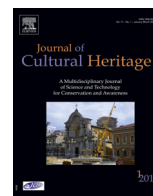




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Original article

## The biocalcarenite stone of Agrigento (Italy): Preliminary investigations of compatible nanolime treatments

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### ABSTRACT

Nanolime is a promising consolidant for the conservation of most historic structures thanks to its high compatibility with carbonate-based substrates. Nanolime can recover the superficial cohesion of deteriorated surfaces thanks to its potential to complete the carbonation process, recreating a thin network of new cementing calcium carbonate. In this paper, the nanolime was produced by an innovative, time and energy-saving and scalable method, and its efficacy was tested preliminarily on biocalcarenite stones from Agrigento. The stones characterization as well as the treatment effectiveness, in terms of protection against water and superficial consolidation, was investigated by several techniques such as X-ray fluorescence, X-ray diffraction, scotch tape test, water absorption by capillarity, mercury intrusion porosimetry, drilling resistance measurement system and colorimeter. Investigations showed that nanolime could guarantee a complete transformation in pure calcite together with a superficial consolidation and a reduction in water absorption.

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### 1. Introduction

Calcareous materials have been one of the main construction materials throughout the ages and proved to be very durable over the centuries. However, they may suffer several degradation processes (e.g. flaking of the surface, powdering and formation of small blisters) that can be recovered through the application of consolidants. Over the last century, several consolidants have been used: silicate-based products or organic consolidants, such as alkoxysilanes, acrylic, epoxy or vinyl resins, have been commonly used in restoration treatments, mainly due to their immediate strength enhancement and ease of application. However, the low physico-chemical compatibility, the lack of bonding between the mineral calcareous matrix and the consolidant material and even the deterioration of the organic consolidant itself, discourages their use and in some cases may compromise the conservation of the monument [1–3]. Inorganic consolidants and, among others, lime-based consolidants present the great advantage of their total chemical compatibility with the calcitic substrate, thanks to their aptitude to react with atmospheric carbonic diox-

ide to produce calcium carbonate (carbonation process). However, traditional lime-based treatments were considered to have some limitations, such as the reduced impregnation depth and the very slow rate of carbonation [4–6]. In order to reduce such limitations, in 2001 Ca(OH)<sub>2</sub> nanoparticles, dispersed in an alcoholic or hydro-alcoholic medium, (nanolimes) were synthesised. So far, nanolimes have been tested on mural paintings, stuccoes and natural stones, and on all the carbonatic-based substrate where a restoration treatment was required [5,7–20]. The efficacy of nanolime dispersions can be affected by several factors, such as the dispersion concentration, solvent type, porosity of the substrates to be treated and relative humidity (RH) conditions. It is commonly agreed that lower concentration of the suspensions (i.e. 5 g/L) help reduce the accumulation of the consolidating product near the surface and significantly improve the yield of carbonation in the pores [16,17]. Furthermore, it has been proved that the concentration and the number of treatments cycles have a significant influence on the strengthening effect, in relation to the stone porosity as well [16,18]. A percentage of residual water content in the dispersing medium (> 10% in volume) clearly enhanced the carbonation process [19]. Recent investigations suggests that nanolime penetrates well in porous materials, but it can be transported back to the surface as the solvent evaporates [20]. Moreover, the type of alcoholic solvent and the RH conditions seem to have an influence

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on the rate of the carbonation reaction, and the formation of different polymorphs of calcium carbonate [21,22]. Currently, nanolimes have been synthesized according to several routes, [10,23–26], where  $\text{Ca}(\text{OH})_2$  was rarely the only reaction product. Washings and purification steps were frequently needed to eliminate the by-products and/or organic compounds, leading to low yield and prolonged synthesis time. The development of a versatile, cost effective and up-scalable method can be essential to the success of introducing nanolime for widespread usage on carbonatic substrates. Recently, an innovative and patented method, based on the ion exchange process, was proposed [27]. This method worked at room temperature and ambient pressure, and it allowed producing, in few minutes and without intermediate steps, pure and crystalline  $\text{Ca}(\text{OH})_2$  nanoparticles in aqueous suspension. The resulting portlandite nanocrystals, less than 100 nm in size, are very reactive, with a complete carbonation process, forming pure calcite in few hours or up to 7 days, depending on solvent, concentration and RH of the environment [28–31]. In addition, the produced nanolime can be dispersed, at different solid concentrations, in mixed water/alcohol (W/A) mixtures in order to improve both the colloidal stability and/or the amounts of consolidant. Specifically, nanolime dispersions in a mixture of 50% water and 50% isopropanol in volume, (W/A=50%), demonstrated to be particularly suitable in optimizing the carbonation process [14,29].

The aim of the present work is to test the effectiveness of this nanolime as a compatible treatment on biocalcarene stones. Specifically, these stones constitute the building material used for most of the buildings of the “Valley of the Temples” in Agrigento – Sicily, Italy, characterized by a documented advanced decay [32–34]. The paper has been divided into three parts:

- synthesis and characterization of the nanolime;
- characterization of the biocalcarene stone from a physicochemical and mechanical point of view;
- testing, in a preliminary way, of different nanolime formulations by varying the solvents and the nanolime concentration. The evaluation of the treatment effectiveness in terms of protection against water and superficial consolidation was properly investigated.

## 2. Research aim

Colloidal  $\text{Ca}(\text{OH})_2$  nanoparticles (also called nanolime) are emerging as effective conservation material for all carbonatic-based substrate. Nanolime can recover the superficial cohesion of deteriorated surfaces, thanks to its potential to complete the carbonation process, recreating a thin network of new cementing calcium carbonate.

In the present paper we report, for the first time, results about the effectiveness of the treatments by a not commercial nanolime on biocalcarene stones from “Valle dei Templi” – Agrigento. In particular, the nanolime is synthesized in laboratory by our original, eco-friendly, one-step and scalable method that provides pure and crystalline nanoparticles in a reproducible way. Moreover, the simplicity and rapidity of this novel procedure provides an ideal opportunity to scale up the nanoparticles production in order to extend their uses in all the application fields where large amounts of such compatible consolidant should be requested. The effectiveness of the nanolime treatments, in terms of reduction of porosity, protection against water absorbed by capillarity and superficial consolidation, is investigated by means of several techniques. The physico-chemical and mechanical characterization of the untreated stones is reported too.

## 3. Material and methods

### 3.1. Synthesis and characterization of nanolime

$\text{Ca}(\text{OH})_2$  nanoparticles were synthesized by an anionic exchanges process, at room temperature and ambient pressure, by mixing under moderate stirring an anion exchange resin with an aqueous calcium chloride solution [27]. The supernatant water of the produced nanolime suspension ( $N_W$ ) was partially extracted and substituted with isopropanol or with 1-butanol. Three nanolime dispersions were prepared: two of them, named  $N_{50\%}$  and  $N_{50\%}^*$ , were characterized by a water/isopropanol mixture, (W/A=50%), and a solid concentration of 5 g/L and 10 g/L, respectively; and the third dispersion, named  $N_B$ , was characterized by a water/1-butanol mixture (W/A=5%) and a solid concentration of 5 g/L. In particular,  $N_B$  was considered to assess its influence on nanolime performance due to its slow evaporation rate. The size, shape and degree of agglomeration of the nanoparticles were determined by transmission electron microscopy (TEM, Philips CM200) and the crystalline phase was analyzed by XRD (PANalytical XPertPRO). Both TEM and XRD samples were prepared diluting the suspension in ethanol under nitrogen atmosphere to avoid the carbonation process. In addition, by means of XRD, we analyzed the carbonation reaction of each dispersion, taking 0.12 mL of nanolime sample, left to dry in air in room conditions ( $T=20 \pm 2^\circ\text{C}$ , R.H.= $50 \pm 5\%$ ), until complete solvent evaporation (about 20 minutes). XRD patterns were recorded in step size of  $0.026^\circ 2\theta$ , in the angular range  $10\text{--}70^\circ 2\theta$ . HighscorePlus software by PANalytical and ICSD and ICDD reference databases were used for the mineralogical identification and to perform the quantitative analysis (Rietveld refinement).

Kinetic stability of the produced suspensions was determined by turbidity measurements, analysing their absorbance at  $\lambda=600\text{ nm}$  by using UV/VIS Spectrophotometer (Lambda 2 Perkin-Elmer). Before the test, nanolimes were sonicated for 20 minutes (Ultrasonic bath by Ultra Sonik 300) to reduce the nanoparticle agglomeration. Measurements were taken for up to 2 hours. The KS % was measured in function of time and was calculated using the following formula:

$$\text{KS \%} = 1 - [(A_0 - A_t)/A_0] \times 100$$

where  $A_0$  is the starting absorbance and  $A_t$  the absorbance at time  $t$ , both evaluated at wavelength 600 nm [35]. The relative kinetic stability (KS %) decreases as result of the nanoparticle settling; values range from 0 (unstable dispersion) to 100 (not settling of the nanoparticles).

### 3.2. The Agrigento's biocalcarene

The stones used in this work, which were obtained from the local quarry of Villaseta, have similar characteristics to the ones used for the construction of the Temples [36]. Chemical, mineralogical and physical features of the stones were studied using different techniques. A general examination was performed using a stereomicroscope (SM, Leica Stereozoom S8APO). The chemical and mineralogical composition was determined by X-Ray Fluorescence (XRF, Philips PW2440), X-Ray Diffraction (XRD, PANalytical XPert PRO) and Attenuated Total Reflectance – Fourier Transform Infrared, (ATR-FTIR, Thermo Nicolet Nexus instrument). In particular, XRF samples were prepared as FP pellets. For XRD measurements, stone samples were milled and sieved through a  $50\ \mu\text{m}$  mesh and placed over a XRD zero-background sample holder; the patterns analysis was performed as reported above. FTIR spectra were collected by 64 scans in the range  $400\text{--}4000\text{ cm}^{-1}$  at a spectral resolution of  $4\text{ cm}^{-1}$ . The obtained FTIR spectrum was identified using the Infrared and Raman users Group (IRUG) libraries, the HR Hummel Polymer and Additives library as well as the ASTER

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