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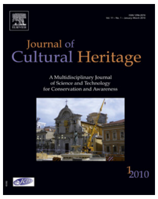

Original article

Understanding the transport of nanolime consolidants within Maastricht limestone

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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 potentialities 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 a 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 was 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.

1. Introduction

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) [1–3]. In fact, the concept of *compatibility* 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 [3].

Organic consolidants such as acrylic and epoxy resins have generally a low durability and compatibility when applied on calcareous substrates [1,2,4]. 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

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lack of more adequate alternatives [5]. 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 in theory much more recommended for limestone, because of their better chemical compatibility [5]. 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* [6,7]. Nanolimes are colloidal alcoholic dispersions with high stability and high lime concentration, facts that can improve the consolidating action [8,9]. 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 [7,8,10–13]. However, when mass consolidation is required, as in the case of render or stone, nanolimes often have poor effectiveness [14,15]. One of the reasons of their limited effectiveness is the accumulation of nanolime at or just beneath the surface [15,16], resulting in a poor consolidating effect in depth.

Nanolime transport mechanism within porous materials, as stone or renders, is barely 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.

2. 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 3.2.1). The effect of carbonation on nanolime deposition was assessed by carrying out the experiments both in air and in a nitrogen-rich environment (Section 3.2.2). 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 3.2.3).

3. Materials and methods

3.1. Materials

3.1.1. Substrate

The Maastricht limestone has been selected as substrate. It is a soft (1.3 to 5 MPa), yellowish limestone ($\approx$95% $CaCO_3$) [17,18], quarried in the Belgian and Dutch provinces of Limburg and used as building material in this part of Belgium and the Netherlands. The Maastricht limestone has a high-porosity (50%) and a unimodal pore distribution (35–40 μm) [19].

Despite its low mechanical strength, Maastricht limestone has generally shown a good durability, probably linked to the dissolution and re-precipitation of carbonates within the limestone pores network, when exposed to atmospheric agents [17,20]. This process was in the past enhanced 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 [21].

Table 1
Overview on the tests performed on different specimen types.

Test procedure	Specimen types identification						
	A1	D1	P1	P2	P3	TA	TB
Absorption test	☐						
Drying test		☐					
Phenolphthalein test			☐	☐	☐		
Macroscopical observation			☐	☐	☐		
Optical microscopy				☐	☐	☐	☐
SEM-EDS						☐	☐

SEM-EDS: scanning electron microscopy coupled with energy dispersive X-ray spectroscopy.

3.1.2. 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 nanoparticles concentration of 25 g/L and is dispersed in ethanol. Nanoparticles have hexagonal plate-like shape and size ranges between 50 and 250 nm [10].

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

3.2. Methods

Maastricht limestone core specimens (4 × 4 cm) were drilled from sound blocks. Different specimens were used for the different tests, as summarized in Table 1.

3.2.1. 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).

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) [22].

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.

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. 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.