# NANOLIME FOR CONSERVATIVE SURFACES TREATMENTS: METHODS OF SYNTHESIS AND CHARACTERISATION

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## Introduction

Thanks to conversion of lime into calcium carbonate, lime water and milk are usually adopted for conservative surfaces treatments. However, some critical aspects concerning the treatments reduced penetration depth, the binder concentration and the incomplete lime carbonatation process still represent undesired limits and hindrances. In order to improve lime treatments, $Ca(OH)_2$ particles with submicrometric dimensions (*nanolimes*) are recently introduced in Cultural Heritage conservation (frescoes, stuccoes,..) [1]. Lime nanoparticles are typically produced by a chemical precipitation process in supersaturated aqueous solutions of the reactants (calcium chloride and sodium hydroxide). To improve nanolime particles dispersion, use of alcoholic solutions in place of aqueous ones was adopted. An alternative nanolime synthesis process involving use of a specific surfactant is presented. The aim of the present work is to analyse the nanolime carbonatation process in relation to some parameters, such as the environmental relative humidity (RH), the suspension concentration and water content respectively. Nanoparticles characterisation according to different techniques including X-ray diffraction (XRD), scanning and transmission electron microscopy (SEM and TEM), and electron diffraction measurements (ED) have been reported. After performing natural lithotypes surfaces treatment with nanolime suspensions, SEM analyses and capillarity tests were performed to evaluate treatment effectiveness [2-3].

## Experimental

*Materials*

Calcium chloride ($CaCl_2$), sodium hydroxide (NaOH), 2-propanol "pro analysi", and deionised water. In case of synthesis process B) also surfactant Triton X-100 have been used.

Two nanolime syntheses process have been followed. According to method A), synthesis have been carried out by adding (drop wise) a NaOH solution into a $CaCl_2$ solution maintained at 90°C. According to method B) Triton X-100 surfactant was previously added to the two base solutions that were later mixed all at once at the fixed temperature of 90°C. The obtained suspension was compared to other ones prepared changing the Triton concentrations added. Both in case of synthesis A) and B), the replacement of given volumes of water with 2-propanol was performed. After exposure of different nanolimes suspensions to fixed environmental conditions (T = 20°C, RH = 70% and 80 % respectively) XRD measurements were performed to determine crystalline phases (data from JCPDS), and to evaluate completeness of the lime carbonatation process. Two different values of the suspension concentration (10 and 1 mg/ml respectively), and various suspension water content (from 100% to 1% in volume) were considered in these investigations. In order to evaluate the protective effectiveness of nanolimes treatments, produced nanolimes have been applied on several lithotypes. First, nanolime alcoholic suspensions were applied on the dry and clean stones surface. Subsequently, Scotch Tape Test (STT) [4] capillarity test [5], and SEM analyses were performed to evaluate treatment efficiency and its penetration depth.

## Results and discussion

TEM micrographs in Fig. 1 shows a typical agglomerate of $Ca(OH)_2$ nanoparticles synthesized according to method A) and kept in plain water suspension: single nanoparticles size was found to range from 50 to 600 nm and ED measurements revealed typical crystalline features of particles.

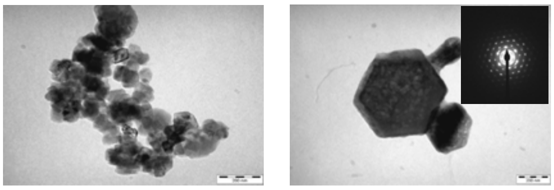

Fig.1 TEM image from aqueous sample (method A)); in the square at the top, ED electron measurement is reported too (*scale bars: 200nm*)

Fig.2 refers to nanolime particles synthesized according to method B) and kept in alcoholic suspensions. In this case single lime particles smaller than 50 nm were recognized, most of which characterised from spherical shape as in [6]. In addition, larger nanoparticles were characterised from regular hexagonal shape and relatively low thickness so to be quite transparent to the electron beam.

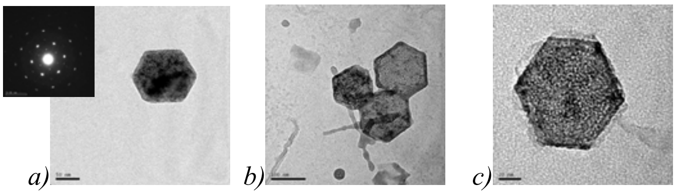

Fig.2 TEM image from method B (alcoholic sample)): a) 0,1g Triton added (*scale bar: 50nm*); b) c) 0,4g Triton added (*scale bar: 100nm and 20nm respectively*)

Elaborating XRD measurements, the ratio among $CaCO_3$ peak areas and the spectrum total area was assumed as index of the carbonatation process efficiency (*yield*). Results showed that degree of carbonation was higher in case of higher environmental relative humidity (RH 80%) (Table 1) and for alcoholic lime suspensions characterised from higher water/alcohol ratios (Table 2).

Table 1. Yield values for different RH conditions and relative exposition time (30% W)

| RH (%) | Time (hours) | Yield (%) |
|---|---|---|
| 70 | 3 | 45 |
| 80 | 3 | 60 |
| 80 | 24 | 100 |

Table 2. Yield values in relation to W% (40% RH)

| % W | Yield (%) |
|---|---|
| 100 | 45 |
| 50 | 70 |
| 30 | 30 |
| 10 | 12 |
| 1 | 1 |

This second result is probably due to the fact that although $CO_2$ diffusivity is higher in alcohol than in water, $Ca(OH)_2$ dissociations and, consequently, $CaCO_3$ formation, is only possible in water.Benefit in water replacement with alcohol was instead confirmed by the suspension with 50% water, where particles dispersion and $Ca(OH)_2$ solubility together maximised the carbonatation process efficiency.
Concerning nanolimes treatments on natural stones, results from capillarity test and STT confirmed that absorbed water ($\Delta Q$) and materials removed from the surface ($\Delta M$) were clearly reduced after treatment (Table 3). Remarkable results were obtained on Pietra Serena stone. Penetration of the nanolime treatment into the stone micropore system is confirmed by SEM images in Fig 3: pores surface coating reduces capillarity water absorption, macropore occlusion is avoided and the natural stones porosimetric system is preserved.

Table 3. STT and capillarity tests results

| **Lithotypes** | **ΔM [%]** | **ΔQ [%]** |
|---|---|---|
| Basalto | -87% | -20% |
| Limestone | -89% | -12% |
| Perla d'Abruzzo | -78% | -13% |
| Pietra di Lecce | -89% | -10% |
| Pietra Serena | -87% | -55% |

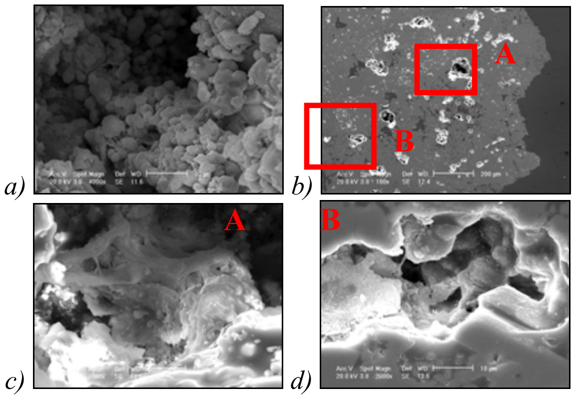


Fig. 3 SEM micrographs on Pietra di Lecce: a) untreated sample; b) treated stone section *(scale bar: 200μm)*; c), d) pores A and B, respectively *(scale bar: 10μm)*.

## Conclusion

Use of surfactant can lead to synthesis of smaller nanolime particles. $Ca(OH)_2$ nanoparticles tend to be more dispersed in alcoholic medium than in plain aqueous suspensions. Nanolime carbonatation process is favourited by high RH conditions and is affected by the suspension water/alcohol ratio. Use of nanolime suspensions was confirmed to be quite a promising in Cultural Heritage conservation, with tested natural stones showing a clear reduction in capillarity absorbed water and improved surface compactness and after nanolime treatments.

## References

[1] Salvadori B., Dei L.; *Langmuir*, **17**, 2371-2374, 2001.
[2] Daniele V., Taglieri G., *J.Cult. Herit.*, **11**, 102-106, 2010.
[3] Daniele V.; Taglieri G.; Quaresima R., *J.Cult. Herit.*, **9**, 294-30, 2008.
[4] ASTM D3359-02, ASTM International, 2002.
[5] NORMAL, UNI 10859, 2000.
[6] Ambrosi M.; Giorgi R.; Salvadori B.; Dei L., *1st Int. Workshop on: Science, Technology and Cultural Heritage,* Venice (Italy) 2004.