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

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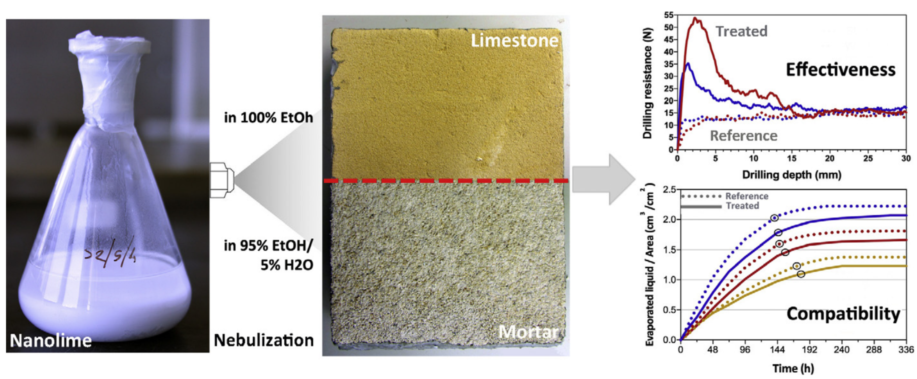
HIGHLIGHTS

- Recover the cohesion loss of limestone and lime-based mortar through compatible nanolime consolidants.
- Synthesis and characterization of new nanolimes, dispersed in different solvents.
- Solvent modification to improve in-depth deposition and effectiveness of nanolimes.
- Evaluation of the mechanical effectiveness and physical compatibility of the nanolime treatment.

GRAPHICAL ABSTRACT



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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.

1. Introduction

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 [1]. Powdering, sanding and chalking are among the most common decay patterns of calcareous materials [2,3]. This implies the loss of cohesion and thus of mechanical strength [4]. The mechanical properties of deteriorated materials can be recovered through the

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application of a consolidation treatment [4]. 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 [3,4].

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) [2,4,5]. 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 [2]. More specifically, the consolidant product should have a short- and long-term stability and decay patterns due to a 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 [6]. 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 [2,4,5,7]. In fact, they form disordered lattices of tetracoordinated silica, with poor chemical bonding to calcitic substrates and tendency to shrink and crack during drying [8].

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 [5,9,10]. Limewater is the most traditional consolidant product, with full chemical compatibility with lime-based substrates [11]; however, limewater has low effectiveness and, due to the low solubility of $Ca(OH)_2$ in water [5,9], 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 [12]. 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 [11].

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 [12–15]. 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 [16].

Nanolimes have proven to recover the superficial cohesion of many different materials [12,13,16,17], but they often show a poor effectiveness when mass consolidation is required, like for example in the case of decayed plasters, renders or lithotypes [1,17,18]. In fact, lime nanoparticles may sometimes deposit or partially migrate back towards the surface during drying, resulting in a poor consolidating effect in depth [1].

Previous research by the authors [19,20] 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 [21] 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 2.2) when applied on highly porous calcareous substrates: Maastricht limestone (sound and weathered) and a lime-based mortar (Sections 2.1 and 3.1). Based on previous research [19–21], 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 4.1). Both nanolime dispersions were applied by nebulization, a methodology widely used in practice (Section 3.2).

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) (Sections 3.4 and 4.3). The compatibility of the treatment was evaluated by measuring the effect of the consolidant on the moisture transport properties (water absorption and drying kinetics, Sections 3.5 and 4.4), on the total porosity by immersion (or open porosity, Sections 3.3 and 4.2) and on the aesthetic properties of the substrates (macro-evaluation by NCS scale, Sections 3.6 and 4.5).

2. Materials

2.1. Substrates

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

2.1.1. 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% $CaCO_3$) limestone, with high-porosity (50%) and a unimodal pore size distribution (35–40 μm) [21–23]. Despite its good durability, it may in some cases show decay in the form of loss of cohesion at the surface (e.g. powdering) [24]. 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 3.3.

2.1.2. 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 Ref. [6]. 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 [6,25]. 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 [26]. 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 [21].