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

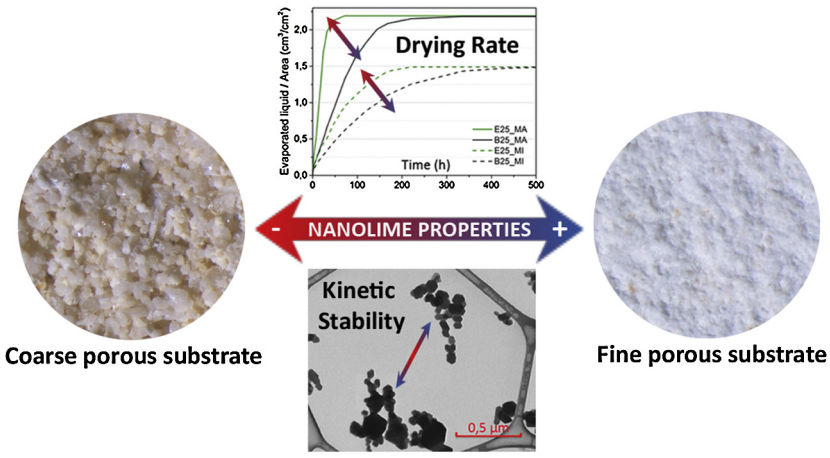
G. Borsoi [a,*], B. Lubelli [a,b], R. van Hees [a,b], R. Veiga [c], A. Santos Silva [d], L. Colla [e], L. Fedele [e], P. Tomasin [f]

[a] Heritage & Architecture Section, Faculty of Architecture, Delft University of Technology, Julianalaan 134, 2628 BL Delft, The Netherlands
[b] Division of Structural Reliability, TNO, Delft, Van Mourik Broekmanweg 6, 2628 XE Delft, The Netherlands
[c] Building Division, National Laboratory for Civil Engineering—LNEC, Av. do Brasil 101, 1700-066, Lisbon, Portugal
[d] Materials Division, National Laboratory for Civil Engineering—LNEC, Av. do Brasil 101, 1700-066, Lisbon, Portugal
[e] Construction Technologies Institute, National Research Council—CNR, Corso Stati Uniti 4, 35127 Padua, Italy
[f] Institute for Energy and Interphases, National Research Council—CNR, Corso Stati Uniti 4, 35127 Padua, Italy

HIGHLIGHTS

- Recover the cohesion loss of limestone through compatible nanolime consolidants.
- Synthesis and characterization of new nanolimes, dispersed in different solvents.
- Model relating solvent properties and porosity of the limestone to be treated.
- Solvent modification to improve in-depth deposition and effectiveness of nanolimes.

GRAPHICAL ABSTRACT



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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 was assessed by Uv–vis spectroscopy. The porosity of the limestones were determined by mercury intrusion porosimetry (MIP), measuring as well their moisture transport properties.

* Corresponding author.
E-mail addresses: gborsoi@lnec.pt, G.Borsoi@tudelft.nl (G. Borsoi).

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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-pore limestones, while for fine 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.

1. Introduction

Calcareous stone when exposed to the severe action of 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) [1–3]. Organic consolidants have no chemical compatibility with calcareous materials, and therefore can be potentially harmful for the treated substrate [1]; 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 [1,4]. Due to low effectiveness of limewater (a traditionally-used $Ca(OH)_2$ aqueous solution) alternatives have been looked for in the last decade, such as the use of alcoholic dispersions of calcium hydroxide nanoparticles, commonly known as *nanolimes* [5–7]. Nanolimes are colloidal alcoholic dispersions of calcium hydroxide nanoparticles with high stability and high lime concentration, facts that can improve the consolidating action [8,9]. Commercial nanolimes have nanoparticles with spherical to hexagonal shape and a size ranging from 50 to 600 nm [4–7,10].

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 preconsolidation and for the recovery of the superficial cohesion [4,5,8–13]. However, when mass consolidation is required, as in the case of thick renders, or porous stones, nanolimes often have poor effectiveness [14–16]. 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 [15,17].

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) [18]. 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 [18].

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.

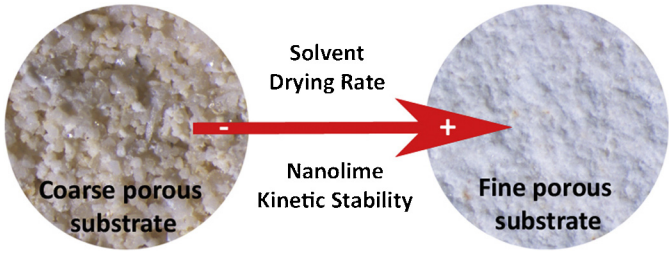

Fig. 1. Graphical representation of the conceptual model developed in order to link the porosity of the substrate with the kinetic stability and drying rate of the solvents (+ = higher, – = lower).

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. 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).

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 4.1.1) and Dynamic Light Scattering (DLS) (Section 4.1.2); the kinetic stability of the nanolimes was studied by Uv–vis spectroscopy (Section 4.1.2). The mineralogical composition of the limestones was determined by X-Ray Diffraction (XRD) (Section 4.2.1). Their porosity and pore size were measured by Mercury Intrusion Porosimetry (MIP) (Section 4.2.1); the moisture transport behaviour was further assessed by measuring absorption and drying (Section 4.2.2).

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.

In order to validate the model, the absorption and drying kinetics of the modified nanolime applied on the two limestone were analyzed (Section 4.4.1). The transport and deposition of the nanolimes applied on the two limestones were studied by phenolphthalein test (Section 4.4.2), optical microscopy (Section 4.4.3) and Scanning Electron Microscopy (Section 4.4.4). Finally, suggestions for fine tuning of the model are proposed in Section 4.3.

2. Materials and methods

2.1. Nanolimes characterization

2.1.1. Synthesis

Nanolimes were synthetized by solvothermal reaction of metallic calcium in water. Metallic granular calcium (99%, by