Deposition of modified nanolimes within calcareous substrates

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Nanolime

**Use:** (Pre)consolidation of historical porous materials

- Recover the lost cohesion
- Spraying
- Brushing
Nanolime

Advantages
• Good compatibility with calcareous materials
• High durability
• High active surface, reactivity, colloidal stability and calcium content
• Operator and environmental friendly

Limits:
• Limited in-depth effectiveness
• Superficial whitening
• Controversial results & few documented case studies on stone consolidation
Research aim

Possible reasons of limited in-depth deposition

- Limited penetration,
  - back-migration,
  - fast carbonation,
  - colloidal stability

• Understanding transport and deposition of nanolime is necessary for improving its effectiveness
Materials & Methods

Substrate: **Maastricht Limestone**

- Lost of cohesion (e.g. powdering)
- 90-95% CaCO$_3$
- Model material (unimodal)
- Widely used in Limburg (NL and Belgium)

Nanolime: **Calosil E25**

- Opal alcoholic dispersions of lime nanoparticles
- Nano to submicron dimension (<50 to 400nm)

Methods:

- **Materials characterization** (MIP, XRD, Uv-Vis, SEM-EDS)
- **Transport** (absorption-drying kinetics)
- **Deposition** (phenolph. test, SEM, AFM, OM)
Characterization of Maastricht limestone

MIP

Moisture transport: Absorption/Drying kinetics of water

XRD

WAC = 1.94 g/cm²s¹/²

≈ 96/120 h
Characterization of Nanolime E25

- **Liquid phase**
- **Dried**

30 mins ultrasonic bath (minimize aggregation phenomena)

- **Uv/Vis**
- **Colloidal stability**
  - Stable/homogeneous up to > 1 week
Transport of nanolime: absorption kinetics

- Fast absorption (< 5mins):
  - water faster than EtOH and E25 → differences in the surface tension and viscosity (presence of nanoparticles)
Transport of nanolime: drying kinetics

50% RH, 20°C

Evaporation rate:

48-72h for E25 and EtOH, step I drying ends at 24h: then, transport by vapour, (nanoparticles can not be transported anymore)
Nanolime: cause(s) of limited in-depth deposition

1. Limited penetration during absorption?
2. Fast carbonation hindering the transport?
3. Back-migration to the drying surface?
1. **Limited penetration** during absorption??

Cross section: **Phenolphthalein test**

❌ No, nanolime penetrates within Maastricht (coarse porous material)
2. Fast carbonation hindering the transport?

- The distribution of nanolime is similar in N\textsubscript{2} and in air
- fast carbonation is not the reason of the limited penetration
3. Transport back to the drying surface?

Setup

![Diagram of transport process]

- Partial back migration is the main reason of the limited deposition in depth.
3. Distribution of nanolimes at different depths

- Nanoparticles are present in depth --> confirm penetration in depth during absorption.
- Accumulation at the drying surface (not at the absorption surface) --> back migration during drying.
3. **Transport back to the drying surface?**

→ **Higher mobility of smaller nanoparticles**
3. **Transport back to the drying surface?**

How to avoid the back-migration and accumulation at the drying surface and improve effectiveness?

The transport and deposition of the dispersions should be adapted to the transport properties of the substrate.

Can this be obtained by modification of the solvent?
New Nanolime - colloidal stability and drying rate

Dispersed Ethanol, isopropanol, butanol, water

![Uv-Vis](image)

Relative Kinetical Stability % vs Time (h)

- H25
- E25
- IP25
- B25

2 weeks

![DLS](image)

Mean Particle Size (nm) vs Time (h)

- B25
- E25
- IP25

![Drying rate](image)

Evaporated liquid/Area (cm^3/cm^2) vs Time (h)

- EtOH_MA
- IpOH_MA
- H2O_MA
- BOH_MA

![Graphs](image)
Depending on the pore networks:

‘Coarse pores’: moderate (kinetical) stability for a proper absorption, fast drying rate for a deposition in depth (without nanolime back-migration)

‘Thin pores’: high (kinetical) stability for a proper absorption, slower drying rate to enhance the deposition of the nanoparticle in depth.
Conclusions

• The main reason of limited in-depth deposition of nanolime in coarse porous substrates as Maastricht limestone has been identified in the back-migration of nanoparticles during drying.

• The high kinetical stability of nanolime dispersed in ethanol favors the back-migration of nanoparticles in coarse porous substrate

• Modifying the transport and/or the kinetic stability of nanolimes according to the properties of the substrate might improve the deposition in depth

• The modification of the solvent is a possibility to control transport and kinetic stability of nanolime in order to favour in-depth deposition.

• At the moment, experiments are going on in order to verify this possibility.
Thanks for your attention!

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Publications

Maastricht limestone:


Lime-based mortars:


Solvent modification (model): Journal of Colloidal Science and Interface
Application methodology: protocol and strategies

++ Effectiveness

++ Effectiveness
Synthesis of new nanolime (bottom-up fabrication)


3. ‘Dispersant method (TX100)’ (2012)
4. ‘Salvadori method’ (2011)