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Cost-effective and sustainable synthetic procedure for aqueous hydroxide/oxide nanoparticles dispersions

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Introduction

The use of nanotechnology is gaining an increasingly attention, particularly in the field of Cultural Heritage conservation, but at now nanomaterials are long way from being routine treatments due to their production processes, often requiring non ambient temperature/pressure with time and energy consuming and low specific yield of production, or to the fact that nanoparticles (NPs) pose concerns regarding human health and environmental risks also in relation to their dispersing medium.

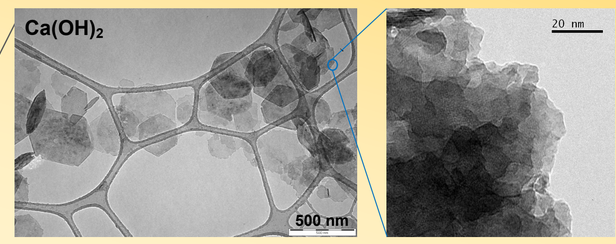
Recently, **we proposed a cost-effective, sustainable and patented synthetic procedure,** allowing us **to produce calcium hydroxide NPs (nanolime), directly in aqueous dispersion,** overcoming the main limitations of synthesis processes found in literature and giving us **the possibility to scale up the NPs production from laboratory to the on-site applications.** This eco-friendly and time-energy saving route is based on an ion exchange process, operates at room temperature, starts from cheap or renewable reactants, without intermediate purification procedures, so reducing the time of synthesis and greatly improving the yield of production. The **produced NPs** appear **pure**, **crystalline** with a **high reactivity**, assuring a complete carbonation process, **in form of pure calcite**, in few hours respect to the commercial products. The aqueous nanolime-based treatments are successfully employed for the conservation of Agrigento's biocalcarenites and they were tested, for the first time, in an on-situ application for the consolidation of an historic mortar, showing a good consolidation effectiveness, no chromatic alteration of the treated surfaces and safety health and environmental conditions. Finally, an innovative and sustainable synthetic procedure, recently patented, to produce iron oxide NPs in aqueous suspension is presented. The synthesis process allows producing both magnetite, maghemite and ferrihydrite NPs characterized by a low toxicity, high stability and unique properties, making them ideal for a wide range of applications such as pigments, gas sensors, catalysts, magnetism, lithium ion batteries, electrochemical capacitors and biomedical field.

Cost-effective and sustainable process for the production of Calcium Hydroxide NPs

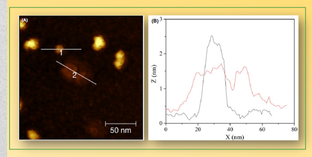
("Synthesis of $Ca(OH)_2$ nanoparticles by means of ion exchange process", *European Patent EP2880101.2016*)

The synthesis process allows to produce **pure and crystalline NPs,** with the **following advantages:**

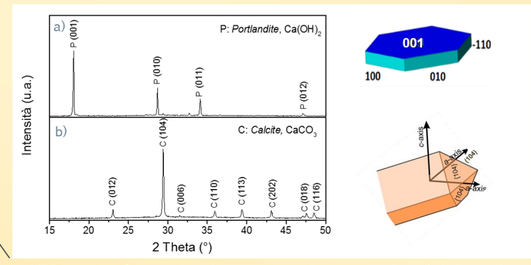
- **Reaction in water at room temperature and pressure**
- **Cheap and renewable reactants**
- **One-step procedure** (without intermediate purification procedures)
- **Reduced time of synthesis (few minutes)**
- **High yield of production**
- **Scalable route for large amount of NPs production** (from few grams to hundreds grams in the same time without changing the characteristics of the obtained product)
- In relation to the specific application, **both the concentration and the dispersing medium** (from water to alcohol) **can be varied**



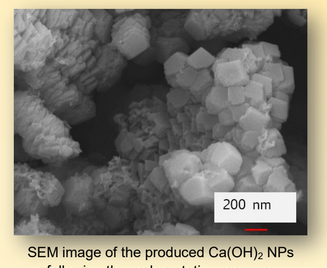
TEM images of the produced $Ca(OH)_2$ NPs, showing a lamellar and hexagonal shape. Each lamella seems to be composed by primary NPs less than 10 nm.



From AFM images the single $Ca(OH)_2$ NPs show a tickness < 3 nm.



XRD spectra of the produced aqueous nanolime suspension. a) drying under nitrogen athmosphere; b) after about two hours of air exposure time (RH < 50%)



SEM image of the produced $Ca(OH)_2$ NPs following the carbonatation process.

Extensive applications of Calcium Hydroxide NPs dispersed in aqueous medium

ECO-COMPATIBLE TREATMENTS ON AGRIGENTO'S BIOCALCARENITE STONES

The effectiveness of the produced aqueous $Ca(OH)_2$ NPs dispersion, as a green and compatible treatment, is evaluated for the superficial consolidation of biocalcarenite stones.

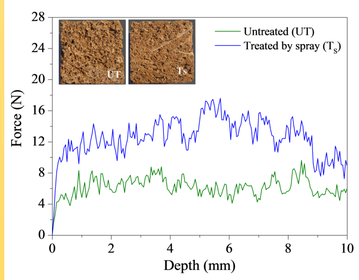
Specifically, the stones constitute the building material used for most of the buildings of the "Valley of the Temples" in Agrigento - Sicily (Italy), characterized by an advanced decay

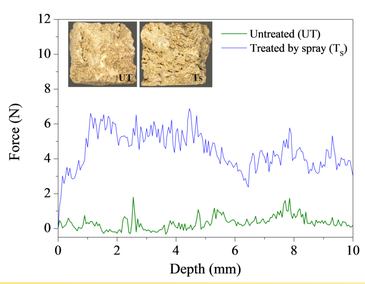
*The **aqueous dispersion** was applied at a **$Ca(OH)_2$ concentration** of **5 g/l**, **until stone saturation**, providing about 150 mg of product for each stone*

We investigated the influence both of the application procedure (**brush** and **spray**) and of the dispersing medium (**alcohol**, **water/alcohol** and only **water**) on the treatment effectiveness.

The **best results** were obtained by using the **spray technique** and the **water as dispersing medium**, revealing:

- **absence of significant white glazing,** visible only by the microscopic observations
- a good **protective efficacy**, both in terms of reduction of water absorbed by capillarity (up to about **20 %)** and in the kinetics of capillary absorption (ΔCA up to 60%).
- **a good increase** of the **superficial cohesion** of the treated stones up to about **85%**
- **a significant mechanical strength increase** up to 10 mm of depth, particularly evident in the most degraded samples.



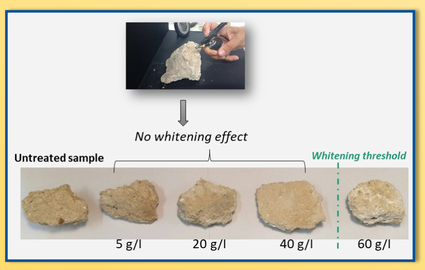


GREEN NANOLIME TREATMENT TAILORED TO CONSOLIDATE THE ORIGINAL MORTAR OF A MEDIEVAL BUILDING

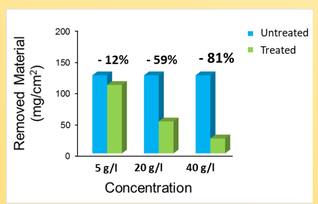
Thanks to the possibility, provided by our patented synthetic route, to scale up the NPs production, we performed the first extensive on-situ application of the nanolime, dispersed in aqueous medium, for the consolidation of the mortar of the main façade of a historic palace "Pica Alfieri" in the center of L'Aquila (Italy).

The nanolime-based treatments were preliminarily tested in laboratory, on the original mortar samples taken from the most degraded areas of the façade. Both the application procedure and the suspension concentration were varied, giving a special attention to limit the chromatic alteration of the treated surfaces .

As required from the operators, the dispersions must be applied on the mortar in ***a single treatment,*** so we decided to apply the ***aqueous nanolime suspension*** by ***aerograph nebulization***, by considering different $Ca(OH)_2$ concentrations.

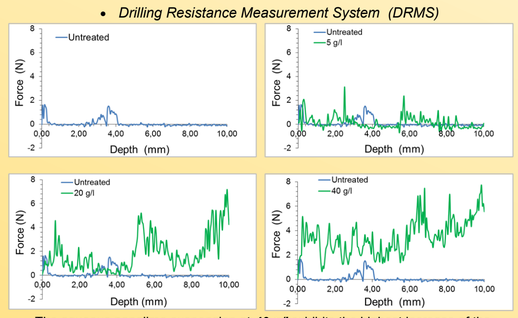


- *Surface adhesion test (STT)*



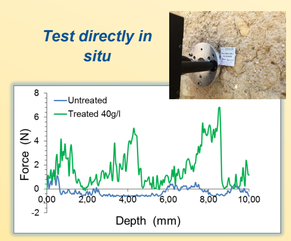
The aqueous nanolime suspension at ***40 g/l*** reveals the highest increase of the superficial cohesion of the treated material

- *Drilling Resistance Measurement System (DRMS)*



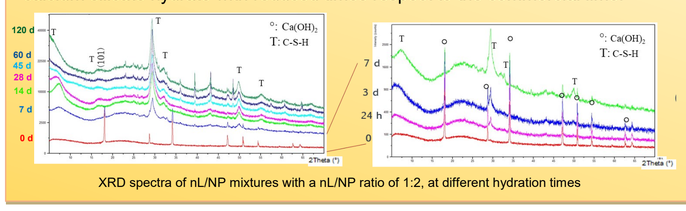
The aqueous nanolime suspension at ***40 g/l*** exhibits the highest increase of the superficial resistance up to al least 10 mm.

Test directly in situ

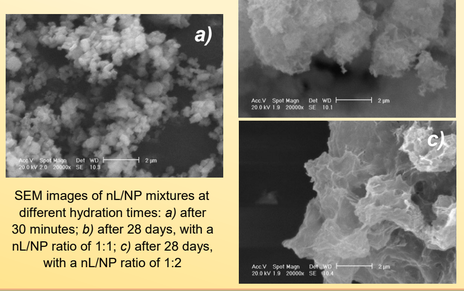


NANOLIME-BASED MIXTURES WITH NATURAL POZZOLAN

Recently, we address ourselves to study the reaction between the produced aqueous nanolime suspension (nL) and the natural pozzolan (NP), considering different nL/NP ratios.The small $Ca(OH)_2$ particles dimensions and their high reactivity tends to promote the reaction with NP, so forming significant amount of calcium silicate hydrate with reduced times respect to the commercial lime.



XRD spectra of nL/NP mixtures with a nL/NP ratio of 1:2, at different hydration times



SEM images of nL/NP mixtures at different hydration times: *a)* after 30 minutes; *b)* after 28 days, with a nL/NP ratio of 1:1; *c)* after 28 days, with a nL/NP ratio of 1:2

FUTURE DEVELOPMENTS

Starting from our cost-effective, sustainable and up-scalable method we will set up a pilot plant to scale NPs' production from lab to industry and to define, optimize and test protocols for extensive applications.

Some References

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[2] Taglieri G, Daniele V, Macera L, Mondelli C, Nano Ca(OH)2 synthesis using a cost-effective and innovative method: Reactivity study, J.Am.Ceram.Soc. 100(12), 5766–5778 (2017)

[3] Daniele V, Taglieri G, Macera L, Rosatelli G, Otero J, Charola A.E, Green approach for an eco-compatible consolidation of the Agrigento biocalcarenites surface, Construction and Building Materials 186, 1188–1199 (2018).

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[5] Macera L, Taglieri G, Daniele V, Passacantando M, D'Orazio F, Nano-Sized Fe(III) Oxide Particles Starting from an Innovative and Eco-Friendly Synthesis Method, Nanomaterials 10, 323 (2020).