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Use of diluted $\text{Ca}(\text{OH})_2$ suspensions and their transformation into nanostructured CaCO_3 coatings: A case study in strengthening heritage materials (stucco, adobe and stone)

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ABSTRACT

In the conservation of heritage materials, the effectiveness of *diluted* nanolime suspensions in consolidating surfaces is scarcely explored. This paper aims to examine the surface modification of stucco, adobe and stone by deposition of $\text{Ca}(\text{OH})_2$ nanoparticles. The nanoparticles were applied in five consecutive coats and transformed into CaCO_3 by atmospheric CO_2 creating a compatible coating with the surface. The coatings were studied by erosion tests (pull-off tests) and examined by scanning electron microscopy (SEM) and optical microscopy. The tests confirmed the surface resistance was clearly improved due to formation of nanostructured cementing CaCO_3 coatings. In addition, the coatings did not practically alter the surface colour due to the diluted nature of the suspensions. To conclude, $\text{Ca}(\text{OH})_2$ nanoparticles-based coatings are appropriate solutions to extend the durability of traditional heritage materials, such as stucco, adobe or stone.

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1. Introduction

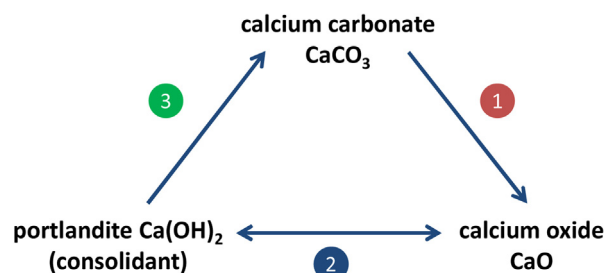
The use of protective coatings is gaining more and more importance in heritage conservation [1–4]. The chemical similarity between the treated surface and the coating is one of the most important aspects in consolidation [5,6]. In this regard, $\text{Ca}(\text{OH})_2$ nanoparticles (nanolime) can be used for consolidating the surface of calcareous materials [6]. Several authors have reported on the synthesis, stability and application of $\text{Ca}(\text{OH})_2$ nanoparticles [7–13]. The suspensions can be stabilised by means of surfactants, short-chain alcohols and sometimes, hydro-alcoholic mixtures [1,9–11]. Nevertheless, important aspects like the *concentration* and purity of $\text{Ca}(\text{OH})_2$ nanoparticles are not explicitly addressed in the scientific literature. The concentration of $\text{Ca}(\text{OH})_2$ is critical for the stability of the suspension, the penetration depth and also, the colour alteration of the surface. In general, *diluted* suspensions are more stable since they are less prone to agglomeration and sedimentation. In addition, diluted nanolime suspensions can be more efficient than concentrated ones as reported by Daniele and Taglieri

[12]. Finally, the lower the nanoparticles concentration the lower colour alteration of the surface.

The synthesis of $\text{Ca}(\text{OH})_2$ nanoparticles can be performed by a precipitation reaction from CaCl_2 and NaOH as reported by several authors [7,9,10,14]. The reaction yields a colloidal precipitate of $\text{Ca}(\text{OH})_2$ and soluble NaCl . The salt must be carefully extracted using appropriate purification methods to avoid efflorescence formation at the surface of heritage materials. After that, the isolated precipitate is dispersed in organic solvents (e.g. alcohols) producing stable suspensions [1,2,9–11,15].

In the maintenance of porous surfaces, laser techniques are used to remove patinas caused by weathering, such as crusts or biological deposits [16–20]. However, laser cleaning is a partially destructive technique that may alter both the surface colour and texture [18–20]. The use of coatings may prevent the surface weathering, thus reducing the accumulation of patinas and the cleaning frequency. In this way, calcareous materials like stuccos or limestone can be consolidated with chemically compatible coatings containing $\text{Ca}(\text{OH})_2$ nanoparticles [5,6,11]. The principle of consolidation is based on a *carbonation* reaction between $\text{Ca}(\text{OH})_2$ and atmospheric CO_2 to form insoluble CaCO_3 (Fig. 1). The consolidation efficiency is greatly affected by atmospheric factors, such as temperature and relative humidity [2]. Besides, the coating's penetration and CO_2 diffusion through the external pores are important factors to increase the efficiency of the treatment.

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- 1 Decarbonation (thermal decomposition of carbonates): $\text{CaCO}_3 + \text{heat} \rightarrow \text{CaO} + \text{CO}_2$
- 2 Hydration: $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$ or dehydration: $\text{Ca(OH)}_2 + \text{heat} \rightarrow \text{CaO} + \text{H}_2\text{O}$
- 3 Carbonation with atmospheric CO_2 : $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$

Fig. 1. Lime cycle and chemical reactions involved in the process. The reinforcing nature of *nanolime* suspensions is explained by a carbonation reaction between Ca(OH)_2 and CO_2 .

This paper is focused on the consolidation efficiency of *diluted* coatings made of pure Ca(OH)_2 nanoparticles dispersed in 2-propanol. The nanoparticles were synthesised in a special reactor controlling the temperature, atmosphere (N_2), purity and addition rate of the reagents. The morphological features of the nanoparticles were examined by TEM and pull-off tests confirmed the surface resistance was clearly improved in coated samples. Microstructural examination revealed formation of new CaCO_3 coatings filling external pores and voids. Finally, the colour remained practically unaltered and the nanoparticles penetrated up to several mm into the studied substrates.

2. Materials and methods

2.1. Synthesis of Ca(OH)_2 nanoparticles and TEM examination

Fig. 2 shows the reactor used in the synthesis of Ca(OH)_2 nanoparticles generated by mixing CaCl_2 and NaOH solutions. The reactor was filled with 50 ml of a NaOH solution and CaCl_2 was added drop by drop from an addition funnel at a rate 1 ml/min, approximately. Milli-Q water ‘type I’ and N_2 atmosphere were used to increase the purity of the precipitate. The temperature was fixed at 70 °C and the colloidal mixture was magnetically stirred throughout the synthesis. The precipitate was cooled to laboratory temperature, kept under N_2 atmosphere (Fig. 2), washed with Milli-Q water, centrifuged and dried. The solid phase was analysed by XRD (Bruker D8 Advance) at 40 kV and 30 mA using $\text{CuK}\alpha$ radiation and the spectra were evaluated with DIFFRAC-EVA and powder diffraction file database PDF4+ (ICDD, 2015).

Diluted suspensions were prepared adding 0.5 g of Ca(OH)_2 to 100 ml of dried 2-propanol (5 g/L). After this, the nanoparticles were dispersed by sonication (20 min) in N_2 atmosphere and stored in hermetically closed flasks using Parafilm®. The nanoparticles were examined by TEM using a high-resolution TEM microscope JEOL JEM-2100 at an accelerating voltage of 200 kV. For TEM examination, sonicated samples containing Ca(OH)_2 nanoparticles were diluted ten times, deposited on 200 mesh grids and rapidly introduced in the chamber of the microscope.

2.2. Samples preparation

Calcium hydroxide, lime type CL-90 [21], and calcitic aggregates provided by Reverté Minerals were used for confectioning lime stucco mortars (Fig. 3a). The grain size of the aggregates ranged from 10 μm to 2 mm and the water mixing was adjusted to obtain adequate workability (19.5% v/v). The mortars were spread out on 12 × 24 cm ceramic tiles at a thickness of 10 mm (Fig. 3b–c). The samples were cured in a climatic box at 20 °C and 90% RH for 48 h

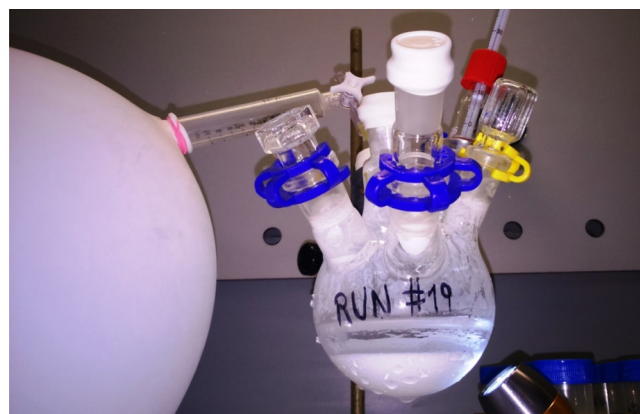


Fig. 2. Reactor containing the synthesised solid, Ca(OH)_2 , kept under N_2 atmosphere.

and, after that, they were stored in laboratory desiccators (23 ± 1 °C and 65% RH) to complete 28 days of curing. The amount of lime was 20% v/v with respect to the whole mortar, which is a normal dose in traditional stuccos (1:4). The adobe specimens were prepared with the same aggregates, using earth as binder (10% w/w) as usual in adobe mixtures. Similarly to the above procedure, the samples were spread out on ceramic tiles; softly dried at 50 °C for 48 h and left to cure for the remaining 26 days under laboratory conditions. The stone specimens were extracted from a sane *Tabaire* block using a 75 mm diameter driller. The resulting cores were cut to obtain sub-samples of 10 mm height and 75 mm diameter as shown in Fig. 3d. The stone is a soft calcarenitic material quarried from Roman times in Spain (Fig. 3e–f). As many other soft rocks, this stone needs consolidation to preserve it from weathering [11].

2.3. Surface resistance and microstructural examination of coatings

The samples were externally coated with diluted suspensions of Ca(OH)_2 (5 g/L). The suspensions were sprayed with an airbrush at a distance of 7 cm measured from the specimens’ surface. The treatment was applied in five consecutive coats leaving 5 min for alcohol evaporation after each coat (Fig. 3e). The internal pressure of the airbrush was regulated at 1.3 bar with a compressor attached to the device [22,23]. After that, the Ca(OH)_2 coatings were left to cure under laboratory conditions (23 ± 1 °C and 90% HR) for 7 days to allow carbonation to happen.

The surface resistance of the deposited coatings was also studied by erosion tests according to the ASTM D3359-08 standard [24,25]. The adhesive strips were weighed before and after conducting the tests with a resolution of ± 0.000001 g. Fifteen data were recorded per sample and the amount of removed material was expressed in $\mu\text{g}/\text{cm}^2$. Reference specimens of stucco, adobe and stone were used for comparative purposes in all the experiments.

The treated materials were metallised with Au and examined by SEM to study the coatings deposited on the surface. The images were captured in secondary electron mode at an accelerating voltage of 5 kV using a Hitachi S-3500N microscope. CaCO_3 coatings are difficult to distinguish from the original components that are often present in calcareous rocks and stuccos. Thus, the coatings were separately examined by SEM using flat cardboards to study both the morphological aspects and thickness of CaCO_3 coatings. The coatings were also studied by optical microscopy using a Dino-Lite AM7115MZT-EDGE microscope equipped with adjustable magnification, polarizer filter and a resolution of 5 Megapixels. The images were captured with DinoCapture 2.0 software to study the coating’s distribution on the surface.

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