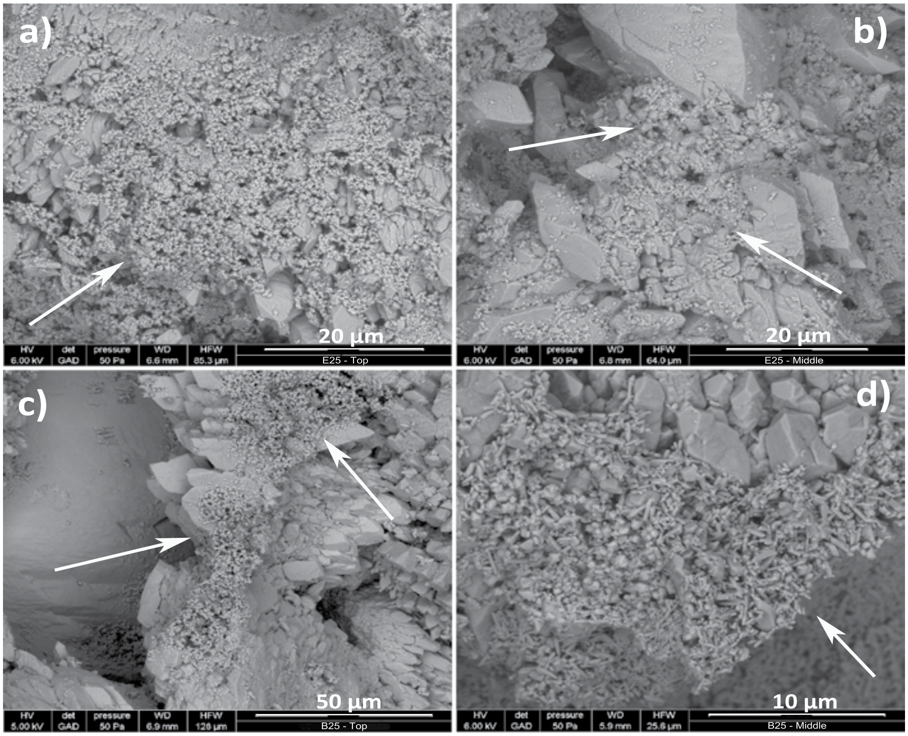

FIGURE 5.11 Fig.11.5 Scanning electron microscopy microphotographs of Maastricht limestone specimen: (a) 0.5 mm and (b) 20 mm in depth (from the drying surface) in the cross section of the specimen treated with E25; (c) 1 mm and (d) 22 mm in depth (from the drying surface) in the cross section of the specimen treated with B25. The arrows indicate the deposits of lime nanoparticles.

§ 5.6 Conclusions

In this work, nanolimes were synthetized by solvothermal reaction of metallic calcium in water, and later dispersed in different solvents (ethanol, isopropanol, butanol, water). The morphology, mean particle size and colloidal stability of the nanolimes were characterized. Results show that, after a proper sonication, colloidal dispersions E25, IP25 and B25 can guarantee stable dispersions up to at least 96 h. Nanoparticles range between 40–800 nm, even if clusters of nanoparticles can be observed in the liquid phase. From these four different solvents, butanol and water give the less stable dispersions.

A conceptual model, aiming at predicting the deposition of lime nanoparticles within the treated limestones, is proposed and validated in this paper. The model is based on the assumption that, by selecting the solvent for the nanolime based on the moisture transport properties of the substrate to be treated and on the kinetic stability of the relative nanolime, an improved deposition of nanoparticles in depth can be obtained.

According to this model, solvents having a high boiling point, as butanol or water (and thus leading to nanolime dispersions with relatively low stability), are expected to improve the deposition of lime nanoparticles in depth in coarse porous materials, as at the studied conditions (50% RH, T = 20° C, air flow <0.1 m/s) no significant back migration is observed. Solvents having lower boiling point, as ethanol and isopropanol (and conferring high stability to the nanolime dispersions), are expected to result into a better penetration and deposition of the nanoparticles in depth in fine porous materials.

The experimental research, carried out on both coarse (Maastricht) and fine (Migné) porous limestones, confirms that the penetration and deposition of nanolimes is strongly influenced by the pore size of the treated material, as suggested by the model.

In the case of coarse porous materials as Maastricht limestone, the nanolime dispersed in butanol showed to be still able to penetrate in depth into the substrate, without having the drawback of back migration of nanoparticles towards the drying surface (as observed with the nanolime in ethanol E25). This resulted in the deposition of nanolime up to 20–25 mm in depth.

In the fine porous Migné limestone, the penetration and in-depth deposition of E25 was slightly better than that of B25, but still quite limited; in fact, even the nanolime dispersions with the highest stability, as the ethanol-based ones, suffer phase separation when applied on such fine porous substrates.

Next to the properties of the nanolime (e.g. concentration, particles size, solvent type, and consequently kinetic stability and reactivity), several other parameters affect the transport and deposition of nanolime in depth, e.g. environmental conditions, application methodology (e.g. capillarity, nebulization, ect.), impregnation depth and amount of consolidant deposited with the treated material. This has to be considered during the consolidation process.

Further fine-tuning of the nanolime dispersion properties is expected to improve the effect of the treatment. In the case of the coarse porous substrates, mixing different solvents (e.g. butanol with percentages of ethanol) might be considered; in the case of the fine porous substrates, further dilution of the ethanol-based dispersion (<25 g/l) might result into a deeper penetration depth.

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6 Optimization of nanolime solvent for the consolidation of coarse porous limestone

§ 6.1 Introduction to the chapter

The model proposed in the previous chapter is fine-tuned here. Nanolimes were dispersed in different mixtures of solvents (i.e. ethanol and water in different percentages) and their properties (drying rate and kinetic stability) studied. The in-depth deposition of the different nanolime dispersions within a coarse porous limestone was investigated. This chapter is based on the paper published in Applied Physics A – Material Science & Processing (doi:10.1007/s00339-016-0382-3) with minor changes to incorporate the suggestions of the PhD committee members.

§ 6.2 Abstract

The potentialities of nanomaterials for application in the field of conservation have been widely investigated in the last two decades. Among nanomaterials, nanolimes, i.e., dispersions of lime nanoparticles in alcohols are promising consolidating products for calcareous materials. Nanolimes are effective in recovering the very superficial loss of cohesion of decayed materials, but they do not always provide sufficient mass consolidation. This limitation is mainly related to the deposition of the nanoparticles nearby the surface of the material. Experimental research has been set up with the aim of improving the in-depth deposition of lime nanoparticles. Previous research by the authors has shown that nanolime deposition within a substrate can be controlled by adapting the nanolimes properties (kinetic stability and evaporation rate) to the moisture transport behaviour of the substrate. Nanolime properties can be modified by the use of different solvents. In this research, nanolime dispersions have been further optimized for application on Maastricht limestone, a coarse porous limestone.

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Firstly, nanolimes were synthesized and dispersed in ethanol and/or water, both pure and mixed in different percentages. Subsequently, based on the kinetic stability of the nanolime dispersions, the most promising solvent mixtures were selected and applied on the limestone. The deposition of lime nanoparticles within the limestone was studied by phenolphthalein test, optical microscopy and scanning electron microscopy. The results confirm that nanolime dispersed in a mixture of ethanol (95 %) and water (5 %) can guarantee a better nanoparticles in-depth deposition within coarse porous substrates, when compared to dispersions in pure ethanol.

§ 6.3 Introduction of the paper

The application of nanotechnology in the field of conservation Science has remarkably increased over the last two decades. Several nanomaterials with cleaning, consolidating and/or protective properties have been developed for the conservation of artworks [Baglioni et al. 2012; Fermo et al. 2014; Cappelletti et al. 2015]. Among nanomaterials, nanolime attracted an increasing interest, due to its potential as consolidating product for calcareous materials, such as frescos, limestones and lime-based renders and plasters. Nanolimes are colloidal alcoholic dispersions of calcium hydroxide nanoparticles, with spherical to hexagonal shape and a size ranging from 50 to 600 nm [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Ziegenbalg et al. 2010; Chelazzi et al. 2013]. Thanks to the nano to submicrometric size of the particles and to the alcoholic solvent, nanolimes have a high reactivity and a high lime concentration, which provide a better consolidating effect than traditional lime-based consolidants (e.g., limewater) [Rodriguez-Navarro et al. 2013; Poggi et al. 2014]. Besides, nanolimes have a better compatibility and durability on calcareous substrates than TEOS-based products (e.g., ethylsilicate), which are commonly used for stone consolidation [Hansen et al. 2003; Toniolo et al. 2010; Ferreira Pinto & Delgado Rodrigues 2012b; van Hees et al. 2014b].

Concerning their consolidation effectiveness, nanolimes have proven to work properly for the pre-consolidation and for the recovery of the superficial cohesion of different materials, such as mural paintings, plasters, paper and wood. [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Borsoi et al. 2012; Rodriguez-Navarro et al. 2013; Baglioni et al. 2013; Poggi et al. 2014]. However, when mass consolidation is required, e.g., in the case of decayed renders or limestone, nanolimes often show a poor effectiveness and sometimes result in the formation of a white haze on the surface [Campbell et al. 2011; Costa & Delgado Rodrigues 2012]. An important reason for their limited effectiveness is related to deposition of nanoparticles at the surface, resulting in a poor consolidating effect in depth [Costa & Delgado Rodrigues 2012; Ghaffari et al. 2012; Ruffolo et al. 2013; Borsoi et al. 2016a].

Previous research has shown that, depending on the moisture transport properties of the substrate, surface deposition may occur not only during absorption but also during evaporation of the solvent, due to a partial back migration of the nanoparticles to the surface [Borsoi et al. 2016a]. This suggests that the approach proposed by the authors in [Borsoi et al. 2016b], i.e., tailoring the kinetic stability and the evaporation rate of nanolime (by modification of the solvent) to the moisture transport properties of the substrate to be treated, can improve nanoparticles in-depth deposition within the substrate. According to this approach, dispersions with lower kinetic stability and lower drying rate should be preferred for application on substrates with very fast moisture transport properties, as they limit back migration of nanoparticles during drying and thereby improve in-depth deposition.

In the research described in this article, this approach has been optimized and validated for Maastricht limestone, a highly and coarse porous limestone.

Lime nanoparticles were synthesized and dispersed in ethanol, water and in mixtures of these two solvents; the kinetic stability (Section 6.5.2) of the dispersions was measured; based on these data, nanolimes dispersed in pure ethanol or in a mixed ethanol–water solvent were selected (Section 6.5.3) and applied on Maastricht limestone (Section 6.5.1). Finally, the in-depth deposition of the lime nanoparticles within the limestone was assessed (Section 6.5.4).

§ 6.4 Materials and methods

§ 6.4.1 Maastricht limestone

The Maastricht limestone is a soft, yellowish limestone (> 95 % $CaCO_3$) [Dreesen & Dusar 2004; Nijland et al. 2006], quarried in the Belgian and Dutch provinces of Limburg and used as building material in the same regions.

Despite its low mechanical strength, Maastricht limestone has generally shown a good durability, probably related to the dissolution and re-precipitation of carbonates within the pore network of the stone, when exposed to atmospheric agents [Dubelaar et al. 2006]. However, Maastricht limestone may in some cases show decay in the form of loss of cohesion at the surface (e.g., powdering, scaling) [van Hees & Nijland 2009].

§ 6.4.1.1 Porosity and pore size distribution

The open porosity and the pore size distribution of Maastricht limestone was assessed by means of mercury intrusion porosimetry (MIP) on one sample. An Autopore IV9500 (Micromeritics) was used to obtain porosity data. Pores in the range 0.01–400 µm could be measured with this instrument. A contact angle of 141° was assumed between mercury and the stone. An equilibration time of 30 s was used between each pressure increase step.

§ 6.4.1.2 Specimens

Cylindrical specimens (diameter: 4 cm, height: 4 cm) were used in this research. Specimens were drilled from sound Maastricht limestone blocks, with an orientation perpendicular to the limestone bedding. Before testing, specimens were dried in the oven at 60°C for 24 h and then conditioned at 20°C and 50% RH.

§ 6.4.1.3 Absorption and drying kinetics

The capillary absorption of water and ethanol in the Maastricht limestone specimens was measured according to EN 15801 [CEN 2009]. A grid was placed in a Petri dish, which was subsequently filled with water or ethanol. The core specimens, sealed with Parafilm M (by Bemis NA, USA) on the lateral sides, were placed with their bottom surface on the grid. During the absorption process, the specimen weight was measured repeatedly till saturation was reached.

The drying rate of the specimens, saturated with water or ethanol, was evaluated by measuring the weight loss over time, in accordance with EN 16322 [CEN 2013].

The absorption and drying tests were carried out in threefold and performed under controlled conditions (50 % RH, T = 20 °C, air speed < 0.1 m/s). Water, ethanol absorption and drying were carried out in sequence on the same specimens, in order to minimize the effect of the stone variability.

§ 6.4.2 Nanolime

§ 6.4.2.1 Synthesis and solvent selection

Nanolimes were synthesized by solvothermal reaction of metallic calcium in water. Metallic granular calcium (p.a. 99 %, by Sigma-Aldrich) was stirred for few hours in dis- tilled water (conductivity <2 µS/cm) within a reactor at T = 90 °C. The aqueous medium was then substituted by centrifuging the colloidal dispersions using an Eppendorf Centrifuge 5810R (rotation speed 8000 rpm, T = 10 min), in order to obtain colloidal dispersions with an equivalent concentration of 25 g/l. The supernatant was subsequently extracted through glass volumetric pipettes and substituted by ethanol (p.a. 99.5 % by Sigma-Aldrich), fresh distilled water (conductivity <2 µS/cm) or mixtures of these solvents.

Ethanol and water were selected as solvents based on the results obtained in previous works [Borsoi et al. 2016a; Borsoi et al. 2016b]. Ethanol is a highly volatile solvent and guarantees a high kinetic stability to the dispersion, whereas water has a higher boiling point and higher surface tension, which results in a low kinetic stability (Table 6.1).

TABLE 6.1 Physical-chemical properties of the selected solvents at T = 20ºC [DDBST].

SOLVENT	DENSITY (g/cm^3)	DYNAMIC VISCOSITY (mPa·s)	BOILING POINT (°C)	DIELECTRIC CONSTANT	SURFACE TENSION (SOLVENT/AIR) (N/m)
Ethanol	0.810	1.214	78.37	24.6	0.0221
Water	1.000	1.002	99.61	80.4	0.0728

TOC

Next to pure ethanol and water dispersion, ethanol-based dispersions mixed with different percentages of water (5–20–50–80 %) were prepared as well (Tab. 6.2). The addition of a percentage of water with the dispersion is expected to decrease the kinetic stability.

TABLE 6.2 Acronyms and solvent composition of the nanolime dispersions considered in this work. (EtOH = ethanol, H_2O = water).

NANOLIME ACRONYM	SOLVENT MIXTURE (IN VOLUME)
H100	100% H_2O
E20H80	20% EtOH, 80% H_2O
E50H50	50% EtOH, 50% H_2O
E80H20	80% EtOH, 20% H_2O
E95H5	95% EtOH, 5% H_2O
E100	100% EtOH

The aim was to produce dispersions with a moderate kinetic stability that can guarantee a homogenous absorption with the substrate, but at the same time limit back migration of nanoparticles to the surface during drying. In other words, when the desired absorption depth is reached, the kinetic stability should decrease and favour nanolime precipitation in depth.

§ 6.4.2.2 Kinetic stability

The kinetic stability of the nanolimes was determined by turbidity measurements, analyzing their absorbance at λ = 600 nm by a UV–Vis spectroscopy (UVmini-1240 UV– Vis Spectrophotometer, by Shimadzu). Before the analysis, the nanolimes were placed in an ultrasonic bath (60 Hz, by VWR symphony Ultrasonic Cleaners) for 60 min, in order to minimize nanoparticle aggregation phenomena. The absorbance at 600 nm was considered as the parameter proportional to the turbidity of the dispersion; its decrease as a function of time is due to particle agglomeration and settling. Before measurement, the nanolimes were placed in an ultrasonic bath (60 Hz, by VWR symphony Ultrasonic Cleaners) for 60 min, to minimize nanoparticle aggregation phenomena; afterward, nanolimes were placed in 10 mm path length plastic cuvettes, which were capped during measurements to avoid solvent evaporation.

The relative kinetic stability parameter (KS %) of the dispersions, defined as the ratio of the optical density of the supernatant liquid (i.e., saturated $Ca(OH)_2$ solution) and of the original dispersion determined at 600 nm, was calculated using the following formula:

$$KS\% = 1-[(A_0 - A_t)/A_0] \times 100 \quad (13)$$

where A_0 = starting absorbance at 600 nm and A_t = absorbance at a given time at 600 nm [Giorgi et al. 2000].

§ 6.4.2.3 Application and assessment of nanolime deposition

Nanolimes E80H20 and E95H5, selected on the basis of the result of the kinetic stability measurements (Section 6.5.3), were applied on the Maastricht limestone specimens by capillary absorption until full saturation. E100 was applied as well for comparison. The bottom surface of the specimens was partially immersed in a Petri dish filled with nanolime and with a grid on the bottom. The wetting front was visually monitored during absorption (Fig. 6.1).

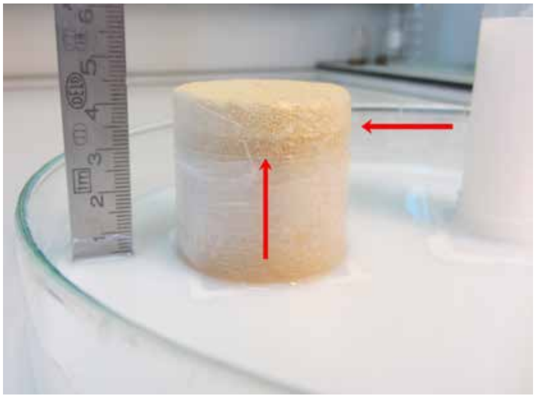

FIGURE 6.1 Nanolime application by capillary absorption until full saturation; the red arrows indicate the wetting front and the homogeneous capillary rising of the nanolime.

Immediately after saturation, the specimens were broken with hammer and chisel in two halves: On one side, the wetting front of the dispersion was visually checked, and on the other side, the distribution of the lime nanoparticles was assessed by phenolphthalein test. This test consists in nebulizing a phenolphthalein solution (1 % phenolphthalein in 60 % ethanol/40 % water) on the fresh cross- section of the specimen and observing the change in colour. Phenolphthalein alcoholic solution is a well-known pH indicator which remains uncoloured for pH <8.2, while pH conditions higher than 9.8 lead to a purple color change. In this case, a purple colour of the substrate indicates the presence of nanolime ($pH_{Ca(OH)2} > 11$). By comparing the results of the phenolphthalein test with the macroscopical observations of the wetting front, separation of the nanoparticles from the solvent during absorption can be assessed.

The deposition of nanolime in the stone after drying was assessed by optical and scanning electron microscope. In order to achieve a full carbonation of the lime nanoparticles [López-Arce et al. 2011], the specimens were stored at 50 % RH and T = 20 °C for at least 4 weeks before microscopy observations.

The drying surface and the cross-section of the specimens were observed by stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to record and analyze the specimens.

Cross-sections were also studied by Scanning Electron Microscope equipped with energy-dispersive X-ray spectroscopy (SEM–EDS). The equipment used (Nova Nano-SEM 650, by FEI) is coupled with a low vacuum solid-state detector BSED (GAD) that allows high resolution imaging (up to 1.4 nm) and a high flexibility of the working conditions (1–30 kV). The v6.2.X software was used to analyse the specimens.

§ 6.5 Results

§ 6.5.1 Substrate characterization

§ 6.5.1.1 Porosity and pore size distribution

Figure 6.2 shows the total open porosity and the pore size distribution of the Maastricht limestone. The Maastricht limestone has a very high porosity (50 %) and an unimodal pore size distribution, with macro pores (30–50 µm).

Because of its high and coarse porosity, Maastricht limestone is expected to quickly absorb large amounts of nanolime dispersions, guarantying the penetration of the lime nanoparticles.

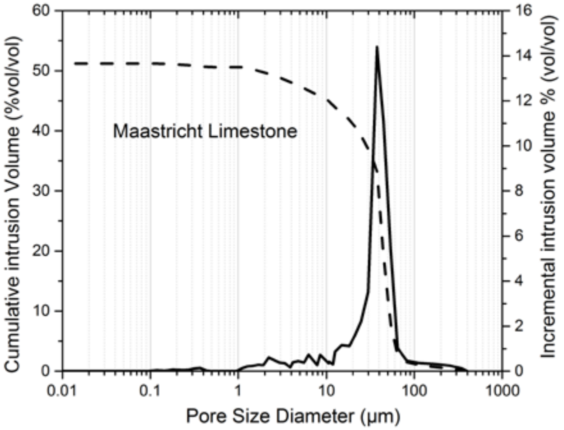

FIGURE 6.2 Pore size distribution (solid) and total porosity (dotted) by MIP of Maastricht limestone.

§ 6.5.1.2 Absorption and drying kinetics

Figure 6.3a reports the absorption kinetics of ethanol and water on Maastricht limestone. As seen, the absorption of H_2O is faster compared to that of ethanol, due to the higher surface tension of water (see Table 6.1).

When observing the drying kinetics (Fig. 6.3b), EtOH evaporates faster compared to H_2O:EtOH completely evaporates in 48–72 h, whereas H_2O takes 7–8 days. This can be explained by the lower boiling point of ethanol; in addition, the higher surface tension of water enhances its retention within the pore network, delaying the drying rate.

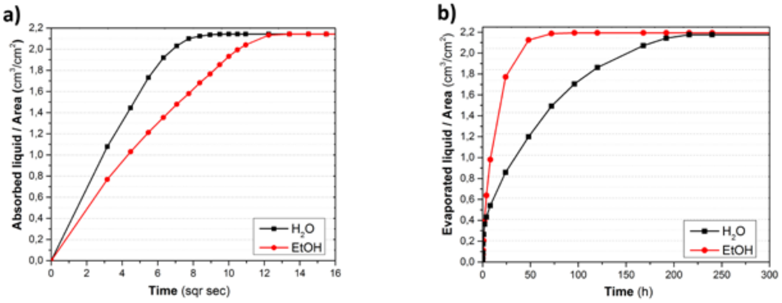

FIGURE 6.3 a) Absorption and b) drying kinetics of water (black line) and ethanol (red line) on specimens of Maastricht limestone.

§ 6.5.2 Nanolimes kinetic stability

The kinetic stability of nanolime dispersions (Table 6.2) was evaluated by UV–Vis spectroscopy, by monitoring the absorbance of the dispersions at 600 nm (Fig. 6.4).

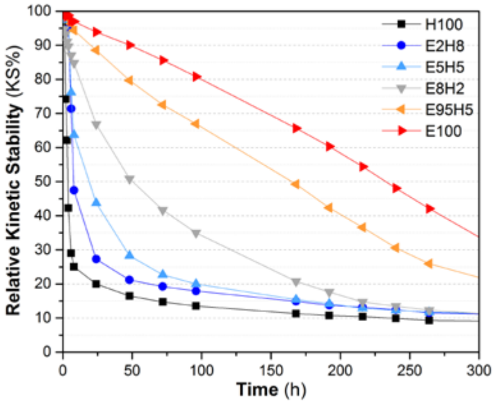

FIGURE 6.4 Relative kinetic stability (KS %) of the nanolimes over time.

The aqueous dispersions (H100) showed a rapid drop in the absorbance, indicating a very low kinetic stability: Lime nanoparticles tend to settle rapidly, with a complete deposition within a few hours. The relative kinetic stability (KS%) for H100 is less than

40% at 4h from the preparation of the dispersion, and around 25 % at 8 h, indicating that most of the nanoparticles have settled at this time. The aggregation phenomena observed for H100 are most probably caused by short-range (attractive) Van der Waals forces [Rodriguez-Navarro et al. 2005; Licchelli et al. 2014].

Differently, E100 shows high kinetic stability, with a slow and constant decrease in the absorbance over time (KS % at 24 and 96 h is, respectively, 91 and 82 %, respectively). This behavior can be explained by the ethanol adsorption onto $Ca(OH)_2$ nanoparticles, which subsequently acquire a similar electrical charge [Giorgi et al. 2000]. The repulsive electrostatic forces between nanoparticles decrease the frequency of collisions leading to aggregation of nanoparticles, which move around in random Brownian motions [Felix 2014]: Sedimentation and particle aggregation are thus prevented [Zheng et al. 2013].

When water is added to the ethanol-based dispersion, the kinetic stability significantly decreases. In the case of E80H20 (20 % water), KS % is still high at 8 h (84 %), but it decreases to 66 % at 24 h and to around 35 % at 96 h. When 5 % in volume of water is added (E95H5), the KS % of the dispersion is 80 % at 48 h, decreasing to 66 % at 96 h. Even a small amount of water is remarkably influencing the kinetic stability of the dispersion.

§ 6.5.3 Selection of the solvent

Based on the results reported in Section 6.5.2, it can be concluded that:

- E100 has a very good stability, and it is known from previous research [Borsoi et al. 2016a; Borsoi et al. 2016b] to easily penetrate in the Maastricht limestone.
- H100, E20H80 and E50H50 have a very low kinetic stability (see Fig. 6.4). This makes the handling of these nanolimes very difficult (nanolime should be used within short time from sonication); moreover, nanoparticle aggregation during absorption is expected. Because of these reasons, these nanolimes are not considered feasible alternatives and will not be further studied.
- E80H20 and E95H5 are expected to be stable enough to be absorbed within the substrate. Their lower kinetic stability in comparison to E100 might enhance precipitation of the nanoparticles at the end of the absorption process, and thereby limit back migration of nanoparticles to the surface.

TOC

Based on the above reported considerations, E80H20, E95H5 and, as comparison, E100, have been selected to be further studied.

§ 6.5.4 Assessment of nanoparticles deposition

E80H20, E95H5 and, as comparison, E100, have been applied by capillary absorption on Maastricht limestone. The penetration of the nanoparticles immediately after absorption as well as their deposition after drying of the solvent has been studied.

§ 6.5.4.1 Phenolphthalein test

The penetration of the nanoparticles immediately after saturation has been studied by phenolphthalein test. Figure 6.5 shows the cross-section of Maastricht limestone specimens, sprayed with a phenolphthalein solution immediately after saturation, respectively, with E100, E95H5 and E80H20.

It can be observed that nanolime E100 homogenously penetrates within the limestone (Fig. 6.5a), saturating the entire section (40 mm) of the specimen.

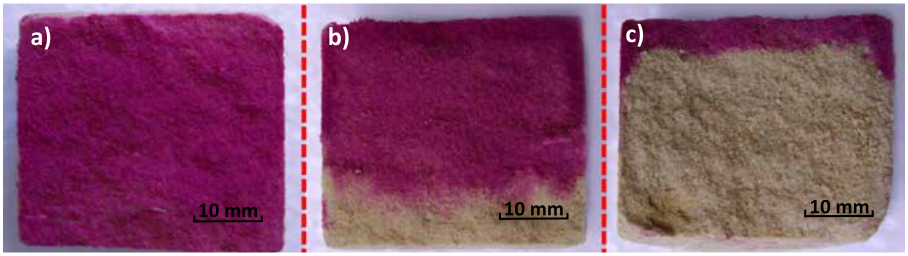

FIGURE 6.5 Pictures of the phenolphthalein test performed on the cross sections of specimens of Maastricht limestone treated by capillary absorption until full saturation with E100 (a), E95H5 (b) and E80H20 (c). The drying surface (which was also the wetting surface) is on the top of the figure.

E95H5 treatment guarantees as well a fast and proper penetration within the limestone (Fig. 6.5b), and no accumulation of nanoparticles at the absorption surface is observed; however, at 28–30 mm in depth, nanoparticles separate from the solvent (no purple color induced by the phenolphthalein is observed after that point), which flows further to saturate the entire section of the specimen. This can be explained by a partial aggregation of the lime nanoparticles within the porous network, during nanolime absorption.

In the case of E80H20, lime nanoparticles penetrate just in the first 5–7 mm in depth in the material (Fig. 6.5c); the low kinetic stability of the nanolime enhances nanoparticles-solvent phase separation, causing deposition near the absorption surface.

§ 6.5.4.2 Optical Microscopy

Maastricht limestone specimens treated with E100, E80H20 and E95H5 were analyzed by optical microscopy. When observing the absorption surfaces, it can be seen that E100 and E95H5 did not leave any white deposit at the surface (Fig 6.6a,b). Conversely, some deposits of lime nanoparticles are observed with E80H20, which formed a whitish patina at the absorption surface (Fig. 6.6c).

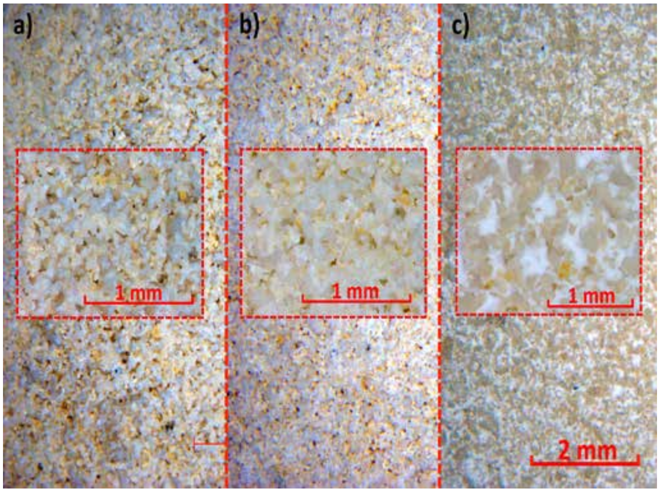

FIGURE 6.6 Microphotographs of the drying surface of Maastricht limestone specimens treated with E100 (a), E95H5 (b) and E80H20 (c), and relative zoom on most significant spots.

When analyzing more in detail the cross-section of the treated limestone specimens, a layer (0.1–0.2 mm thick) highly enriched in lime nanoparticles can be seen at 0.5 mm from the evaporation surface of the specimen treated with nanolime E100 (Fig. 6.7a). Clusters of lime nanoparticles are barely visible in depth in the specimen. As observed in a previous study [Borsoi et al. 2016a], the high kinetic stability and evaporation rate of the ethanol-based nano- lime can, in coarse porous stone, favor the migration of nanoparticles back to the surface during drying, causing an accumulation of nanolime just beneath the evaporation surface.

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Differently, a more homogeneous in-depth distribution of the lime nanoparticles can be observed within the cross-section of Maastricht limestone treated with E95H5. Clusters of lime nanoparticles can be identified up to 18–20 mm from the absorption surface (Fig. 6.7b).

In the case of E80H20, a deposit of lime nanoparticles can be observed at the absorption surface of the treated specimen (Fig. 6.7c). Sporadic and heterogeneously distributed clusters of nanolime are identified up to 6–8 mm in depth in the specimen, confirming the results obtained by phenolphthalein test.

On the basis of the optical microscopy results, it is can be concluded that E95H5 guarantees a deeper in-depth deposition of nanoparticles and it is thus a much better option than E80H20. Because of this reason, further SEM observations were only carried out on treatments with E95H5 and E100.

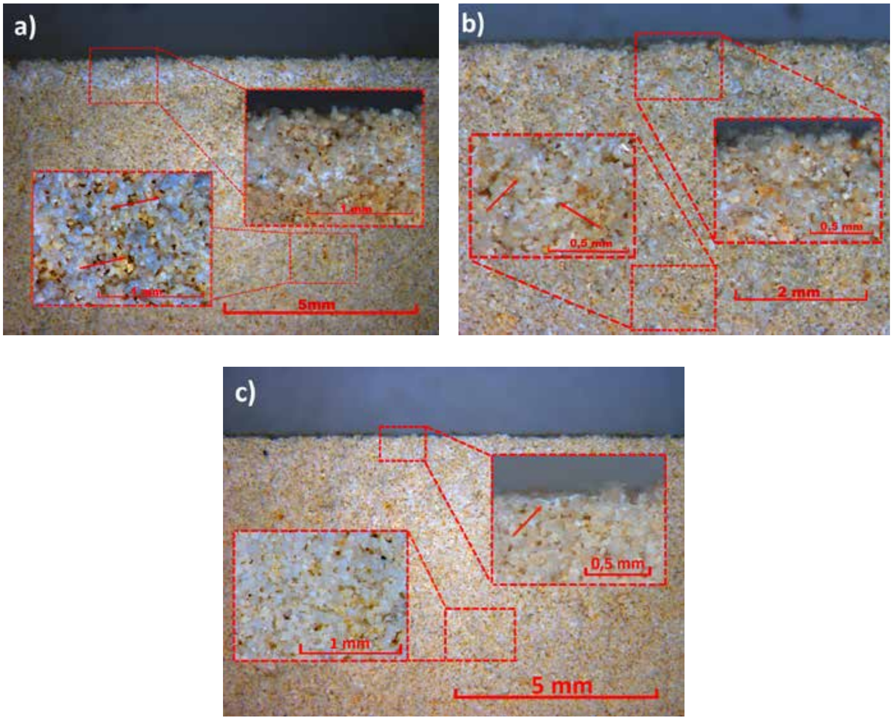

FIGURE 6.7 Microphotographs of the cross-sections of the Maastricht limestone specimens treated with E100 (a), E95H5 (b) and E80H20 (c), and relative zoom on most significant spots. The arrows indicate the deposits of lime nanoparticles.

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§ 6.5.4.3 SEM-EDS

More detailed microstructural observations on the deposition of nanolime within the treated specimens were performed by SEM-EDS.

The SEM analysis of E100 treatment confirms a significant nanolime deposition nearby the drying surface, at 0.5 mm in depth (Fig. 6.8a). In fact, at this location agglomerated primary microclusters (generally with a size of 2–3 μm) formed larger secondary nanolime deposits (up to 50 μm in some cases). In addition, local depositions of lime nanoparticles are identified deeper in the cross-sec- tion: At 20 mm from the drying surface, sporadic clusters of nanolime particles are visible (Fig. 6.8b).

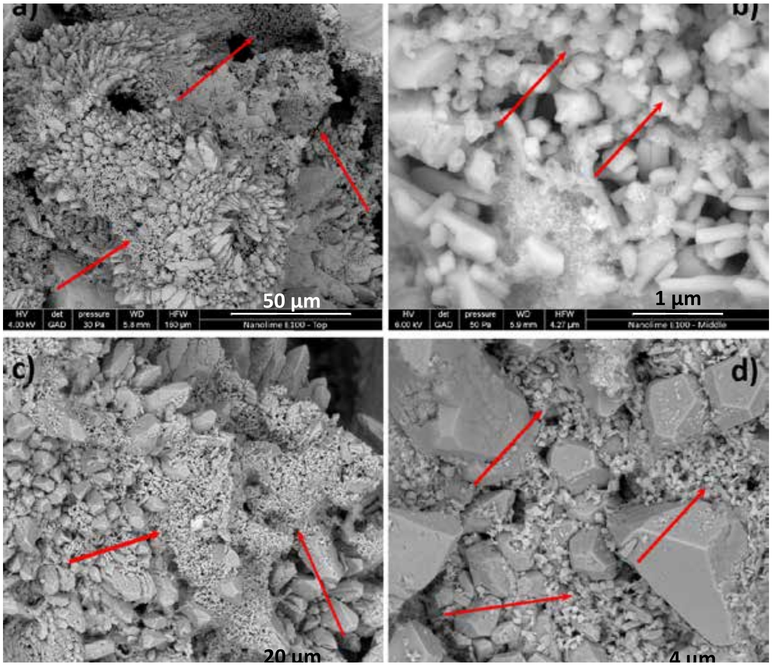

FIGURE 6.8 SEM microphotographs of Maastricht limestone cross sections after the treatment with E100 (a, b) and E95H5 (c, d). The images correspond to different deposition depths from the drying surface: 0.4 mm (a); 18 mm (b); 0.5 mm (c) and 18 mm (d). The arrows indicate the deposits of lime nanoparticles.

The SEM-EDS analysis of the limestone specimen treated with E95H5 shows nanolime deposits up to 25–27 mm in depth (Fig. 6.8d), more homogeneously distributed than in the case of E100; lime nanoparticles have a squared to hexagonal plate-like shape and dimensions ranging between 10 and 300 nm, which mainly agglomerate in larger clusters. Nanolime deposition just beneath the surface (Fig. 6.8c) is much less than in the case of the specimen treated with E100, confirming the optical microscopy observations. Deeper in the specimens (35–40 mm), the presence of nanoparticles is limited, in accordance with the results obtained by phenolphthalein test.

§ 6.6 Discussions and results

Previous research by the authors showed that very stable nanolime dispersions (dispersed in pure ethanol) may lead, in coarse porous substrates, to nanolime deposition near the surface, due to back migration of the nanoparticles during drying [Borsoi et al. 2016a]. Based on these results, a model for the choice of suitable nanolime has been developed, relating the stability of nanolime dispersion to the moisture transport properties of the substrates [Borsoi et al. 2016b]. According to this model, less stable dispersions would be more suitable for coarse substrates (i.e., with fast water absorption and drying), whereas very stable dispersions could be more successfully used on fine porous substrates. The stability of the nanolime dispersion can be modified by an appropriate choice of the solvent.

In this research, this model has been further developed and validated in the case of Maastricht limestone, a coarse porous limestone.

Newly synthesized nanolime particles were dispersed in different solvents: pure ethanol, pure water, and water– ethanol mixtures with different ratios. The aim was to define the optimal solvent mixture, i.e., with a kinetic stability sufficient to guarantee a homogeneous absorption of the nanolime within the substrate but, at the same time, to avoid back migration of the particles to the surface during drying.

The results of the colloidal stability of the nanolimes showed that, as expected, ethanol-based dispersion (E100) have a very high kinetic stability. The addition of water, even in small amount, has been shown to remarkably reduce the stability. Nanolimes with more than 20 % (in volume) of water were considered to be not sufficiently stable for the time needed to perform application. Based on these results, ethanol-based nanolimes with 5 %

(E95H5) and 20 % (E80H20) of water were selected and applied on Maastricht limestone. Nanolime E100 was applied as well for comparison.

Nanolime E100 showed a good penetration but also back migration of nanoparticles during drying, confirming previous results [Borsoi et al. 2016a]. Nanolime E80H20 led to slight surface deposition of nanoparticles during the absorption phase; besides, separation of the nanoparticles from the solvent was observed during absorption. This suggests that this percentage of water is too high (i.e., too low kinetic stability of the nanolime) to guarantee proper absorption, even in a very coarse substrate as the Maastricht limestone.

Conversely, nanolime E95H5 showed a proper penetration during the absorption and, thanks to the lower kinetic stability of the dispersion in comparison to E100, back migration was limited and nanoparticles deposited in depth.

It can be concluded that coarse porous substrates, such as Maastricht limestone, can be optimally consolidated in depth by the use of a nanolime dispersed in ethanol and a limited amount of water (5 %). These results validate the model [Borsoi et al. 2016b] and confirm that knowledge on moisture transport properties of the substrate is required for a successful in-depth consolidation treatment.

Research is ongoing to assess the consolidating effectiveness of the selected nanolime and to translate the results of this laboratory research, carried out by capillary absorption till full saturation of the specimens, to the practice, where other application methodologies (i.e., nebulization or brushing) are used. The final aim is to provide restorers and professionals in the field with guidelines for the choice and application of nanolime on calcareous substrates.

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7 Application protocol for the consolidation of calcareous substrates by the use of nanolimes: from laboratory research to practice

§ 7.1 Introduction to the chapter

In this chapter, the application procedure of nanolime dispersions was studied, this step being a crucial one for a successful consolidation. Based on the results of previous research, nanolimes dispersed in pure ethanol and a mixture of ethanol (95 %) and water (5 %) were applied on two coarse porous substrates, Maastricht limestone and lime-based mortar. Nanolime dispersions were applied by capillary absorption (a method commonly used for laboratory tests) or by nebulization (a method widely used in situ). The aim was to provide an application protocol for restorers and professionals in the field. This chapter is based on the paper published in Restoration of Buildings and Monuments - Materials Science, Conservation of Architectural Heritage, Sustainable Construction (https://doi.org/10.1515/rbm-2016-0008) with some minor changes, to incorporate the suggestions of the PhD committee members.

§ 7.2 Abstract

Calcareous materials such as limestone and lime-based mortars, widely used in the built heritage, are often subjected to degradation processes that can lead to loss of cohesion and material loss. Consolidation of these materials with liquid products via the surface is a common practice; however, the most used consolidation products (e.g. TEOS-based) show a poor physical-chemical compatibility with calcareous substrates.

For application on calcareous materials, the so-called nanolimes, i.e. dispersions of lime nanoparticles in alcohols, are an alternative to TEOS-based products, thanks to their chemical compatibility with lime-based substrates.

Nanolimes can help to recover a superficial loss of cohesion. However, their in-depth consolidation effect is not always satisfactory. Previous work has shown that a better deposition of lime nanoparticles in depth can be achieved in coarse porous materials by adapting the properties of the nanolime dispersion (kinetic stability and evaporation rate) to the moisture transport properties of the substrate, through optimization of the solvent.

In this paper, freshly synthetized nanolimes were dispersed in pure ethanol and/or in binary mixture of ethanol (95%) and water (5%). These nanolimes were applied on Maastricht limestone and on a lime-based mortar by capillary absorption (a method commonly used for laboratory tests) and by nebulization (a method widely used in situ).

The aim of this research is to fill the gap between laboratory tests and on site application, providing an application protocol for restorers and professionals in the field.

The research shows that results obtained by application by capillary absorption do not always correspond to those obtained by nebulization. This fact should be considered when deciding on the use of a consolidation surface treatment in practice.

§ 7.3 Introduction of the paper

Consolidation is a common practice in the conservation of artwork and of growing importance in the conservation of the built heritage. Research has been going on for decades in this field, however, there is still a lack of compatible and effective products, especially when dealing with calcareous materials, such as limestone or lime-based mortars [Delgado Rodrigues 2001; Delgado Rodrigues 2010; Borsoi et al. 2012; Ferreira Pinto & Delgado Rodrigues 2012; Slížková & Frankeová 2012].

The progresses in material science, colloid science and interface science has introduced a new insight in the field of conservation, by delivering nanomaterials with improved properties [Baglioni et al. 2013]. Due to their potentially high performance, several nanomaterials with cleaning, consolidating and/or protective properties have become available for the conservation of movable and immovable artworks [Baglioni et al. 2012]. One of the most studied nanostructured consolidants concerns the group of the so-called nanolimes, that show interesting consolidating properties and full chemical compatibility with calcareous materials [van Hees et al. 2014b].

Nanolimes are colloidal dispersions of calcium hydroxide nanoparticles, with spherical to hexagonal shape and a size ranging from 50 to 600 nm, generally dispersed in ethanol or isopropanol [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Ziegenbalg et al. 2010; Chelazzi et al. 2013]. Thanks to the nano to submicrometric size of the particles and to the alcoholic solvent, nanolimes have a high reactivity and a high lime concentration, which provide a better consolidating effect than that of traditional lime-based consolidants, such as limewater [Doehne & Price 2010; Rodriguez-Navarro et al. 2013; Poggi et al. 2014]. Besides, nanolimes have a better compatibility and durability, when applied on calcareous substrates, than TEOS-based (tetraethyl orthosilicate) products, e.g. ethylsilicate, commonly used for stone consolidation [Hansen et al. 2003; Toniolo et al. 2010; Ferreira Pinto & Delgado Rodrigues 2012b; van Hees et al. 2014b].

Nanolimes have proven to work properly for the pre-consolidation and for the recovery of the superficial cohesion of different substrates such as mural paintings, stone, renders, paper and wood [Giorgi et al. 2000; Ambrosi et al. 2001a; Dei & Salvadori 2006; Campbell et al. 2011; Borsoi et al. 2012; Rodriguez-Navarro et al. 2013; Poggi et al. 2014]. However, when mass consolidation is required, e.g. in the case of decayed plasters, renders or limestone, nanolimes often show a poor effectiveness [Campbell et al. 2011; Costa & Delgado Rodrigues 2012] and sometimes result in the formation of a white haze on the surface [Ghaffari et al. 2011; Ruffolo et al. 2013; Borsoi et al. 2016a].

An important reason for their limited effectiveness is related to the fact that lime nanoparticles may deposit on the surface during absorption or partially migrate back towards the surface during drying, resulting in a poor in-depth consolidating effect [Costa & Delgado Rodrigues 2012; Ruffolo et al. 2013; Borsoi et al. 2016a].

Research by the authors [Borsoi et al. 2016b; Borsoi et al. 2016c] showed that nanolimes can be tailored on the moisture transport properties of the material to be treated by fine-tuning their solvent. According to this approach [Borsoi et al. 2016b], dispersions with lower stability and higher drying rate, as those obtained by the addition of low percentages of water to the ethanol solvent, are more effective for application on substrates with very fast moisture transport properties: in fact, the lower stability of these dispersions can limit back migration of the particles to the drying surface and favors their precipitation in depth, improving the consolidation effect.

Another crucial aspect for the success of consolidation, is the application procedure [Ferreira Pinto & Delgado Rodrigues 2008a; Delgado Rodrigues 2010]; this includes application method, number of applications and time interval between applications. Despite the application procedure can strongly affect the effectiveness of the consolidation action, its influence has been barely tackled by researchers [Delgado Rodrigues 2010]; the difference between application procedure used in laboratory and in practice complicates the direct translation of laboratory results to the field [Ferreira Pinto & Delgado Rodrigues 2008a; Delgado Rodrigues 2010]. In fact, while the application of a consolidant by capillary absorption is widely used as standard laboratory method (due to its reliability and reproducibility) [Ferreira Pinto & Delgado Rodrigues 2008a; Ferreira Pinto & Delgado Rodrigues 2012a; Slížková & Frankeová 2012], *in situ* application usually involves methods such as brushing, pipetting, nebulizating or poulticing [Doehne & Price 2010].

In this research, two nanolimes were synthetized and dispersed in pure ethanol and in a mixture of ethanol (95 % in volume) and water (5% in volume) (section 7.4.2). Pure ethanol was chosen as this is usually the solvent in commercial products, while the ethanol-water mixture was selected, based on previous research [Borsoi et al. 2016b; Borsoi et al. 2016c], in order to have an improved in-depth deposition on coarse porous limestone.

We investigated the effectiveness of these nanolime dispersions on two lime-based substrates (section 7.4.1) by different application procedures: full-and partial saturation by capillarity and partial saturation by nebulization. In the case of the application by nebulization, multiple applications were performed, and the optimal time interval between applications was identified (section 7.4.3).

The comparison of these application methodologies allowed to relate laboratory results to conservation practice, and therefore to provide an improved nanolime application protocol for restorers and professionals in the field (section 7.5.3).

§ 7.4 Materials and methods

§ 7.4.1 Substrates

§ 7.4.1.1 Maastricht limestone and lime-based mortar

The Maastricht limestone is a soft, yellowish limestone (> 95% $CaCO_3$) [Dreesen & Dusar 2004; Nijland et al. 2006], quarried in the Dutch and Belgian provinces of Limburg and used as building material in the same region. Despite its low mechanical strength, Maastricht limestone shows generally a good durability, probably linked to the dissolution and reprecipitation of carbonates within the pore network of the stone, when exposed to atmospheric agents [Dubelaar et al. 2006]. However, Maastricht limestone may in some cases show decay in the form of loss of cohesion at the surface (e.g. powdering, scaling) [van Hees & Nijland 2009].

For the experimental research described in this article, cylindrical specimens (diameter: 4 cm, height: 4 cm) were drilled from sound (freshly quarried) Maastricht limestone blocks.

Lime-based mortar specimens were prepared using commercial CL90 hydrated lime (H100 by Lusical, Portugal) and a siliceous sand. The sand used was a mixture of three different calibrated siliceous fractions, named A12, A20 and A30 (by Areipor, Portugal), in proportion 0.66:1:1 (in volume). The grain size distribution of the sand can be found in [Borsoi et al. 2012]. A binder/aggregate ratio 1:4 in volume was chosen in order to obtain a weak mortar with a high porosity, similar to an old render needing consolidation [Borsoi et al. 2012; Pascoal et al. 2015].

A water:binder ratio of 2:1 (by mass) was adopted for this mortar in order to obtain an optimal workability, in accordance with EN 1015-3 [CEN 1999]. Prismatic mortar specimens (16x4x4cm) were produced and stored under controlled conditions (T=20°C, 65% RH) for over 1 year. Then the prismatic specimens were cut in cubes of 4 cm side, which were used in this work.

§ 7.4.1.2 Characterization of the substrates

The open porosity and the pore size distribution of Maastricht limestone and lime-based mortar were assessed by means of Mercury Intrusion Porosimetry (MIP) on one sample for each substrate type. An Autopore IV9500 (by Micromeritics, USA) was used to obtain porosity data. A contact angle of 141º was assumed between mercury and the material. An equilibration time of 30 s has been used between each pressure increase step and measurement of the intruded volume [Lubelli et al. 2015]. Pores in the range 0.01–400 µm can be measured with this instrument.

The presence of pores larger than 400 µm in the mortar, was assessed by microscopic observations on polished cross sections. Mortar specimens were dried for 12 h at 60° C and then vacuum impregnated with an epoxy resin (resin-hardener ratio 3:1), with the addition of a blue dye (Keystone Oil Blue Dye, by Logitech, UK). The dye increases the contrast between pore voids and aggregate or binder when observing polished sections, thus helping in the identification of the pore sizes and their distribution. Impregnated cross sections were polished with abrasive Al_2O_3 slurries (15 and 9 µm) and with three diamond abrasive dispersions (6, 3 and 1 µm). The polished cross sections were observed with a stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to analyze the specimens.

The capillary absorption of water in the Maastricht limestone and in the lime-based mortar specimens was measured, according to EN 15801 [CEN 2009]. The specimens, sealed with Parafilm M (by Bemis NA, USA) on the lateral sides, were partially immersed in a petri dish, filled with water and with a grid on the bottom. During the absorption process, the specimen weight was measured until saturation was reached.

The drying rate of the specimens, saturated with water, was evaluated by measuring the weight loss over time, in accordance with EN 16322 [CEN 2013].

The absorption and drying tests were carried out in threefold and performed under controlled conditions (50 % RH, T=20° C, air speed < 0,1 m/s).

§ 7.4.2 Nanolime

Nanolime with an equivalent concentration of 25 g/l were synthetized by solvothermal reaction of metallic calcium in water, as described in [Borsoi et al. 2016b; Borsoi et al. 2016c] and dispersed in two different solvents: ethanol (p.a. 99.5% by Sigma-Aldrich) (nanolime dispersion E100) and a mixture of ethanol (95% in volume) and deionized water (5% in volume) (nanolime dispersion E95H5).

These solvents were selected based on the results obtained in previous work [Borsoi et al. 2016a; Borsoi et al. 2016b]. Ethanol is a highly volatile solvent and guarantees a high kinetic stability to the dispersion, whereas water has a higher boiling point and higher surface tension, which results in a low kinetic stability. The addition of a small amount of water has been shown by previous research by the authors to guarantee a moderate kinetic stability, sufficient for the nanolime to be properly absorbed [Borsoi et al. 2016a; Borsoi et al. 2016b; Borsoi et al. 2016c]. Thus, when the necessary absorption depth is reached, the decreased kinetic stability can favour nanolime precipitation in depth and avoid back transport [Borsoi et al. 2016c].

§ 7.4.3 Nanolimes application methodologies

Nanolimes were applied by capillary absorption and nebulization. Capillary absorption was performed following two different protocols, full saturation and partial saturation (here identified as surface impregnation), of the treated specimens up to 20 mm in depth.

The aim was to compare an application protocol widely used for laboratory purposes (capillary absorption till full saturation) with an application method commonly adopted in the practice of conservation (nebulization), which is generally done to obtain a partial saturation of the treated substrate. In order to allow a comparison between these two different methods, an 'in-between' method (surface impregnation by capillarity) was used as well.

Application by capillary absorption until full saturation was carried out by immersing the bottom surface of the specimens in the nanolime dispersions, until the liquid reached the opposite surface of the specimen.

Surface impregnation by capillary absorption was carried out by immersing the upper surface of the specimen in an amount of nanolime dispersion sufficient to saturate the outer 20 mm. The necessary amount was determined by preliminary tests.

Application by nebulization was carried out with a manual spray nozzle on the upper surface of the specimens. The same amount of nanolime used for surface impregnation by capillary absorption was sprayed at each application by nebulization on the specimen, in order to facilitate the comparison between these application methods; up to 5 consecutive applications were performed with this method (see also [van Hees et al. 2017]). An optimal interval (48h) between applications was chosen based on preliminary tests.

All experiments were carried out in threefold under controlled conditions (50% RH, T = 20°C, air speed < 0.1 m/s).

Finally, the amount of nanolime dispersion (kgm^{-2}) in contact or wetted with the product was monitored over time [van Hees et al. 2014b; Peruzzi et al. 2003].

§ 7.4.4 Assessment of the penetration and in-depth deposition of nanolime treatment

The penetration of the lime nanoparticles immediately after absorption in the treated specimens was assessed by phenolphthalein test. The specimens were broken with hammer and chisel in two halves, analysing on one side the wetting front of the dispersion and on the other side the distribution of the lime nanoparticles by phenolphthalein test. This test consists in nebulizing a phenolphthalein solution (1% phenolphthalein in 60% ethanol / 40% water) on the cross section of the specimen and observing the change in colour. Phenolphthalein alcoholic solution is a well-known pH indicator, which remains uncoloured for pH < 8.2, while pH conditions higher than 9.8 lead to a purple colour change. In this case a purple colour of the substrate indicates the presence of nanolime ($pH_{Ca(OH)2} > 11$). By comparing the results of the phenolphthalein test with the macroscopic observations of the wetting front, the possible separation of the nanoparticles from the solvent during absorption can be assessed.

Additionally, in order to assess the deposition of nanolime in the stone after drying, the drying surface and the cross section of the treated specimens were observed with a stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to record and analyze the specimens.

§ 7.5 Results

§ 7.5.1 Substrate characterization

§ 7.5.1.1 Porosity and pore size distribution

Fig. 1.7 shows the total open porosity and the pore size distribution of the two calcareous substrates considered in this research. The Maastricht limestone has a very high porosity (50 vol%) and a unimodal pore size distribution, with macro pores (30 to 50 µm). The lime-based mortar has a total porosity of 28 vol%, with a heterogeneous pore size distribution, including meso (0.2 - 1 µm), macro (20 - 100 µm) and coarse pores (100 - 400 µm). The high total porosity and the presence of a large volume of coarse pores (≈ 20% of the pores >100 µm) indicates that this mortar can simulate an altered and decayed plaster or render [Thomson 2004].

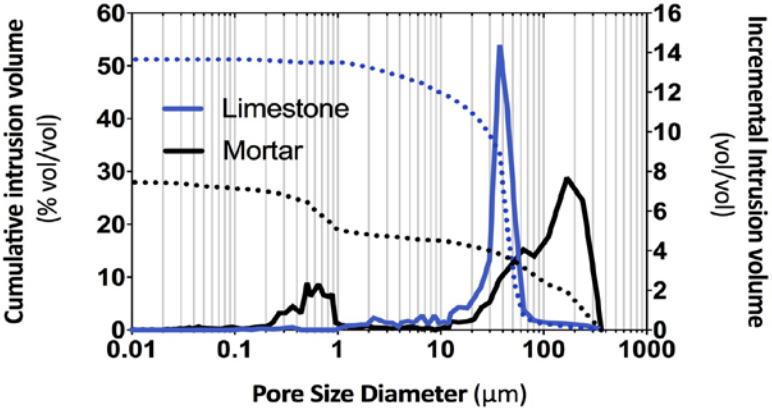

FIGURE 7.1 Pore size distribution (solid) and total porosity (dotted) by MIP of Maastricht limestone (blue) and lime-based mortars (black).

The presence of pores larger than 400 µm (up to 1.5 mm) in the mortar was evaluated by microscopy observations on a cross section (Fig. 7.2). It is generally assumed that pores ranging from 1 to 100 µm act as capillary pores, whereas pores > 100 µm generally contribute to the water permeability through gravity (e.g. percolation) or wind driven water ingress [Hunt & Ewing 2008].

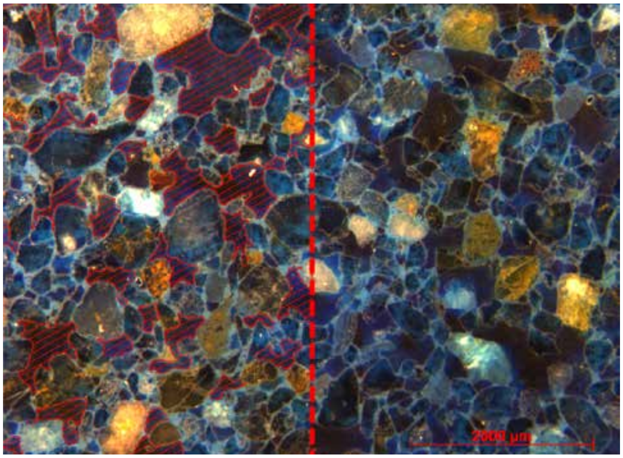

FIGURE 7.2 Polished cross section of the lime-based mortar: the blue colour identifies the resin, and thus the pores/voids in the mortar; pores larger than 400 µm were identified with a red contour in the left part of the image.

§ 7.5.1.2 Water absorption and drying kinetics

Fig. 7.3a reports the water absorption kinetics on Maastricht limestone and on lime-based mortar. The absorption of water within Maastricht limestone is slightly faster than in lime-based mortar, due to the higher porosity and the absence of small pores in this limestone. Furthermore, the total amount of water absorbed by the Maastricht limestone is considerably higher, due to the higher open porosity of the limestone, compared to that of the mortar.

When observing the drying kinetics (Fig. 7.3b), the drying rate of the mortar is slightly slower than that of the limestone, mainly due to the presence of small pores in the mortar. In fact, water completely evaporates in 7-8 days for Maastricht limestone and in 8-9 days for lime-based mortars.

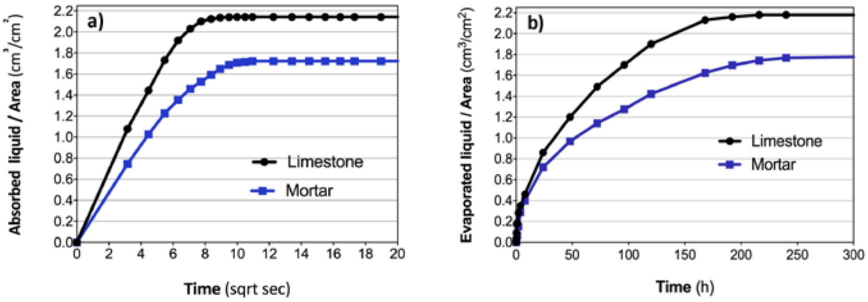

FIGURE 7.3 a) Absorption and (b) drying kinetics of water on specimens of Maastricht limestone (black line) and lime-based mortar (blue line).

§ 7.5.2 Nanolime absorption

Three procedures were used for the application of the nanolimes to the two considered substrates, as described in section 7.4.3. The average amount of nanolime dispersions (E100 and E95H5) applied by the different application procedures and absorbed within specimens of Maastricht limestone and lime-based mortar are presented in Tab. 7.1.

TABLE 7.1 Amount of nanolime dispersion absorbed by capillary absorption (full saturation and surface impregnation) and nebulization (surface impregnation) and standard deviations after a single application.

SUBSTRATE	NANOLIME	AMOUNT OF PRODUCT ABSORBED (kg/m^2) PER APPLICATION PROCEDURE		
		Full saturation by capillary absorption	Surface impregnation by capillary absorption	Surface impregnation by Nebulization
Maastricht limestone	E100	12.59 ± 0.12	6.04 ± 0.22	5,44 ± 0.53
	E95H5	12.64 ± 0.21	6.21 ± 0.24	5.49 ± 0.19
Lime-based mortar	E100	10.22 ± 0.23	6.01 ± 0.29	5.32 ± 0.44
	E95H5	10.37 ± 0.54	6.07 ± 0.21	5.43 ± 0.49

When comparing the different substrates, it can be seen that the higher total porosity of the limestone allows a higher amount of absorbed nanolime, when compared to the lime-based mortar. In addition, nanolime E95H5 leads to a slightly higher amount of absorbed dispersion (in weight), due to its higher density, when compared to nanolime E100.

Surface impregnation by capillary absorption resulted in the absorption of slightly higher amounts of product, when compared to impregnation by nebulization, confirming the results reported in [Ferreira Pinto & Delgado Rodrigues 2008a]. In the case of the limestone, capillary absorption until full saturation led, as expected, to almost twice the amount of the nanolime absorbed by surface impregnation. This trend was not observed in lime-based mortar specimens, as these specimens could not be fully saturated by capillarity (see as well section 7.5.3.1).

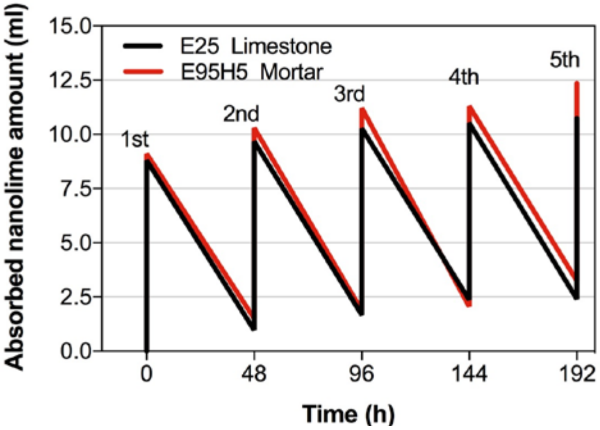

FIGURE 7.4 Graph showing consecutive applications by nebulization (with 48 h intervals) of E100 on Maastricht limestone and of E95H5 on lime-based mortars, comparing the amount of nanolime absorbed and retained in the substrates.

The application by nebulization was performed 5 times. After several trials, the optimal interval between two subsequent applications was defined at 48 h, as shown in fig. 7.4. In fact, an almost complete evaporation of the alcoholic solvent (≈ 90%, in volume) is achieved within this interval. This can avoid that the excess of solvent from previous applications favours the migration of the nanoparticles back towards the surface during the drying process [Borsoi et al. 2016a], decreasing the in-depth deposition of the nanoparticles within the pores network and thus the consolidation action.

§ 7.5.3 Assessment of nanolime deposition

§ 7.5.3.1 Full saturation by capillary absorption

Fig. 7.5 shows the cross section of limestone (fig. 7.5a,b) and lime-based mortar (fig. 5.7c,d) specimens, sprayed with a phenolphthalein solution after saturation respectively with E100 and E95H5. It can be observed that nanolime E100 penetrates easily within the limestone (fig. 7.5a), saturating the entire section (40 mm) of the specimen. E95H5 treatment guarantees as well a good penetration within the limestone (fig. 7.5b); however, at 28-30 mm in depth, nanoparticles separate from the solvent (no purple color induced by the phenolphthalein, indicating the presence of $Ca(OH)_2$ nanoparticles is observed beyond this depth), which flows further to saturate the entire section of the specimen.

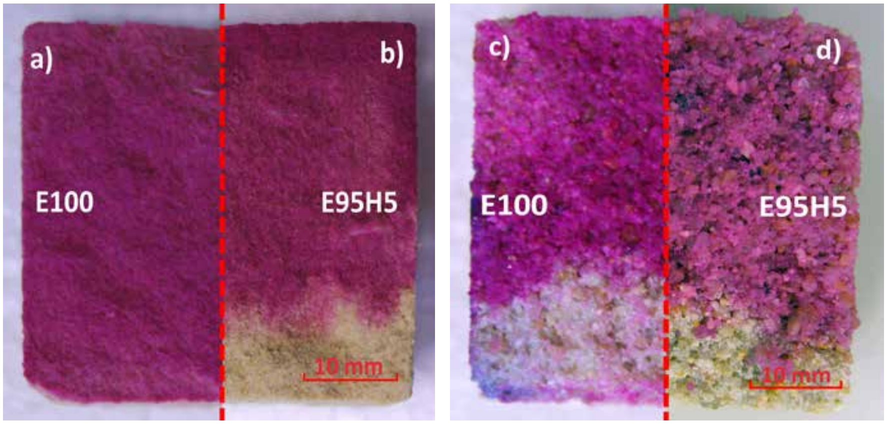

FIGURE 7.5 Pictures of the phenolphthalein test performed on the cross sections of Maastricht limestone specimens treated by capillary absorption until full saturation with E100 (a) and E95H5 (b) and of lime-based mortars treated with E100 (c) and E95H5 (d). The absorption surface is at the top of the figures.

In case of the lime-based mortar, both nanolimes E100 and E95H5 cannot saturate the entire section of the specimen (fig. 7.5c,d). In addition, nanoparticles separate from the solvent at 25-30 mm in depth, while the solvent flows slightly further. In this case, the slower absorption of the mortar (due possibly to the pores > 100 µm, which do not act as capillary pores) when compared to the limestone can destabilize the dispersion, enhancing nanoparticle deposition.

No accumulation of nanoparticles at the absorption surface was observed for either of the substrates. With this application methodology, both nanolime dispersions can properly penetrate both substrates.

§ 7.5.3.2 Surface impregnation by capillarity

Nanolime deposition after absorption was assessed also for specimens treated by surface impregnation (up to 20 mm in depth) (fig. 7.6).

In the case of Maastricht limestone, it was observed that, as expected, both nanolimes can penetrate up to 20 mm within the limestone pore network (Fig. 7.6a,b). When comparing the wetting front and the nanolime deposition (by phenolphthalein test), it can be observed that the solvent moved slightly further if compared to the lime nanoparticles. Neither nanolimes showed any accumulation at the absorption surface.

In the case of the lime-based mortar, both nanolimes penetrated up to 20 mm inside the specimen (Fig. 7.6c,d). The in-depth distribution of the nanoparticles is slightly more heterogeneous if compared to that within the treated limestone specimens, mainly due to the presence of bigger pores in the mortar specimens. By comparing the wetting front and phenolphthalein test of both E100 and E95H5, the solvent penetrates further in depth in the specimen, similarly to what was observed on the lime-based mortar treated by full saturation (section 7.5.3.1). Also in this case no accumulation of lime nanoparticles was observed at the absorption surface.

§ 7.5.3.3 Surface impregnation by nebulization

When analysing the Maastricht limestone specimens, treated with 5 consecutive applications by nebulization with E100, it can be seen that E100 properly penetrated up to 20 mm after five applications, with no nanolime accumulation at the absorption surface (fig. 7.7a). E95H5 treatment worked properly during the first application; however, the penetration of following treatments was hindered by the accumulation of the nanolime nearby or at the absorption surface (Fig. 7.7b). This deposition was due to the lower kinetic stability of nanolime E95H5, when compared to E100 [Borsoi et al. 2016c].

When considering the lime-based mortar, both E100 and E95H5 penetrated into the substrate for each of the five consecutive applications (Figs. 7.7c,d). However, the dispersions tend to percolate deeper than 20 mm, due to the very coarse pores present in the mortar.

After drying of the specimens, the cross sections of both Maastricht limestone and mortar were observed by optical microscopy, in order to detect nanoparticles deposition. The stereozoom microscope images of the Maastricht limestone specimens show that, after 5 treatments with nanolime E100, lime nanoparticles are well distributed within the treated 20 mm; only few heterogeneously distributed clusters of lime nanoparticles were detected (Fig. 7.8a), mostly in the first 5-8 mm from the surface; besides, a layer (0.1-0.2 mm thick) with a slightly higher concentration of lime nanoparticles is visible in proximity of the wetting front (Fig. 7.8a). This thin layer can be attributed to a deposition of the nanoparticles, which separate from the solvent in proximity of the wetting front, as observed in section 7.5.3.2.

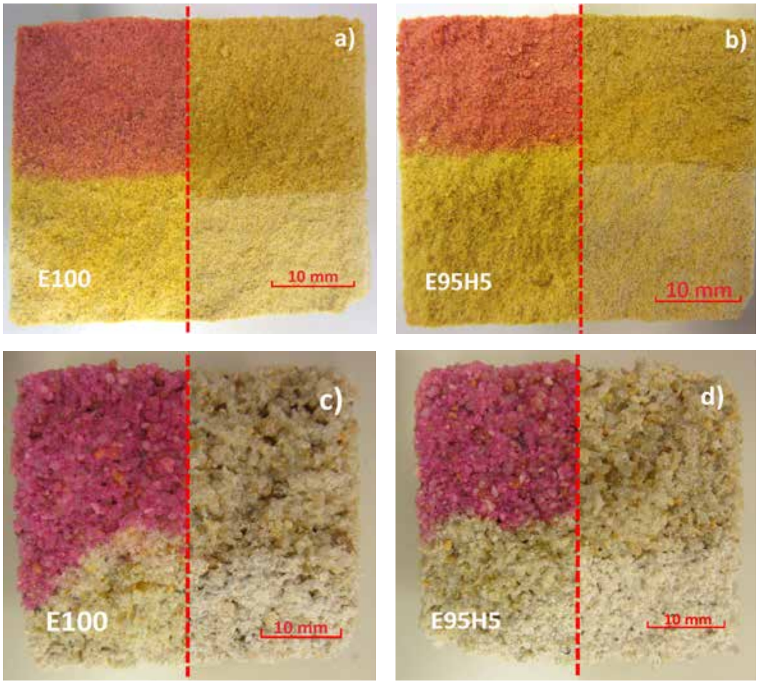

FIGURE 7.6 Pictures of the cross sections of Maastricht limestone specimens treated by surface impregnation by capillarity with (a) E100 and(b) E95H5 and of the lime-based mortar treated with (c) E100 and (d) E95H5. The absorption surface is on the top of the specimens. One half of each specimen has been sprayed with phenolphthalein (purple colour).

The cross section of Maastricht limestone after 5 treatments with nanolime E95H5, shows a remarkable accumulation of lime nanoparticles at the absorption surface (Fig. 7.8b); also in this case, the accumulation can be explained by the lower kinetic stability of nanolime E95H5, when compared to E100. Besides, some clusters of nanoparticles can be randomly observed up to 10-12 mm in depth in the section (Fig. 7.8b).

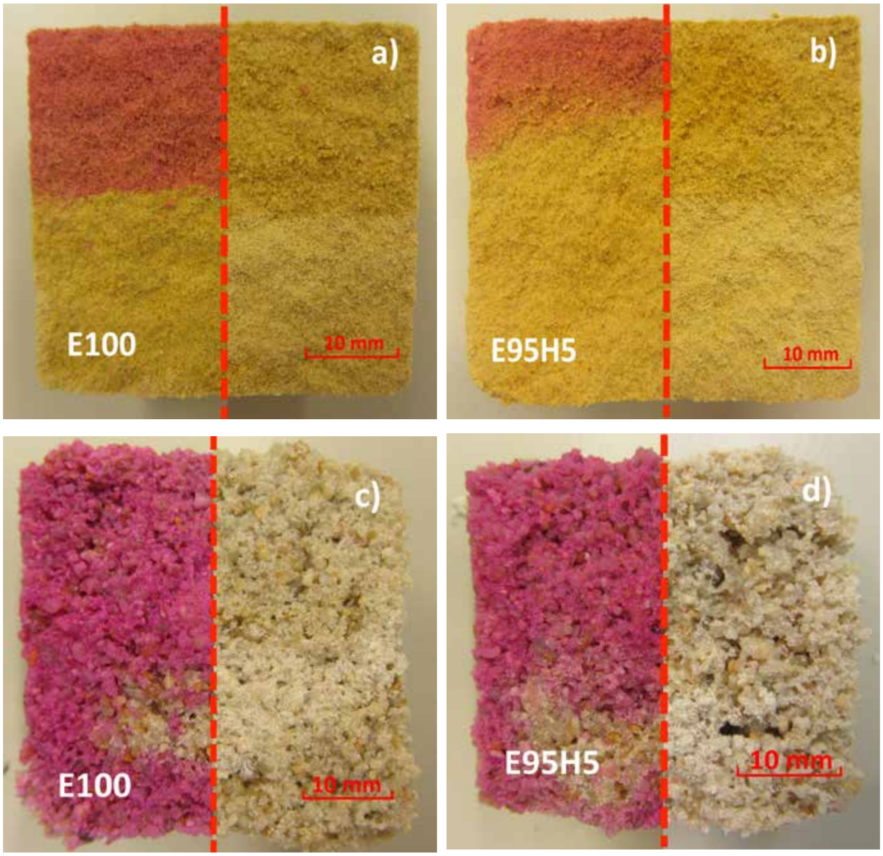

FIGURE 7.7 Pictures of the cross section of Maastricht limestone specimens after 5 treatments by nebulization with E100 (a) and E95H5 (b), and of the lime-based mortars treated with E100 (c) and E95H5 (d). The absorption surface is on the top of the figures. One half of each specimen is treated with phenolphthalein (purple colour).

TOC

Micropictures of the cross section of lime-based mortars treated 5 times with E100 (Fig. 7.9b) and with E95H5 (Fig. 7.9c) showed deposition of nanolime in the pores. In fact, whereas untreated specimens showed a heterogeneous distribution of the binder with wide pores and microcracks (Fig. 7.9a), specimens treated with E100 and E95H5 had a slightly more compacted matrix, with partial pore filling and a moderate binder increase due to the deposition of the lime nanoparticles. When comparing the two nanolime treatments, a more homogeneous consolidation effect was observed in the case of E95H5, especially in the first 10 mm in depth in the cross section. The deposition of the nanoparticles in depth in the case of E95H5 can be explained by the presence of very coarse pores in the mortar, which allow a proper penetration of this nanolime. At the same time, the lower kinetic stability of E95H5, when compared to nanolime E100, avoids back migration of the nanoparticles towards the absorption surface [Borsoi et al. 2016a].

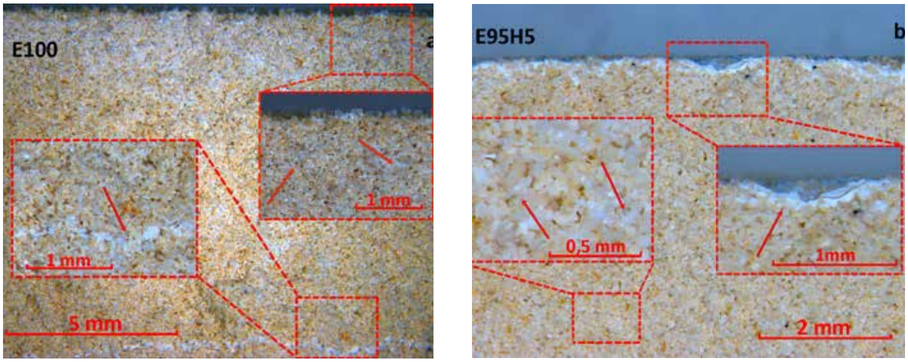

FIGURE 7.8 Micropictures of the cross sections of Maastricht limestone specimens (nebulization treatment): (a) treated with E100, with details on clusters of lime nanoparticles at 5–8 mm in depth and a thin layer of nanolime at 20 mm in depth (arrows); (b) treated with E95H5, with details of the superficial accumulation of nananolime and of clusters of nanoparticles at 8 mm in depth (arrows).

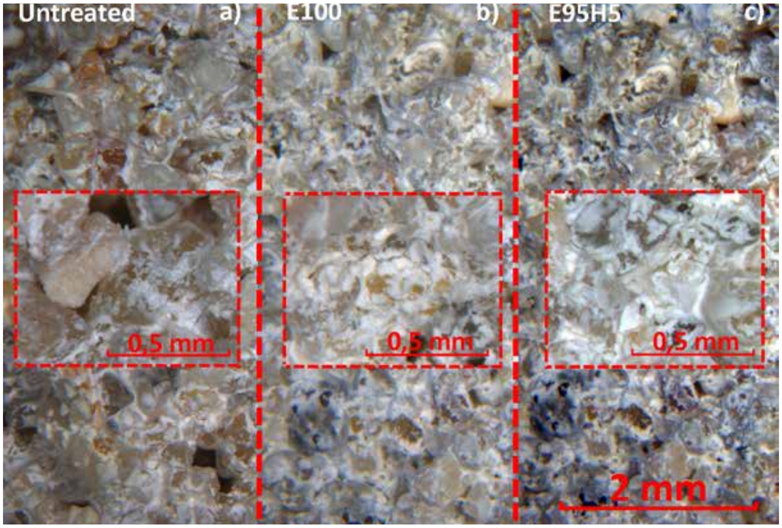

FIGURE 7.9 Micropictures of the cross section of lime-based mortars and details on the most significant spots: untreated (a), and after 5 applications by nebulization of E100 (b) and E95H5 (c).

§ 7.6 Discussion and conclusions

In this paper, freshly synthetized nanolimes were dispersed in pure ethanol (E100) or in ethanol-based mixture with 5% of water (E95H5) and applied to two calcareous substrates, coarse porous Maastricht limestone and lime-based mortar.

Different application methodologies were used: full saturation and surface impregnation by capillarity, both common and reliable laboratory methods, and surface impregnation by nebulization, a method mainly used on site in conservation practice. The comparison of these application methodologies allows to provide an application protocol for restorers and professionals in the field.

The results of the tests, resumed in tab. 7.2, show that an effective in-depth treatment of Maastricht limestone can be obtained both with E100 or E95H5 if a single application by capillarity until full impregnation is performed; however, E100 treatments may result on this substrate in partial nanolime backmigration during drying, as was shown in chapter 4; therefore, E95H5 is more recommended with this application methodology on this substrate since it can guarantee a more homogeneous nanolime in-depth deposition, due to the lower stability and drying rate of E95H5 dispersion, when compared to E100.

E100 treatment on the other hand, is recommended if a surface impregnation by nebulization is adopted (up to 5 applications). In fact, due the lower kinetic stability of the E95H5 nanolime, nanoparticles partially accumulate at or near the absorption. Thus, when considering multiple applications by nebulization, E100 instead of E95H5 is recommended for an optimal treatment of Maastricht limestone.

When considering lime-based mortars, their coarse pores and insufficient capillary pressure (in large pores) impede a full saturation by capillarity with either type of nanolime. Surface impregnation by nebulization (up to 5 applications) appears a more suitable application methodology for this substrate: in fact the lower stability of E95H5 nanolime in comparison to E100, prevents back migration of nanoparticles towards the drying surface and leads to their precipitation in depth (Tab. 7.2).

These results show that fine-tuning of the solvent of the nanolime, based on the properties of the substrate to be treated, can improve the in-depth deposition of lime nanoparticles. From the comparison of application methods, it becomes clear that the results from laboratory application methods cannot always be directly translated to application methods used in practice. The consolidation treatment should be therefore fine-tuned based on the properties of the material to be treated and on the selected *in situ* application methodology: based on these two parameters, an appropriate solvent or solvent mixture can be selected.

TABLE 7.2 Correlation between application methodology, type of nanolime and substrate to be treated. ✓= suitable treatment (deposition in depth), X = not suitable treatment (no deposition in depth due to nanoparticle back migration), // = not suitable treatment (no deposition in depth due to insufficient penetration of the nanoparticles)

APPLICATION PROCEDURE		MAASTRICHT LIMESTONE		LIME-BASED MORTAR	
Application methodology	Number of applications	E100	E95H5	E100	E95H5
Full saturation by Capillarity	1	X	✓	//	//
Surface impregnation by Capillarity (20 mm in depth)	1	✓	✓	✓	✓
Surface impregnation by Nebulization (20 mm in depth)	1	✓	✓	X	✓
Surface impregnation by Nebulization (20 mm in depth)	5	✓	//	X	✓

The validity of the above mentioned approach will be assessed in the next chapter by evaluating the consolidation effectiveness (expressed as strengthening of the treated layer) and compatibility (assessed as effect of the consolidation on the moisture transport properties of the substrate) of these nanolimes, applied with an improved application protocol.

TOC

8 Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties

§ 8.1 Introduction to the chapter

This chapter focuses on the evaluation of the effectiveness and compatibility of nanolimes with improved properties, applied following an optimized protocol on fresh and weathered Maastricht limestone and a lime-based mortar. This chapter is based on the paper published in Construction and Building Materials (doi:10.1016/j.conbuildmat.2017.03.097) with some minor changes, in order to incorporate the suggestions of the PhD committee members.

§ 8.2 Abstract

Surface consolidation is a common practice in the conservation of the built heritage. However, the effectiveness of consolidation of calcareous materials is often doubtful, due to the lack of effective and compatible consolidation products. Dispersions of calcium hydroxide nanoparticles in alcohol, the so-called nanolimes, can recover the superficial consolidation of calcareous substrates. Nevertheless, they are often not able to guarantee an in-depth consolidation.

Previous research by the authors has demonstrated that the effectiveness of nanolime can be improved by fine-tuning the properties and the application protocol of the dispersions, based on the moisture transport properties of the material to be treated.

In this paper, we verify the consolidation effectiveness and physical compatibility of the developed nanolimes, when applied on coarse porous calcareous materials like Maastricht limestone and lime-based mortars. The results show that a suitable mass

consolidation can be achieved with nanolimes, while maintaining a good compatibility with the substrate material.

§ 8.3 Introduction of the paper

A significant part of the built heritage is constituted by calcareous and lime-based materials, which have demonstrated their durability over the centuries. These materials, however, may be subjected to degradation phenomena (e.g. salt crystallization, frost action, biological growth) that can lead to surface decay [Borsoi et al. 2016a]. Powdering, sanding and chalking are among the most common decay patterns of calcareous materials [van Hees et al. 2014b; van Hees et al. 2017]. This implies the loss of cohesion and thus of mechanical strength [4]. The mechanical properties of deteriorated materials can be recovered through the application of a consolidation treatment [Toniolo et al. 2010]. This intervention is meant to recover the cohesion of the grain structure and so the adhesive forces across the mineral surfaces by introducing a new binding agent and forming organic or inorganic bridges [Toniolo et al. 2010; van Hees et al. 2017].

A consolidation treatment should fulfil three main requirements: effectiveness (i.e. improvement of the mechanical strength), compatibility (with the treated substrate) and durability (resistance to different damage mechanisms) [Hansen et al. 2003; Toniolo et al. 2010]. A treatment can be considered compatible if it does not lead to technical (material) or aesthetic damage to the historical materials and is at the same time as durable as possible [van Hees et al. 2014b]. More specifically, the consolidant product should have a short- and long-term stability and decay patterns due to differential aging between the consolidated and unconsolidated areas of the substrate should be avoided.

Organic consolidant products (e.g. acrylics and epoxy resins) are easy to apply, flexible, and have good adhesion to the substrate, but they often lack physical-chemical compatibility with the substrate [Borsoi et al. 2012]. TEOS-based (tetraethyl orthosilicate) and silica-precursor consolidant products (e.g. ethyl silicate), widely used for the consolidation of stone and mortars, can penetrate deeply into porous materials, but have low chemical compatibility with calcareous substrates, showing in some cases also low effectiveness and durability [Hansen et al. 2003; Toniolo et al. 2010; Ferreira Pinto & Delgado Rodrigues 2012b; van Hees et al. 2014b]. In fact, they form disordered lattices of tetrahedrally coordinated silica, with poor chemical bonding to calcitic substrates and tendency to shrink and crack during drying [Wheeler 2005].

Inorganic consolidants (e.g. lime-based or barium-based treatments) are a suitable alternative to organic compounds, thanks to their compatibility with calcareous substrates and good durability [Hansen et al. 2003; Doehne & Price 2010; Delgado Rodrigues & Ferreira Pinto & Delgado Rodrigues 2016a]. Limewater is the most traditional consolidant product, with full chemical compatibility with lime-based substrates [Drdácký & Slížková 2008]; however, limewater has low effectiveness and, due to the low solubility of $Ca(OH)_2$ in water [Hansen et al. 2003; Doehne & Price 2010], a large number of applications is necessary. Additionally, limewater has often low penetration and the lime deposited within the treated surface shows sometimes low or incomplete carbonation.

In the last two decades, the progresses in colloid science have introduced new nanostructured materials with improved properties. Among them, the so-called nanolimes, i.e. dispersions of lime nanoparticles in alcohols, have acquired an increasing interest due to their consolidating properties and physical-chemical compatibility with calcareous materials [Giorgi et al. 2000]. The consolidation effectiveness and material strengthening is obtained thanks to the penetration of the calcium hydroxide nanoparticles into the treated material and their subsequent carbonation [Drdácký & Slížková 2008].

Nanolime dispersions are opal fluids containing stable calcium hydroxide nanoparticles, with spherical to hexagonal shape and a size ranging from 50 to 600 nm, dispersed in an alcoholic medium [Giorgi et al. 2000; Dei & Salvadori 2006; Ziegenbalg et al. 2010; Chelazzi et al. 2013]. The high active surface of the nanoparticles ensures a high reactivity, and the alcoholic solvent a high stability and lime concentration, thus providing a proper consolidating action [Rodriguez-Navarro et al. 2013].

Nanolimes have proven to recover the superficial cohesion of many different materials [Giorgi et al. 2000; Dei & Salvadori 2006; Campbell et al. 2011; Rodriguez-Navarro et al. 2013], but they often show a poor effectiveness when mass consolidation is required, like for example in the case of decayed plasters, renders or lithotypes [Campbell et al. 2011; Costa & Delgado Rodrigues 2012; Borsoi et al. 2016a]. In fact, lime nanoparticles may sometimes deposit or partially migrate back towards the surface during drying, resulting in a poor consolidating effect in depth [Borsoi et al. 2016a].

Previous research by the authors [Borsoi et al. 2016b; Borsoi et al. 2016c] suggests that the use of binary solvent mixtures (e.g. ethanol and water) can enhance a more homogeneous nanoparticles in-depth deposition in highly and coarse porous calcareous substrates. Nanolimes can thus be tailored for a specific substrate by fine-tuning their solvent. According to this approach, dispersions with lower stability and higher drying rate should be preferred for application on substrates with very fast moisture transport properties (and thus with higher total porosity and coarse pore size distribution), in order to improve in-depth deposition. The application procedure is another crucial factor that has been previously studied [Borsoi et al. 2017a] and that should be taken in account for an optimal result.

In this paper, we verified the effectiveness and compatibility of freshly synthetized nanolimes (section 8.4.2) when applied on highly porous calcareous substrates: Maastricht limestone (sound and weathered) and a lime-based mortar (section 8.4.1 and 8.5.1). Based on previous research [Borsoi et al. 2016b; Borsoi et al. 2016c; Borsoi et al. 2017a], pure ethanol was selected as solvent for the nanolime to be applied on specimens of sound and weathered Maastricht limestone, and a binary mixture of solvents (95% ethanol-5% water) was used in the case of application on lime-based mortars (section 8.6.1). Both nanolime dispersions were applied by nebulization, a methodology widely used in practice (section 8.5.2).

The mechanical effectiveness of the consolidation action in depth was assessed by measuring the hardness of the substrate, before and after consolidation, by means of Drilling Resistance Measurement System (DRMS) (section 8.5.4 and 8.6.3). The compatibility of the treatment was evaluated by measuring the effect of the consolidant on the moisture transport properties (water absorption and drying kinetics, section 8.5.5 and 8.6.4), on the total porosity by immersion (or open porosity, section 8.5.3 and 8.6.2) and on the aesthetic properties of the substrates (macro-evaluation by NCS scale, section 8.5.6 and 8.6.5).

§ 8.4 Materials

§ 8.4.1 Substrates

Nanolime consolidants have been tested on both sound and weathered Maastricht limestone and on lime based mortar.

§ 8.4.1.1 Maastricht limestone

Maastricht limestone is a building material quarried and mainly used in the Belgian and Dutch provinces of Limburg. It is a soft, highly pure (> 95% CaCO3) limestone, with high-porosity (ca. 50%) and a unimodal pore size distribution (30–50 µm) [Nijland et al. 2006; Lubelli et al. 2015; Borsoi et al. 2017a]. Despite its good durability, it may in some cases show decay in the form of loss of cohesion at the surface (e.g. powdering) [van Hees & Nijland 2009]. The Maastricht limestone used in this research comes from the quarry of Sibbe, in the Netherlands.

The effectiveness of the nanolimes was verified also on weathered Maastricht limestone, from the medieval Castle of Keverberg, situated in the village of Kessel (North Limburg, Netherlands). These blocks, which show a severe weathering of the surface (i.e. powdering), were recently removed from the external façade of the castle during a restoration campaign. The porosity of this weathered limestone was investigated as reported in section 8.5.3.

§ 8.4.1.2 Lime-based mortar

Lime-based mortar specimens were prepared using a commercial CL90 hydrated lime (H100 by Lusical, Portugal) and a siliceous sand. The sand used was a mixture of three different, calibrated sands (by Areipor, Portugal), in proportion 0.66:1:1 (in volume), as presented in [Borsoi et al. 2012]. A binder/aggregate ratio 1:4 in volume was chosen in order to obtain a weak mortar with a high porosity, similar to an old render needing consolidation [Borsoi et al. 2012; Pascoal et al. 2015]. A water:binder ratio of 2:1 (in mass) was adopted for this mortar in order to obtain an optimal workability, in accordance with EN 1015-3 [CEN 1999]. The lime-based mortar has a high porosity (29%), with a heterogeneous pore size distribution, including meso (0.2 - 1 µm), macro (20 - 100 µm) and coarse pores (100 - 400 µm). The high total porosity and the presence of a large volume of coarse pores (≈ 20% of the pores >100 µm) indicates that this mortar can simulate an altered and decayed plaster or render [Borsoi et al. 2017a].

§ 8.4.2 Synthesis and solvent selection of nanolime

Lime nanoparticles with an equivalent concentration of 25 g/l were synthetized, as described in [Borsoi et al. 2016b; Borsoi et al. 20176c]. Ethanol (p.a. 99.5% by Sigma-Aldrich) and distilled water (conductivity < 2 µs/cm) were selected as solvents, based on the results obtained in previous works [Borsoi et al. 2016a; Borsoi et al. 2017a]. Ethanol is a highly volatile solvent and can guarantee a high kinetic stability to the dispersion, whereas water has a higher boiling point and higher surface tension, which results in a low kinetic stability. Based on results obtained in previous research [Borsoi et al. 2016b; Borsoi et al. 2016c; Borsoi et al. 2017a], two nanolime consolidants were selected: a nanolime dispersed in pure ethanol (identified as E100) for the treatment of the sound and weathered limestone, and a nanolime dispersed in an ethanol (95%) – water (5%) mixture, identified as E95H5, for application on lime-based mortars specimens. In the latter case, the addition of small amount of water is known to guarantee a moderate kinetic stability, sufficient for the nanolime to be properly absorbed. Thus, when the necessary absorption depth is reached, the decreased kinetic stability can favour nanolime precipitation in depth and avoid back transport to the drying surface [Borsoi et al. 2017c].

§ 8.5 Methods

§ 8.5.1 Specimen preparation

Cylindrical specimens (diameter: 4 cm, height: 4 cm) and prismatic blocks (15 cm side, 4 cm height) were drilled or cut from sound Maastricht limestone blocks blocks (with orientation perpendicular to limestone bedding). Cubic specimens (diameter: 4 cm, height: 4 cm) and prismatic blocks (15 cm side, 4 cm height) were cut from bigger blocks of weathered Maastricht limestone. Both the sound and weathered limestone blocks were covered on the lateral sides with an epoxy resin (Wapex 105 by Sikkens, The Netherlands), in order to avoid any percolation of the dispersion or evaporation of the solvent from the lateral sides.

Prismatic mortar specimens (16x4x4cm) of lime-based mortars were produced and cut in cubes of 4 cm side. In addition, a single mortar layer of 1.5 cm thickness was applied on fired-clay bricks (28x19x4 cm). All specimens were stored under controlled conditions (T = 20° C, 65% RH) for more than 1 year.

The type of specimens and number of replicas used in the different tests (described in the next sections) is resumed in Tab. 8.1.

TABLE 8.1 Overview on the tests performed on different specimen types and number of replicates.

TEST PROCEDURE	MATERIAL, NUMBER AND SIZE OF SPECIMEN	
	Sound and Weathered Maastricht limestone	Lime-based mortar
Open porosity	3 (samples with size 2 x 1cm)	3 (samples with size 2 x 1 cm)
DRMS	10 measurements on 1 block (size 15 x 15 x 4 cm)	10 measurements on 1 mortar applied on brick (size 29 x 17 x 2cm)
Absorption and drying kinetics	3 (core specimens size 4 x 4 cm)	3 (prismatic specimens size 4 x 4 cm)
NCS Scale	10 measurements on 1 block (size 15 x 15 x 4 cm)	10 measurements on 1 mortar applied on brick with size 29 x 17 x 2 cm
Optical microscopy	10 observations on 1 block (size 15 x 15 x 4 cm)	10 observations on 1 mortar applied on brick with size 29 x 17 x 2 cm

§ 8.5.2 Application of nanolime

Nanolimes were applied by nebulization, an application method commonly adopted in the practice of conservation [Doehne & Price 2010]. The application protocol was optimized in order to reach a good penetration and deposition in depth, as described in [Borsoi et al. 2017a].

Application by nebulization was carried out with a trigger spray nozzle, calibrating the nanolime necessary depending on the substrate. The amount of nanolime used for a single nebulization application was 0.787 ± 0.052 l/m^2 for sound and weathered limestone and 0.779 ± 0.022 l/m^2 for mortar respectively. The nebulization was repeated up to 10 consecutive applications, in order to improve the consolidation effect. The interval between consecutive applications was set at 48h, as within this interval an almost complete evaporation of the alcoholic solvent is achieved [Borsoi et al. 2016a; Borsoi et al. 2017a]. This timespan can guarantee a deposition of the nanoparticles within the porous network and so avoid that the excess of solvent between consecutive applications would influence the deposition of the nanoparticles.

The applications were performed under controlled conditions (50% RH, T = 20°C, air speed < 0.1 m/s). The treated specimens were then stored at 65% RH, T = 20°C, air speed < 0.1 m/s for over 3 months, in order to enhance the carbonation of the nanoparticles. In fact, the carbonation of the $Ca(OH)_2$ nanoparticles and thus the strengthening effect on the treated substrates is speeded up at RH > 50% [Daniele et al. 2008]; higher RH conditions give rise also to the formation of $CaCO_3$ polymorphs (e.g. vaterite, aragonite, calcite and/or amorphous calcium carbonate - ACC) and/or monohydrocalcite (MHC) with higher crystallinity and particle size [Daniele et al. 2008; López-Arce et al. 2011; López-Arce et al. 2013], when compared to the polymorphs obtained at lower RH (<50%).

§ 8.5.3 Measurement of the pore filling

The degree of pore filling due to consolidation influences the moisture transport behaviour of the treated material and it may thus negatively affect damage processes like salt crystallization and freeze-thaw.

A first, indicative degree of pore filling was calculated based on the following assumptions:

- at the used T and RH of curing of the treated specimens (20° C/ 65% RH), stored for over 3 months, the formation of mainly calcite is expected, as well as other anhydrous (aragonite, vaterite or amorphous calcium carbonate - ACC) and hydrated (monohydrocalcite - MHC) Ca-carbonates [López-Arce et al. 2011; López-Arce et al.2013; Saharay et al. 2013]. However, ACC is an instable and transition phase [Saharay et al. 2013] and it will be converted into anhydrous polymorphs.
- the density of calcite (2,711g/cm^3) and that of vaterite (2,645 g/cm^3) are comparable, whereas aragonite (2,944 g/cm^3) and MHC (2,241 g/cm^3) have different values. Thus, the degree of pore filling in the treated substrate was obtained by considering the Ca-carbonates with the lower density (MHC) and that with the higher density (aragonite). This range of values can be representative of all the possible Ca-carbonate formations.
- All the nanolime particles deposit in the outer 20 mm of the specimen.

The calculated values were then compared to the measured values in order to assess the degree of pore filling due to consolidation. Water absorption measurements under vacuum [RILEM 1980] were thus carried out on the substrates before and after consolidation in order to determine the open porosity.

Samples were dried in an oven at 60 ± 5 °C for 24h, till constant mass. After drying to constant mass (M1), the samples were put within an evacuation vessel, applying a pressure of 400 mbar for 24h, in order to eliminate the air contained in the pores of the samples. Distilled water (at T=20ºC) was then slowly introduced into the vessel, maintaining afterwards the vacuum for additional 24h. The samples were then stabilized and maintained at atmospheric pressure for additional 24h. Finally, the samples were weighed immersed in water (hydrostatic weighting, M2), and, after a quick wipe with a shammy cloth, in air (M3).

The open porosity values (vol %) of the treated and untreated substrates were calculated (in %), using the following equation:

$$\text{Open Porosity (\%)} = \frac{\text{M3} - \text{M1}}{\text{M3} - \text{M2}} \text{ x } 100 \qquad (14)$$

Measurements were carried out in threefold. In the case of the treated substrates, samples were collected in the outer layer of the specimens (0-20 mm from the treated surface), in order to be representative of the treated area.

§ 8.5.4 Assessment of the consolidation effectiveness by DRMS

The consolidation action in terms of in-depth strength increase was assessed by Drilling Resistance Measurement System (DRMS). This method is generally considered suitable for evaluating the consolidation performance, particularly in soft stones [Ferreira 2004; Ferreira Pinto & Delgado Rodrigues 2012a; Nogueira et al. 2014]. The test consists of drilling a hole at a defined constant revolution speed *x* (rpm) and constant penetration rate *v* (mm/min), and measuring the penetration force needed as a function of depth [Ferreira Pinto & Delgado Rodrigues 2012a; Nogueira et al. 2014].
Drilling tests were performed with the drilling device DRMS Cordless, developed by SINT Technology (Italy) [Valentini et al. 2008]. The drilling machine is equipped with two precision motors able to keep a predefined rotation speed and to guarantee a predefined penetration rate [Ferreira Pinto & Delgado Rodrigues 2004]. The force, Fd (N), which corresponds to the thrust to be exerted on the drill to drive the bit [Nogueira et al. 2014], is measured continuously by a load cell and a graph showing the force versus depth is

displayed after the test [Valentini et al. 2008]. A drill bit of 5 mm diameter and made with the application of a polycrystalline diamond plaque was adopted [Valentini et al. 2008]. All acquired data are recorded and can be processed with a dedicated software. All tests were performed on both limestone and lime-based mortars with the same drilling parameters ($v/\omega = 40/40$ mm/min/rpm), which were defined by previous tests [Lubelli et al. 2015]. Holes were drilled up to 30 mm in the case of the Maastricht limestone, 16mm for the lime-based mortars, thus over the penetration depth of the nanolime and the depth where the consolidation effect of the treatment might be expected.

DRMS measurements were carried out in twofold in all the treated and untreated substrates (sound and weathered limestone, mortar) performing 10 drillings in every specimen. In the case of the Maastricht limestone, the average of these measurements was used as criterion to assess the mechanical strength improvement (Tab. 8.2). The increase of the drilling resistance can be easily analyzed by comparing the resistance profiles before and after treatment [Ferreira Pinto & Delgado Rodrigues 2012a]. Besides, DRMS measurements on weathered Maastricht limestone specimens from the site, before and after treatment, allowed to verify the penetration depth of the consolidant on weathered stone but also to assess the compatibility of the consolidation effect. The consolidation effect can be defined as optimal (the consolidated weathered material has a strength, F_{cw}, comparable to that of the sound stone, F_s), insufficient ($F_{cw} << F_s$) or excessive ($F_{cw} >> F_s$) [van Hees et al. 2004b].

TABLE 8.2 Properties of the substrates and details of the relative DRMS measurements.

SUBSTRATE	PROPERTIES	CONSOLIDATION	DRMS PARAMETERS	TYPE OF DRMS ANALYSIS
Sound Maastricht limestone	Undamaged blocks (15 x 15 x 4 cm) from quarry	Untreated block	$v/\omega = 40/40$ mm/min/rpm, 30 mm in depth	Average of 10 drilling measurements (on the same block)
		Block treated with E100		
Weathered Maastricht limestone	blocks with weathered surface (15x15x4 cm), from Keverberg Castle	Untreated block		
		Block treated with E100		
Lime-based mortar	Mortar layer (29 x 17 x 1,5 cm) applied on brick substrate	Untreated specimen	$v/\omega = 40/40$ mm/min/rpm, 16 mm in depth	Average of the lowest values of every 2mm segment of 10 drilling measurements (on the same block)
		Specimen treated with E95H5		

In the case of the mortar, the use of DRMS poses some problems in relation to the interpretation of the data. In fact, lime-based mortars are materials composed of aggregates (usually harder than the paste), paste (which includes binder crystals and

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voids) and the interface between aggregates and paste (usually called the interfacial transition zone, ITZ) [Nogueira et al. 2014]. The high heterogeneity of the mortars and the systematic presence of abrasive components (especially quartzite aggregates) complicate the interpretation of the DRMS data. Thus, a direct comparison of DRMS profiles before and after consolidation can hardly be done, given the extreme background noise introduced by the high resistance peaks of the quartz aggregate particles [Delgado Rodrigues & Costa 2016b].

A typical profile of a soft mortar has a baseline with forces varying within a more or less narrow band and a series of intercalated peaks with significantly higher values: the baseline can be attributed to the binding matrix, while the peaks are due to the presence of the aggregate [Delgado Rodrigues & Costa 2016b]. A method for the elaboration of DRMS data measured on mortar has been recently proposed by Delgado Rodrigues & Costa [Delgado Rodrigues & Costa 2016b]. This method splits the drilling profile in several segments, which are then analysed independently. An algorithm, which excludes the high peaks that are attributed to the aggregate, is used for the analysis of the consolidated mortars: only the lowest values are considered and averaged. Following this approach, we considered segments of 2 mm, which consist of 20 measurements (one each 0.1mm) registered by the software. Within this 2 mm segment, the 5 lowest values were selected (25th percentile) and then averaged. Finally, the averages of the lowest peaks of every segment are plotted in one graph, allowing the comparison between a treated and an untreated lime-based mortar. In addition, we considered 10 different drilling measurements and averaged the force values obtained from the lowest peaks of every segment of every drilling measurement, in order to evaluate the consolidation action on a wider scale.

§ 8.5.5 Measurement of the water absorption and drying

The water absorption and drying kinetics of the sound and weathered Maastricht limestone and of the lime-based mortar specimens were measured before and after the treatment with nanolime, in order to assess the compatibility of the treatments. The capillary absorption of water in the sound (core specimens 4 cm diameter and 4 cm height) and weathered (cubic specimens of 4 cm side) Maastricht limestone, and in the lime-based mortar specimens (cubic specimens of 4cm side) was measured; the water absorption coefficient (WAC) was calculated according to EN 15801 [CEN 2009]. The specimens, sealed with Parafilm M (by Bemis NA, USA) on the lateral sides, were partially immersed with their treated side in a petri dish, filled with water and with a grid on the bottom. During the absorption process, the specimen weight was measured until saturation was reached.Once saturated, the specimens were allowed to dry through the treated surface; the drying rate was evaluated by measuring the weight loss over time, in accordance with EN 16322 [CEN 2013]. The absorption and drying tests were carried out in threefold and performed under controlled conditions (50 % RH, T = 20° C, air speed <0.1 m/s).

§ 8.5.6 Evaluation of chromatic alteration

In order to assess any possible chromatic alteration (e.g. whitening) due to the nanolime treatment, treated and untreated specimens were visually observed and photographs were taken, using a WX220 Compact Camera (by Sony, Japan). Chromatic variations on the treated specimens were evaluated with the NCS (Natural colour System) Scale [NCS].

In addition, the surface of treated and untreated specimens was observed with a stereomicroscope Zeiss Stemi SV 11. Images were recorded with a Zeiss AxioCam MRc5 digital microscopy camera. The AxioVision 4.8 software and its interactive measurement tools were used to record and analyze the specimens.

§ 8.6 Results and discussion

§ 8.6.1 Absorption of nanolime dispersions

The nanolime dispersions were nebulized till any white haze was macroscopically visible on the treated surface, up to maximum 10 applications. In the case of the sound limestone, 7 applications were performed, as after this number of applications a white haze appeared on the treated surface. In the case of the weathered limestone and of the lime-based mortar, 10 nanolime applications were performed, and no whitening was macroscopically observed on the treated substrates.

The optimal interval between application by nebulization was defined at 48 h, as almost complete evaporation of the alcoholic solvent (≈ 90%, in volume) is achieved within this timespan. This procedure can prevent that the excess of solvent from previous applications would favour the migration of the nanoparticles back towards the surface during drying [Borsoi et al. 2016a].

The amount of E100 and E95H5 nanolime dispersions (l/m²) absorbed at each application by specimens of Maastricht limestone (both sound and weathered from Kessel) and of lime-based mortar is given in Tab. 8.3.

A similar amount of nanolime dispersion was absorbed at each application by the specimens. In the case of the sound Maastricht limestone (7 applications), the specimens absorbed between 8.21 l/m² (1st application) and 7.42 l/m² (7th application) of E100 nanolime. The calculated content of lime nanoparticles, expressed as the weight of product per volume (kg/m³), after 7 applications is 0.689 kg/m³ (Tab. 3.8). The weathered limestone specimens (10 applications) absorbed between 7.81 l/m² (1st application) and 7.23 l/m² (10th application) of E100 nanolime dispersion. The final content of lime nanoparticles deposited in the stone is considerably higher (0.924 kg/m³) when compared to that of the sound limestone, due to the higher number of applications.Lime-based mortars (10 applications) absorbed between 8.11 l/m² (1st application) and 7.54 l/m² (7th application) of E95H5 nanolime, resulting in a lime nanoparticle content of 0.981 kg/m³.

TABLE 8.3 Total amount of nanolime dispersion and nanoparticle content absorbed, and foreseen porosity reduction in the treated part of the substrates.
* this amount has been calculated considering the penetration depth of the nanolime (20mm in all the substrates).

SUBSTRATE	NANOLIME	NANOLIME DISPERSION ABSORBED ± STANDARD DEVIATION (l/m²)	LIME NANOPARTICLE CONTENT* (kg/m³)
Sound Maastricht limestone	E100	5.516 ± 0.223 (7 applications)	0.689 (7 applications)
Weathered Maastricht limestone	E100	7.548 ± 0.201 (10 applications)	0.924 10 applications)
Lime-based mortar	E95H5	7.797 ± 0.216 (10 applications)	0.981 (10 applications)

§ 8.6.2 Pore filling

Nanolime, like other consolidation treatments, is expected to partially fill the pores of a material and lead thereby to a small reduction of its porosity. First, an indicative measure of the degree of pore filling has been calculated, based on the assumptions mentioned in section 8.5.3. Then the actual degree of pore filling has been experimentally assessed by means of open porosity tests. Calculated and measured data are reported in Tab. 8.4. It can be observed that for all substrates the calculated pore filling is higher than the actual pore filling measured in the specimens. This difference might be due to the nanolime penetration also partially deeper than the outer 20 mm (layer considered in the calculation). When considering the measured data, it can be observed that:

- the open porosity of the untreated sound limestone (around 47%) is higher than that of the untreated weathered limestone (44.7%). This can be justified either by natural differences between Maastricht stone quarried in different times or by the partial occlusion of the pores at the very surface of the weathered limestone due to calcite dissolution/re-precipitation processes, typically found with this coarse porous limestone [van Hees & Nijland 2009], especially when exposed to weathering.
- both the treated sound and weathered limestone show a small reduction of the total porosity (respectively around 2% and 3%). In the case of the lime-based mortar specimens, the reduction of the total porosity is higher (4.6%) than that of the treated limestone specimens.

TABLE 8.4 Open porosity (vol%) of treated and untreated substrates and comparison measured/calculated pore filling.
* this range of values has been calculated by considering the nanoparticle content in the treated layer, the porosity of the substrates, the carbonation of calcium hydroxide (which implied a volume increase of around 37%) and the density of the Ca-carbonates with the lower density (MHC, 2.241 g/cm^3) and that with the higher density (aragonite, 2.944 g/cm^3).

SUBSTRATE	MEAN OPEN POROSITY ± STANDARD DEVIATION (%)	MEASURED PORE FILLING (POROSITY UNTREATED – POROSITY TREATED) (%)	CALCULATED PORE FILLING (%) DUE TO TREATMENT*
Untreated sound Maastricht limestone	47.02 ± 0.08	+ 2.16	+ 2.64 / 3.74
Treated sound Maastricht limestone	44.86 ± 0.24		
Untreated weathered Maastricht limestone	44.71± 0.25	+ 3.03	+ 3.43 / 4.51
Treated weathered Maastricht limestone	41.68 ± 0.59		
Untreated lime-based mortar	30.57 ± 0.21	+ 4.62	+ 5.51 / 6.71
Treated lime-based mortar	25.94 ± 0.04		

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§ 8.6.3 Effectiveness of consolidation - DRMS results

When analysing the sound Maastricht limestone, the untreated specimen has a homogeneous matrix with strength values of 12 to 15 N (Fig. 8.1). The block treated with E100 shows a remarkable increase of the mechanical strength (varying between 20 and 80%) in the treated layer. The penetration depth of the treatment is about 18 mm. The highest strength values were measured in the outer 2-4 mm, showing an over-strengthening at this depth. When analysing the untreated weathered Maastricht limestone block (Fig. 8.1), it is possible to observe that the outer 4 mm show a lower strength, due to weathering.

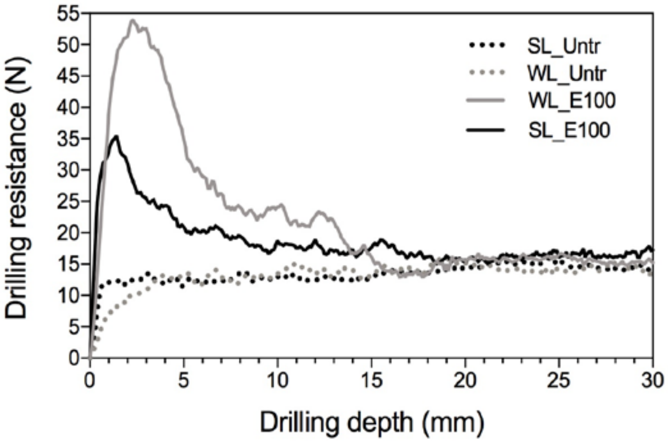

FIGURE 8.1 Drilling resistance profile of sound (SL) and weathered (WL) Maastricht limestone, untreated (dashed line) and treated with E100 (solid line). All profiles are an average of 10 measurements.

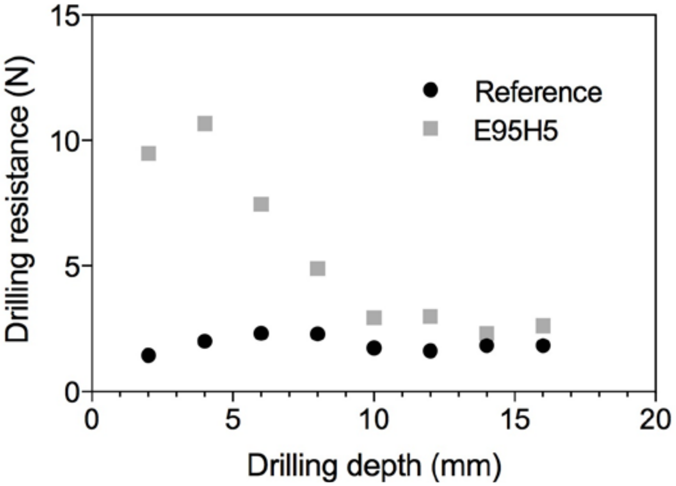

FIGURE 8.2 Drilling resistance profile of untreated and treated (with nanolime E95H5) lime-based mortar specimens. Markers represent average (10 measurements) of the arithmetic mean of the lowest values of every 2 mm segment.

E100 treatment (10x) results in a notable consolidation effect within the weathered limestone, up to 15 mm in depth. Also in this case the highest increase in strength is measured in the outer layer (6 mm). When comparing the strength of the weathered layer after consolidation with the strength of the unweathered stone (in the depth of the same block), it is possible to conclude that the nanolime treatments, although very effective, has strengthened too much the outer layer of the stone (2 to 3 times the values the sound limestone). In this case a lower number of applications would have led to a more compatible consolidation effect.

Analyzing the two treated limestones, in the weathered limestone a more heterogeneous in-depth distribution of the lime nanoparticles and a higher strength increase at the absorption surface can be observed. This difference can be attributed to the different absorption behaviour of the weathered stone, (decohesion of the outer, weathered layer) and the higher number of nanolime applications.

The methodology described in section 8.5.4 was adopted in order to examine the DRMS profiles of the treated and untreated mortars. The obtained data confirmed a consolidation action within the treated specimen, mostly up to 8-10 mm in depth (Fig. 8.2): an increase of the mechanical strength was observed (with values ranging 5 to 11 N), compared to the untreated specimen (1,5 to 2,5 N). The consolidation action is confined mostly in the outer 6-8 mm.

§ 8.6.4 Effect of treatment on water absorption and drying

The moisture transport properties of treated and untreated core specimens were assessed in order to evaluate the compatibility of the nanolime consolidant with the substrates (Fig. 8.3).

The total water amount absorbed within the weathered limestone is considerably lower (around 20% in volume) than that absorbed within the sound limestone. This difference can be attributed to lower open porosity of the stone from Kessel in comparison to that from the quarry (as seen in section 8.6.3). Such differences in porosity have been observed in Maastricht limestone before [van Hees & Nijland 2009] due to natural variations.

When comparing the untreated with the treated specimens, the results show that water absorption by capillarity of sound Maastricht limestone specimens treated with E100 is slower than that of the untreated specimen. The treated specimen takes around 3 minutes to be completely saturated with water, whereas 1 minute is necessary for the untreated specimens. A similar trend is observed with the weathered limestone: the specimens treated with nanolime E100 are completely saturated in slightly more than 4 minutes, while the untreated specimens are saturated in about 90 seconds.

Also in the case of the lime-based mortar, the nanolime treatment induced a delay of the water absorption; the specimens treated with nanolime E95H5 are completely saturated within 5 minutes, whereas it takes about 2 minutes for the untreated specimens to be saturated.

Additionally, it can be observed that a slightly smaller amount of water was absorbed within all the treated substrates, due to the pore filling induced by the nanolime treatments, in accordance with the results of section 8.6.2.

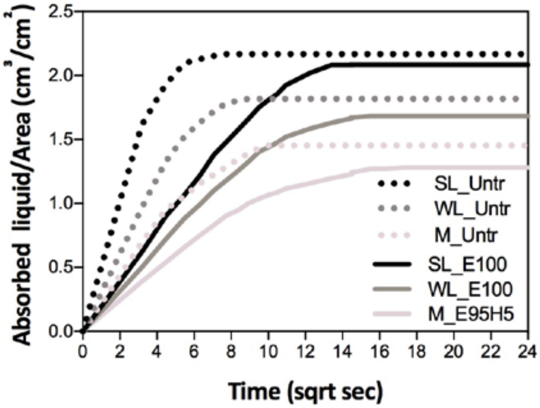

FIGURE 8.3 Comparison of the capillary absorption curves (in volume) of water of treated (solid line) and untreated (dashed line) specimens of sound Maastricht limestone (SL, black line), weathered Maastricht limestone (WL, dark grey line) and lime-based mortar (M, light grey line).

The water absorption coefficient (WAC) of treated and untreated specimens is presented in Tab. 8.5. It can be seen that the WAC of the treated sound limestone has a reduction of around 36% when compared to the untreated specimens; a slightly higher reduction is observed in the case of the weathered limestone (44%), probably due to the higher number of applications (10). In the case of the lime-based mortar, the reduction is around 40%.

In order to assess compatibility, the following criterion can be considered: after treatment the WAC should not increase and not differ too much from that of the untreated material [van Hees et al. 2014b; Snethlage 2013]. Nanolime treatment fulfills the first requirement, as they do no increase the WAC; in fact, a moderate reduction of the WAC (around 40% of the original value for all the 3 substrates) was measured.

TABLE 8.5 Water absorption coefficient (WAC) of treated and untreated substrates.

MATERIAL	WAC ($kg/m^2h^{1/2}$)
Untreated Sound Limestone	2.482 ± 0.067
Treated Sound Limestone	1.577 ± 0.156
Untreated Weathered Limestone	2.207 ± 0.183
Treated Weathered Limestone	1.275 ± 0.199
Untreated Mortar	1.753 ± 0.187
Treated Mortar	1.048 ± 0.264

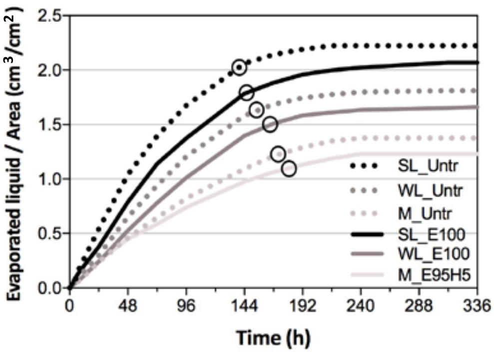

FIGURE 8.4 Drying curves (in volume) of water of treated (solid line) and untreated (dotted line) specimens of sound Maastricht limestone (blue line), weathered Maastricht limestone (yellow) and lime-based mortar (red line). The black circles indicate the critical liquid content and the end of the first step of drying.

The drying curves (Fig. 8.4) show that the water absorbed by treated and untreated, sound limestone specimens evaporates within about the same time span. In the drying curves, two stages can be observed: in the 1st stage of drying, called the constant drying period, the drying front is at the surface and the drying rate is relatively constant and controlled by the external conditions [Hall & Hoff 2012]. This first phase ended in around 144 h in the case of both the treated and untreated sound limestone. In the 2nd stage of drying, identified by the change in the slope of the drying curve, the liquid water content can no longer support the demands of the evaporation flux. The drying front recedes progressively into the material and the properties of the substrate control the rate of drying [Hall & Hoff 2012]. In this second stage of drying, where drying occurs in the vapor phase, most of the water has already evaporated. In this step, some delay can be observed in the case of the treated limestone. Untreated sound limestone specimens completely dried in about 8 days, whereas the treated specimens need up to 10 days.

A similar trend is observed in the case of the weathered limestone. In the case of the mortar specimens, no significant differences in the drying rate are observed between treated and untreated specimens, which completely dried in 9-10 days.

Summarizing, it can be concluded that nanolime treatments do not cause drastic alteration of water transport properties in the studied substrates. Therefore, the risk of harmful consequences and future decay of the substrate caused by differential moisture transport properties between treated and untreated layer is low [Zornoza-Indart et al. 2016].

§ 8.6.5 Influence of the treatments on the aesthetical aspect

The sound and weathered limestone blocks and the lime-based mortar were observed macroscopically, before and after the treatment with nanolime. NCS indexes measurements were considered to evaluate any possible macroscopical chromatic alteration of the treated specimens.

In the case of the sound limestone (Fig. 8.5a), identified with the NCS indexes S0530-G80Y and S0540-G80Y, no white patina was observed at the drying surface after 6 applications of nanolime E100 (Fig. 8.5c); some whitish haze was visible only after the 7th application (Fig. 8.5b), when compared to the untreated specimen, being the specimen identified with the NCS indexes S0530-G80Y, S0520-G80Y and S0510-Y. This slight whitening is due to lime nanoparticles accumulated nearby the surface. This white patina is not homogeneously distributed on the surface, and an accumulation is visible in the center of the specimen (Fig. 8.5d).

When considering the weathered limestone (NCS indexes: S0530-G80Y and S0540-G80Y), the surface is more irregular than that of the sound limestone, and it shows powdering and loss of cohesion (Fig. 8.6a,c). After 10x treatment with nanolime E100, the specimen shows a more homogeneous surface (Fig. 8.6b) and no significant chromatic alteration (NCS indexes: S0530-G80Y and S0520-G80Y). In fact, even if a higher number of applications was performed compared to the sound limestone (10 instead of 7), no white patina is observed at the surface (Fig. 8.6d).

The untreated mortar specimen, identified by the NCS indexes S0500-N and S0502-Y, presents a whitish, highly porous surface (Fig. 8.7a,c).

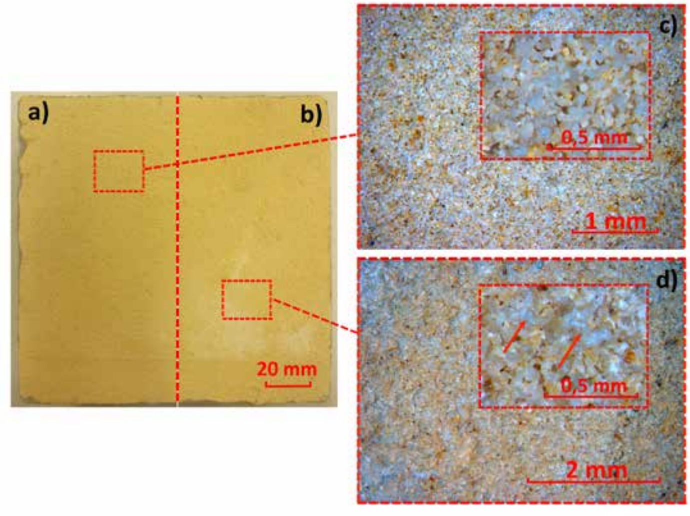

FIGURE 8.5 Pictures of the drying surface of a) untreated and b) treated (7 applications with E100) blocks (15 x 15 x 4 cm) of sound Maastricht limestone; c, d) relative microphotos on the most significant spots. The arrows indicate the deposits of lime nanoparticles.

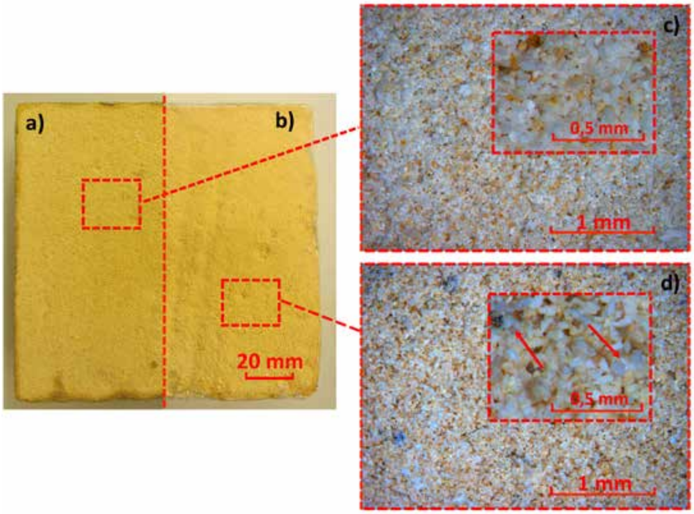

FIGURE 8.6 Pictures of the drying surface of a) untreated and b) treated (10 applications with E100) blocks (13 x 13 x 4 cm) of weathered Maastricht limestone; c, d) relative microphotos on the most significant spots. The arrows indicate the deposits of lime nanoparticles.

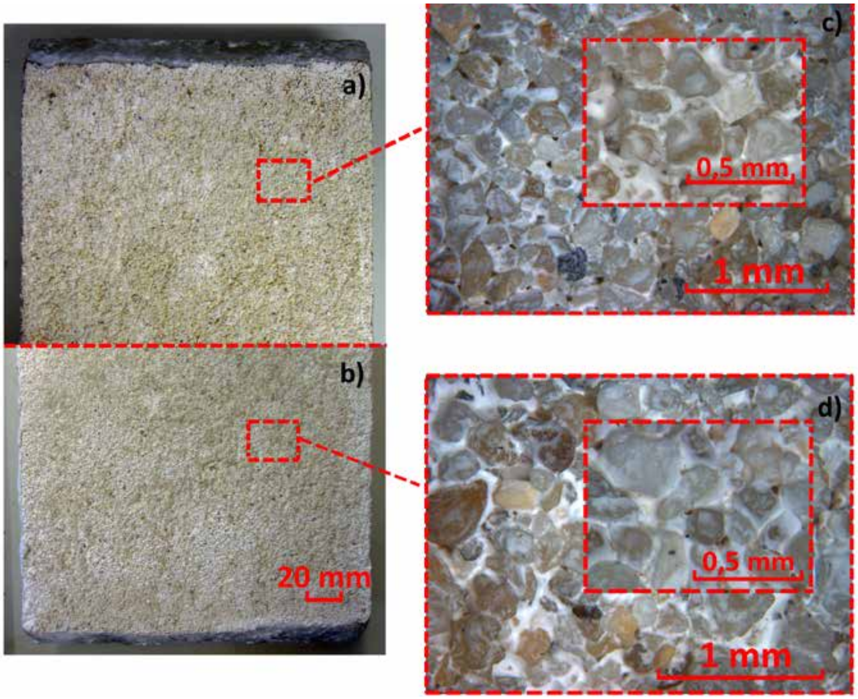

FIGURE 8.7 Pictures of the drying surface of a) untreated and b) treated (10 applications with E95H5) lime-based mortar layer applied on a brick (29 x 17 cm); c, d) relative microphotos on the most significant spots.

The treated specimen shows a more homogeneous surface and no chromatic alteration or white patina is macroscopically visible (Fig. 8.7b) (NCS index: S0500-N). Looking more in detail to the microstructure, it can be observed that lime nanoparticles partially filled the superficial pores and enriched the binder of the original matrix (Fig. 8.7d) [Borsoi et al. 2012].

In the case of the weathered limestone and of the lime-based mortar, the variations observed in the treated specimens are not macroscopically perceptible and thus the treatments demonstrate to respect the chromatic parameters of the substrates.

§ 8.7 Conclusions

In this research the effectiveness and compatibility of freshly synthesized nanolimes with fine-tuned solvent [Borsoi et al. 2016b; Borsoi et al. 2016c] and applied according to an optimized protocol [Borsoi et al. 2017a], was assessed on Maastricht limestone (both sound and weathered) and on lime-based mortar.

In the case of the sound and weathered Maastricht limestone, the results showed that nanolime E100 (dispersed in 100% ethanol) can guarantee a consolidation action up to ca. 16 mm in depth, with a maximum effect in the outer 5-6 mm.

The de-cohesion of the outer layer of the weathered stone allowed for a higher number of applications when compared to the sound limestone, without any whitish patina appearing at the drying surface.

Also in the case of lime-based mortar specimens, treated with nanolime E95H5 (nanoparticles dispersed in a binary mixture of 95% ethanol - 5% water), a considerable consolidation was observed, which led to an increase of the mechanical strength up to 8-10 mm in depth.

Based on these results, it can be concluded that a significant strengthening effect can be obtained by the use of the developed nanolime dispersions on coarse porous lime-based substrates. A higher strengthening effect measured at the very surface of the specimens might be necessary to compensate for the weakness of strongly weathered substrates. The strengthening effect may be adapted to the decohesion of the substrate by adjusting the number of nanolime applications.

In spite of the considerable strengthening effect, the treatment only moderately altered the total porosity and the moisture transport properties of the investigated substrates.

The nanolime treatments tested in this work showed to have a good effectiveness and compatibility when applied for consolidation of highly porous, calcareous substrates like Maastricht limestone and lime mortar. Future research should evaluate the effect of the treatment on the durability related to decay processes (e.g. salt crystallization and freeze-thaw resistance) of the treated materials.

9 Conclusions and discussion

§ 9.1 Conclusions

This dissertation has focused on the effectiveness and compatibility of so-called nanolime consolidants, i.e. calcium hydroxide nanoparticles dispersed in alcohols. Colloidal dispersions of nanolime have been proposed in the last decade for the consolidation of calcareous materials such as frescos, limestone and lime-based renders and plasters.

These products generally are able to ensure a proper superficial consolidation and a high reactivity and thus carbonation. However, when mass consolidation is required (as often is the case of limestone and mortars), the mechanical effectiveness of nanolime treatments is still doubtful and contradictory results on their physical compatibility are found in literature (Chapter 2).

One of the main aims of this PhD research was to better understand the most important influencing factors and subsequently improve the effectiveness and compatibility of nanolime dispersions. A first step towards this objective, consisted in gaining a better understanding of the transport and deposition processes of nanolime particles within porous materials.

The transport of a commercial nanolime (CaloSil E25) within a coarse porous substrate (Maastricht limestone) was investigated (Chapter 4) in order to clarify the role of the different mechanisms (absorption, phase separation, back transport and carbonation) involved in the transport and deposition of nanolime dispersions. This research clarified the process of accumulation at the surface: in the case of porous limestones, the absorption of nanolime is not hindered, thus no accumulation at the surface occurs during the absorption phase. However, lime nanoparticles tend to migrate back towards the surface with the solvent during drying. This migration, favoured by the high volatility of the solvent and high kinetic stability of the dispersion, results into a thin layer of lime nanoparticles beneath the drying surface. Experiments carried out in N_2 atmosphere, showed that carbonation does not play a relevant role in this case.

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The observed accumulation of the nanoparticles nearby the drying surface may be a limitation for the achievement of an effective in-depth consolidation. Additionally, accumulation of nanoparticles at the surface may limit the penetration of successive consolidant applications and it may result sometimes in an unwanted white haze. Solutions to tackle this problem were looked for in the following phases of the research.

The results of the study on transport of nanolime in Maastricht limestone suggest that the main factors influencing the deposition are both the stability of the dispersion and the moisture transport in the substrate. The first is mainly affected by the particle size and concentration and by the type of solvent; the second is the result of the pore size distribution of the substrate and of the environmental conditions.

Consequently, a better in-depth deposition of the nanoparticles and thus a more effective consolidation can therefore be obtained by fine tuning the kinetic stability of the nanolimes to the moisture transport properties of the substrate.

The possibility of optimization of the kinetic stability of the dispersions by an appropriate selection of a solvent was investigated (Chapter 5).

Nanolime particles were synthetized by solvothermal reaction of metallic calcium in water (a synthesis method which can be easily set-up and guarantees a good yield, as seen in chapter 5) and were dispersed in different solvents (ethanol, isopropanol, butanol, water). The type of solvent showed to strongly affect the kinetic stability of the dispersions: nanolime dispersed in ethanol and isopropanol are stable for several days after proper sonication, dispersions in butanol are slightly less stable, whereas dispersions in water have a very low kinetic stability (few hours for complete nanoparticle-solvent phase separation).

Based on these analytical observations, a conceptual model was developed: this model supposes that an improved nanoparticle in-depth deposition can be obtained by selecting the solvent of the nanolime dispersions based on the following two factors: a) the moisture transport properties of the substrate to be treated; b) the kinetic stability of the relative nanolime. According to this model, solvents having a high boiling point (and thus a slow evaporation) and leading to dispersions with low kinetic stability, such as butanol or water, are expected to improve nanoparticles in-depth deposition within coarse porous materials. Conversely, solvents having a lower boiling point (and thus a fast evaporation), such as ethanol and isopropanol, and giving high stability to the nanolime dispersions, are expected to result in a better penetration and nanoparticles in-depth deposition within fine porous materials.

The model was experimentally validated on Maastricht (coarse-porous) and Migné (fine-porous) limestone. The results show that, as expected, nanolime dispersed in butanol penetrates into the Maastricht limestone, leading to in-depth deposition (up to 20–25 mm) and no back migration of nanoparticles towards the drying surface. In the Migné limestone, the best results were obtained by the use of nanoparticles dispersion in ethanol; however, due to the very slow liquid transport in this fine porous stone, some deposition of nanoparticles during absorption was observed (due to phase separation). These experiments validate the model and confirm that the optimization of the properties of the nanolime (e.g. concentration, particle size, solvent type, and consequently kinetic stability and reactivity) to the moisture transport properties of the substrate can significantly improve the transport, in-depth deposition and thus the effectiveness of the lime nanoparticles in a coarse porous substrate. The model will need further fine tuning for very fine porous substrates.

The model was then further developed in order to fine-tune the in-depth deposition of lime nanoparticles within coarse porous substrates (Chapter 6). Instead of butanol (which by the way has higher cost and toxicity for the operator and the environment, when compared to water), nanolime dispersions in a mixture of ethanol and different percentage of water were prepared. The stability of these dispersions was assessed. Based on the results and on the moisture transport properties of the Maastricht limestone, a mixture of 95% ethanol and 5% water (identified here as E95H5) was selected as the most suitable for application on this coarse porous limestone. In fact, the experiments showed that E95H5 has a proper penetration during the absorption and, thanks to the lower kinetic stability of the dispersion in comparison to nanolimes dispersed in pure ethanol, back migration was limited and nanoparticles deposited in depth. These results further validated the proposed model.

Next to the characteristics of the nanolime dispersion and of the substrate, also the environmental conditions and the application protocol can affect the transport and deposition and thus the effectiveness of the consolidation action. The application protocol includes the application method (e.g. nebulization, capillarity, brushing), the amount of consolidant applied, the procedure of application (e.g. absorption until saturation, wet on wet, the number of applications) and any other measure taken to ensure an effective and compatible consolidation.

In this research, different applications methods were compared: full saturation by capillary absorption, a widely used and reliable laboratory method, and surface impregnation (i.e. partial saturation) by nebulization, a method mainly used on site in conservation practice (Chapter 7).

The comparison of these application methods aimed at translating laboratory results into advice for practice, and thus at contributing to the definition of an application protocol for restorers and professionals in the field.

Laboratory research was carried out by applying nanolime in ethanol and in an ethanol-water mixture on Maastricht limestone and on a lime-based mortar. The lime mortar allowed to validate the model on a lime-based coarse porous substrate with multimodal pore size distribution. The research showed that the results obtained, may differ depending on the application method. For example, in the case nebulization is used on Maastricht limestone, nanolime dispersed in pure ethanol (E100) gives better results (in-depth deposition without white haze), than nanolime in a mixture of ethanol and 5% water (E95H); the opposite of what occurs in the case of application by capillary impregnation. This underlines the importance of fine-tuning the nanolime consolidant (i.e. select an appropriate solvent or solvent mixture for the nanolime dispersion) based also on the application method.

Finally, the effectiveness and compatibility of the nanolimes (E100 and E95H5), applied on Maastricht limestone (both fresh and weathered) and lime mortar according to an optimized protocol (multiple applications by nebulization) was assessed (Chapter 8).

The hardness of the surface of the stone and the mortar, before and after consolidation, was considered as a measure of the consolidation effectiveness. The hardness was measured using the Drilling Resistance Measurements System (DRMS) (Chapter 8). The DRMS results show that nanolime E100 penetrated and consolidated all substrates, up to a significant depth (16 mm respectively 8-10 mm in the case of the Maastricht limestone and lime mortar), with a maximum effect in the outer 5-6 mm. In all substrates the pore filling was limited (maximum of 5% in the mortar).

Thanks to this limited pore filling, no significant effect on the moisture transport was measured in spite of the considerable consolidation effect. This minor effect on moisture transport proves the good physical compatibility of this treatment with the tested substrates.

Based on these results, it can be concluded that significant strengthening effect can be obtained by the use of the modified nanolime dispersions on coarse porous lime-based substrates such as Maastricht limestone and lime mortar, using an optimized application protocol. The nanolime treatments showed to have also a good compatibility, with a minor variation of the moisture transport properties and no significant visual chromatic alteration of the treated surface.

Summarizing, it can be concluded that nanolimes, if adequately fine-tuned to the substrate properties and the application procedure, can offer a suitable alternative to the widely used TEOS-based products for application on lime-based substrates. In fact, nanolimes can provide a good consolidating effect while ensuring good chemical and physical compatibility with lime-based substrates.

§ 9.2 Outlook

This research studied both the effectiveness and the compatibility of the developed nanolimes. An important aspect, which has not been investigated, concerns the durability of the nanolime treatment, i.e. the resistance of the treated substrate towards degradation processes such as freeze-thaw cycles, salt crystallization, thermal and hygric stresses. Based on the measured low percentage of pore filling and on the minor effect of the nanolime on the moisture transport of the treated materials, a good durability of the treated material to frost and salt crystallization decay can most probably be expected. Accelerated laboratory tests would allow to verify this and quantify to what extent the nanolime treatment can affect the durability of the treated substrate.

Another aspect related to the durability of the treated substrate, still to be investigated is the possible difference in solubility (e.g. in acid rain) between the original lime-based substrate and treated substrate with deposited nanolime, in order to know whether any undesired degradation patterns might develop.

Furthermore, as seen as well in the review (Chapter 2) and in Chapter 7, the long-term storage of nanolime dispersions, the curing conditions (e.g. relative humidity) after treatment and the water content of the to be treated substrate can favour the formation of other calcium carbonates (e.g. aragonite, vaterite, monohydrocalcite), rather than calcite. These calcium carbonates have different morphology and physical properties (e.g. density, solubility) compared to calcite, which could affect the long-term stability and durability of the treated substrate. It would therefore be important to investigate the influence of these polymorphs on the long-term effectiveness and compatibility of the treated substrate.

Another issue which needs further investigation is the treatment of fine porous limestone: experiments showed that even very stable dispersions (like nanolime in ethanol) at the used concentrations (25g/l) cannot easily penetrate in (very) fine porous substrates and will lead to surface deposition. Future research could lead to adapting the proposed model also for finer porous substrates; in these cases the use of lower concentrations may offer a solution.

It should be mentioned that, apart from the assessment of the effectiveness of the treatment by means of DRMS, most tests were carried out in the laboratory on fresh substrates. It is known that the properties of a weathered material differ from those of a sound one and this can significantly affect both the choice of the nanolime product and the results of the treatment. Additional tests on weathered substrates as well as a survey of field cases can provide important and useful information on the effectiveness, compatibility and durability of these treatments under real conditions, as already is shown in the case of the weathered Maastricht limestone specimens collected in the castle of Keverberg (Kessel, Southern Netherlands).

Although recent studies showed the low toxicity of the nanolime dispersions during application, further research should be carried out considering also the possible long-term harmfulness on human health of the colloidal dispersions. Moreover, the use of near-zero toxicity solvent (e.g. additivated water-based solvents, dialkyl carbonates, etc.) might be also considered for the future to improve the safety of the operators.

Another interesting subject of research for product development concerns the possibility of mixing lime nanoparticles with other nanomaterials with polyvalent features. This could give additional properties to nanolime consolidants: e.g. titanium oxide nanoparticles could provide photocatalytical and thus self-cleaning properties, silica nanoparticles might increase the strengthening effect and favour chemical compatibility with e.g. siliceous aggregates in mortar, etc.

As shown, nanolime products have numerous promising possibilities and further research is necessary to explore and exploit them at the best for the conservation of our cultural heritage.

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Appendix A Recommendations for the use of nanolime on calcareous substrates

The effectiveness of nanolime dispersions was shown to be strongly affected by the stability of the nanolime dispersion and by the moisture transport properties of the substrate. Besides, a series of other factors, such as the application method, the amount of product applied, the water content in the substrate, the environmental conditions, can affect the results.

In order to help restorers and professionals in the field in successful application of nanolime products, some recommendations on the storage, preparation and a possible protocol for the application of nanolime dispersion are given in the next pages.

Storage

Nanolime dispersions should be used as soon as possible after their synthesis, in order to reduce nanoparticle aggregation and possible hydroxide-to-alkoxide conversion (which has a deleterious effect on the product). However, being this option often not feasible, it is highly recommended to store nanolime in a cabinet at low temperature: this reduces the viscosity of the alcoholic solvent and thus the collisions between the nanoparticles. Additionally, the hydroxide-to-alkoxide conversion is temperature-dependent and is reduced at low temperature.

Nanolime dispersions are highly flammable and thus need to be kept away from heat sources or oxidizers.

As specified also by the producers of commercial nanolimes, the shelf life of nanolime depends on the dispersion concentration, ranging from 3 months (with nanolime of 25g/l) to 1 year (with nanolime of 5g/l). Over this timespan, irreversible aggregation phenomena can take place, which may reduce the effectiveness of the nanolime products.

Preparation

It is necessary to vigorously stir nanolime dispersions, immediately prior to their application. In fact, nanoparticles are often partially or completely settled on the bottom of the container already after 1 week of storage. Even when no deposition on the bottom is visible, it is highly recommended to proceed to sonication (i.e. a ultrasonic bath at e.g. 60Hz) of the dispersions for at least 10 minutes (possibly maintaining the dispersions temperature ≤ 20°C); this step is important for reducing possible aggregation phenomena and obtaining a more homogeneous particle size distribution.

Nanolime properties

Solvent selection

As seen in the previous chapters, ethanol-based (or isopropanol-based) nanolimes are suitable for the consolidation of calcareous substrates, due to the high kinetical stability of these dispersions.

The addition of small percentage of water (e.g. 5% in volume) in the dispersion can be considered when treating substrates with high porosity and coarse or macro-pores (e.g. Maastricht limestone or the 1:4 lime-based mortars studied in this work), depending on the adopted application methodology (see also chapter 7).

Concentration

The concentration of the nanolime needs to be chosen based on the properties of the materials to be treated. Very high concentrations (e.g. 50g/l) are not recommended, since they can lead to whitening on the treated surface.

In the case of coarse porous substrate (pores ≥ 10 µm), like Maastricht limestone and the lime-based mortars studied in this dissertation, concentration ≤ 25 g/l are recommended. For fine porous substrates, lower concentrations can be beneficial.

Instead of a single application at higher concentration, in some cases several applications at lower concentration (1 to 25 g/l) might be performed. The application of dispersions with increasing concentrations, starting from very diluted dispersions, can be also considered.

In any case, the nanolime effectiveness and compatibility needs to be verified through preliminary trials in laboratory and on site.

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Substrate properties and pre-application care

In order to achieve a proper consolidation action on calcareous substrates, it is necessary to know the properties of the substrate to be treated. In particular, the knowledge of the moisture transport properties (drying and absorption kinetics) of the treated substrate is highly recommended for the optimization of the nanolime solvent. Additionally, MIP (Mercury Intrusion Porosimetry) or BET analysis (by nitrogen absorption) can precisely define the total porosity and the pore size distribution of the materials to be treated.

As seen in the previous section, substrates with high porosity and macro and coarse pores (e.g. Maastricht limestone or the 1:4 lime-based mortars studied in this work) are generally characterized by a fast absorption and drying rate. These substrates can be treated easily and nanolime generally penetrates in depth within their pore network, but the drying rate needs sometimes to be slowed down in order to minimize nanoparticle migration back towards the drying surface and to increase the in-depth deposition of the lime nanoparticles. As water decreases nanolime kinetic stability and drying rate, the addition of small percentage of water to the solvent can be beneficial in these cases (see also chapter 5 and 6)

Conversely, substrates with low porosity and micro-pores (e.g. Migné limestone) have slower absorption and drying rate. In the case, lime nanoparticles are barely penetrating within this very compact and micro-porous substrate, and lower concentrations might be more effective in these cases.

Additionally, the presence of moisture in the substrate has to be carefully evaluated. In fact, since even small water amounts can destabilize nanolime dispersions, it is necessary to proceed to at least a partial removal of the moisture, by artificially drying the surface (e.g. through proper ventilation or moderate heating) and, whenever possible, minimize capillary rise or other causes of moisture. A preliminary application of ethanol (which is soluble in water and will quickly evaporate) on the surface to be treated can help to reduce the moisture content at the surface of the substrate to be treated.

In the presence of salts, desalination (e.g. by poulticing) are highly recommended in order to remove these harmful compounds which may hinder the penetration and in-depth deposition of the lime nanoparticles. Additionally, the presence of hygroscopic salts can negatively affect the durability of the consolidated material.

Environmental conditions

Relative humidity, temperature and air speed have a major impact on the effectiveness of a consolidation action, especially when dealing with highly reactive nanoparticles. It is thus necessary to monitor and control the environmental factors, in order to minimize strong climatic variations at least 2-3 weeks after the application of nanolime (necessary for the carbonation of most of the lime nanoparticles).

As mentioned above, nanolime dispersions should be preferably applied on a dry surface (or at least a surface with low moisture content. However, after application, nanolime treatments should be preferentially cured at RH ≥ 65%), since the presence of some moisture and CO_2 is promoting the carbonation of the nanoparticles. Additionally, at higher RH%, the formation of thermodynamically stable calcite is promoted, whereas at lower RH%. metastable vaterite, aragonite, monohydrocalcite or amorphous calcium carbonate are favoured. It is known that calcite guarantees a more efficient and durable strength increase, when compared to the other calcium carbonates.

Next to air RH, temperature and air speed should be also monitored and controlled during and after the application of the nanolime dispersion, in order to control the evaporation of the solvent and thus favour nanoparticles in-depth deposition. In fact, ethanol vapour pressure exponentially increases over 25ºC, thus the temperature should be kept as much as possible below this value.

The solvent evaporation is equally influenced also by air speed, which should be controlled and maintained within reasonable values (<1 m/s).

Application

Nebulization is a feasible method for the application of nanolime. Application by brush is a valid alternative. The amount of nanolime to be applied should be defined both by laboratory tests and in situ trials, after assessment of the substrates properties.

In the laboratory tests presented in this dissertation, a nanolime amount of about 5 l/m^2 was used on the highly porous substrates (limestone and lime-based mortars), in order to achieve a saturation of the specimens up to 20mm in depth. However, these substrates are extremely porous, thus a proper amount generally may ranges from 0,1 to 3 l/m^2 per application, depending on the substrate properties. In this way, a proper consolidation action, with minor effects on the moisture transport properties of the treated substrates, can be achieved. In any case, the suitable amount of nanolime should be fine-tuned by preliminary trials in laboratory and on site.

The number of applications and the interval between applications are other important issues. In this dissertation, nanolime was applied up to 7x on sound Maastricht limestone and up to 10x on weathered Maastricht limestone and lime-based mortars.

Depending on the type and state of conservation of the substrate to be treated, the strengthening effect may be adapted by adjusting the number of nanolime applications. Since 7 and 10 nanolime applications induced an excessive strengthening effect respectively on limestone and mortars (chapter 8), it can be supposed that 3 to 5 applications are sufficient to achieve a proper in-depth consolidation action in these substrates.

An interval of at least 24 h between every applications is recommended in order to allow (almost) complete evaporation of the solvent, as well as the deposition and partial carbonation of the nanoparticles. In this way, there is a minimal amount of solvent that is interfering in the penetration of successive applications, and a proper consolidation action can be achieved in a reasonable timespan (around 1 week).

For the safety of the operators, it is recommended to use masks, gloves and eye protectors. Sufficient ventilation (but with an air speed not higher than 1-1.5 m/s) during nanolime application is recommended.

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Curriculum vitae

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Work Experience	
July 2005 – December 2005	Trainee as laboratorial technician Physical-chemical analysis, diagnostic for restoration purposes (e.g. cleaning, consolidation, protection actions) on historical building materials
	Ducale Restauri S.N.C., Venice, Italy
March 2009 – September 2009	Trainee with Erasmus Placement Fellowship Analysis and diagnostic of traditional building materials (mainly lime-based renders and plasters) Materials Department, National Laboratory for Civil Engineering (LNEC), Lisbon, Portugal
May 2010 – May 2013	Temporary Research Associate LIMECONTECH project– Conservation and durability of historical renders: compatible technics and materials
	Building Department, National Laboratory for Civil Engineering (LNEC), Lisbon, Portugal
June 2013 – October2016	Ph.D. Fellow Nanotechnologies applied to the conservation of historical lime-based render. Final dissertation delivered, defence planned in May 2017.
	Technical University of Delft, The Netherlands; collaboration with TNO (Delft, The Netherlands) and LNEC (Lisbon, Portugal)

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Education and Academic Degrees

October 2002 – April 2006	Bachelor in Chemical Science and Technology for the Conservation and Restoration, Cá Foscari University of Venice; Main field of Study: Chemistry; Final note: 104/110 Physical-chemical analysis of traditional, historical and modern materials (Build heritage; museum artefacts; archaeological finds)
October 2006 – December 2009	Master in Chemical Science for the Conservation and Restoration; Cá Foscari University of Venice and University of Lisbon; Main field of Study: Chemistry; Final note: 110/110 cum laude
	Analytical and material chemistry, development of building materials, diagnostic for the restoration of the built heritage and museum artefacts.
August 2007 – March 2008	Socrates-Erasmus fellowship at the Science Faculty of the University of Lisbon (Portugal), master in Analytical Chemistry

Main areas of interest and research

Analytical chemistry applied to Building materials (e.g. lime, aggregates, traditional and modern additives) and museum artefact (e.g. wood, bone, metals, plastic, pigments, organic and inorganic additives).
Synthesis and characterization of building materials and for the conservation of the built heritage, with specialization in nanomaterials (e.g. nanolime, nanosilica).
Knowledge of analytical techniques and physical-mechanical tests as: XRD, thermal analysis (TG, DTA, DSC), optical and electron microscopy (SEM-EDS, AFM), spectroscopic analysis ((Uv-Vis, FTIR, DLS), porosimetry (MIP), rheometry, potentiometry, mechanical analysis (flexural and compressive strength, hardness, elastic modulus, etc.), artificial aging tests (Uv-IR, freeze-thaw, salts)

Personal Skills and Competences

Publications	10 publications in peer-reviewed journals, e.g. Colloids and Surfaces A, Journal of Cultural heritage, Applied Physics A, Construction and Building Materials, Microscopy and Microanalysis. Presentations in around 30 international conferences; invited speaker in 5 events (conferences and workshops)
Coordination and review	Coordination and development of 4 master thesis of students of Chemistry and Civil Engineering (at LNEC, Lisbon, Portugal) Organization of 3 conferences at LNEC (Lisbon, Portugal) Corresponding member of CIB endorsed Student Chapter of the Civil Engineering and Architecture Department (DECivil) at IST-Technical University of Lisbon, Portugal. Reviewer in international Journals as RCS Advances, Colloids and Surfaces A, Journal of Cultural Heritage
Languages	Italian (mother tongue), English (C1, as in Common European Framework of Reference for Languages), Portuguese (C1), Spanish (B1), French (A1)
Computer skills	Optimal knowledge of Office tools Good knowledge of graphics softwares as Photoshop, Illustrator Good knowledge of graphing and data analysis software as Prism, Origin Good knowledge of specific software for analytic techniques, as XPERT for XRD analysis, SetSoft 2000 for TG-DTA analysis, INCA for SEM-EDS, etc.)
Other Skills and interests	Cooperation in the socio-political youth group "Il Citofono" at Spresiano (Tv, italy); Basic and advanced course of documental and digital photography Participation in amateur football and basketball teams in Spresiano (Italy), Lisbon (Portugal) and Delft (The Netherlands). Driving license: B

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List of Publications related to the PhD project

Peer-reviewed papers

1 Borsoi, G., Lubelli, B., Hees, R. Van, Veiga, R., Silva, A., Understanding the transport of nanolime consolidants within Maastricht limestone, Journal of Cultural Heritage 18 (2016) 242-249.

2 Borsoi, G., Lubelli, B., Hees, R. Van, Veiga, R., Silva, A. S., Fedele, L., Colla, L., Tomasin, P., Effect of solvent on nanolime transport within limestone: How to improve in-depth deposition. Colloids and Surfaces A: Physicochemical and Engineering Aspects, 497 (2016) 171–181.

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4 Borsoi, G., Lubelli, B., Hees, R. Van, Veiga, R., Silva, A., Application Protocol for the Consolidation of Calcareous Substrates by the Use of Nanolimes: From Laboratory Research to Practice, Accepted for publication December 2016, http://doi.org/10.1515/rbm-2016-0008.

5 Borsoi, G., Lubelli, B., Hees, R. Van, Veiga, R., Silva, A., Evaluation of the effectiveness and compatibility of nanolime consolidants with improved properties, Construction and Building Materials, 142 (2017) 385–394.

Conferences, Seminars, Workshops

1 Borsoi, G., Veiga, R., Santos Silva, A., Effect of nanostructured lime-based and silica-based products on the consolidation of historical renders, in 3rd Historic Mortars Conference 11-14 September 2013, Glasgow, Scotland.

2 Borsoi, G., Veiga, R., Santos Silva, A., Nanostructured lime-based and silica-based materials for the conservation of ancient renders: an open challenge, in 1st International conference on innovation in art research and technology - InArt13, 10-13 July 2013, Hercules Laboratory - University of Evora, Evora, Portugal.

3 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, A., Nanolime deposition in Maastricht limestone: back-migration or accumulation at the absorption surface?, in Proceedings of the 15th Euroseminar on Microscopy Applied to Building materials, 17-19 June 2015, p. 77-86 Delft University of Technology, Delft, The Netherlands.

4 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, A., Deposition of modified nanolimes within calcareous substrates, in Workshop Green Conservation of Cultural Heritage, CNR, Rome 27-28 October 2015.

5 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, A., Nanostructured lime-base materials for the conservation and restoration of historical renders: Advantages, limitations, progresses, 3rd Workshop CIB-SC DeCivil, Instituto Superior Técnico, Lisbon, Portugal, 11 September 2015.

6 Borsoi, G., Lubelli, B., Hees, R. Van, Colla, L., Fedele, L., Tomasin, P., Veiga, R., Silva, A. S., Modified nanolimes: synthesis, structure and colloidal stability, in 1st International Conference on Science and Engineering in Arts, Heritage and Archaeology – SEAHA, July 14-15th, 2015, University College, London.

7 Borsoi, G., Lubelli, B., Van Hees, R., Nanostructured lime-base materials for the conservation and restoration of historical stone and renders, Inside Materials - Newsletter Delft Centre for Materials - March 2015.

8 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, Nanostructured lime-base materials for the conservation and restoration of historical renders: Advantages, Limitations, progresses, 3rd COMPAT - Workshop CIB-SC DeCivil – 11 Sept 2015, IST, Lisbon.

9 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, Consolidação de revestimentos históricos com nanocal: vantagens, limites, progressos, in V Jornadas FICAL – Forum Iberico da Cal, 23-25 May 2016, LNEC, Lisbon.

10 Borsoi, G., Van Hees, R., Lubelli, B., Veiga, R., Santos Silva, Consolidation of calcareous substrates with nanolime: advantages, limitations, progresses up-to-date, in WTA International PhD Symposium, September 2017, Delft, The Netherlands.