CRISTINA DE NARDI, GERALD ZIEGENBALG

# *Advancing Heritage Conservation: Evaluating Healing Agents for Mimetic Self-Healing Technologiesevaluating an innovative nanolime dispersion in 3D printed vascular self-healing systems*

## 1. Introduction

Climate change is subjecting our built heritage to increasingly severe hazards, highlighting the need for innovative masonry repair technologies to ensure long-term resilience. A range of traditional intervention strategies, such as repointing and bed joint reinforcement, are available to repair damage in masonry structures[1]. However, these methods have a limited lifespan and are often ineffective[2]. There is a growing interest in self-healing technologies for historic masonry, driven by the need to preserve heritage structures while maintaining their original materials and aesthetics. Incorporating self-healing properties helps minimise frequent repairs, reducing maintenance costs and ensuring the long-term stability of historic buildings. In this context, researchers are investigating different strategies, including bio-based healing agents[3], mini vascular networks in mortar[4], and autonomous crack repair mechanisms[5]. Choosing the right healing agent is essential for a vascular system's success. It must be stable over time, trigger self-healing moratrs, have low viscosity for efficient flow and crack penetration, be compatible with historic materials, and be non-toxic for environmental and construction safety. Nanolime, a dispersion of calcium hydroxide nanoparticles in alcohols, is widely used for consolidating historic masonry and modifying mortars or grouts[6]. Its small particle size allows deep penetration, but challenges such as rapid alcohol evaporation and formation of metastable carbonates require careful post-treatment. To enhance its effectiveness, nanolime can be combined with silicic acid esters (SAE)[7]. This combination improves surface consolidation by forming an adhesive bridge between calcium hydroxide and silica gel while also accelerating SAE hydrolysis.

This study evaluates the potential of an innovative nanolime dispersion, termed Adv-NL, created by combining the commercial product CaLoSiL® with SAE for use as a healing agent. Specifically, it aims to assess its suitability for encapsulation while meeting key requirements for self-healing technologies in built heritage contex: (i) long-term stability in liquid form, (ii) chemical compatibility with carriers to prevent alterations in their mechanical properties.

## 2. Materials and methods

Longevity tests were performed on tubular capsules (inner diameter = 4 mm, length 40 mm, double wall thickness 0.25 × 2 mm) printed from clear Polylactic acid (PLA) filament (2.75 mm in diameter) purchased from Verbatim®, using an Ultimaker2+® printer with a 0.25 mm nozzle. The tubular capsule design and the main printing parameters are reported in Figure 1.

---

1 Valluzzi et al. 2005.
2 Harding P. 2023.
3 Vučetić et al. 2023.
4 De Nardi et al. 2024.
5 De Nardi et al. 2017.
6 Rodriguez-Navarro et al. 2018.
7 Ziegenbal 2024.

| Printing parameters | |
|---|---|
| nozzle | 0.25 mm |
| layer height | 0.06 mm |
| support type | buildplate |
| bottom_layers | 8 |
| cool_fan_speed | 80 |
| infill_sparse_density | 100 |
| support_infill_rate | 2 |
| support_z_distance | 0.25 |
| top_bottom_pattern | grid |
| top_bottom_thickness | 0.06 mm |
| top_layers | 5 |
| wall_line_count | 16 |
| wall_thickness | 0.25 mm |
| xy_offset | 0 |

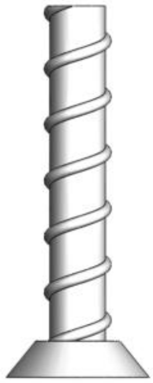

Figure 1. Design of tubular capsules and corresponding printing parameters.

Capsules were filled with approximately 0.7 mL of advanced nanolime dispersion (Adv-NL) provided by IBZ-Salzchemie GmbH & Co. KG (Germany), sealed with silicone, and broken at 7, 14, 21, and 28-day intervals to evaluate the physical condition of both the healing agent and the PLA polymer. Capsules were stored in laboratory condition (20° ± 5, RH ~ 45 %). Over 4 weeks, 12 were tested, with 3 opened at each interval.

## 3. Results

The results of the Adv-NL longevity tests are summarised in Table 1. It is important to note that changes in both the viscosity of the healing agents and the PLA polymer were assessed through visual inspection, providing only a qualitative approximation of any variations. The letters L, G, and S indicate the following states: Liquid (L) – no noticeable change, Gel (G) – beginning to exhibit solid-like behavior, and Solid (S) – fully solidified. The polymer's consistency was evaluated by breaking the capsules and observing the fracture behavior: Brittle (B) indicated a brittle rupture, while Ductile (D) suggested a more flexible failure, which was considered a sign of early polymer degradation.

From the results, it can be seen that the Adv-NL solution remained liquid throughout the 28-day period, without any noticeable change in viscosity. No significant alterations in the PLA polymer were observed, as it consistently exhibited brittle fracture behavior. However, a decrease in volume was detected ( ~10%), suggesting a possible partial absorption of the Adv-NL into the polymer matrix or gradual evaporation over time. This could indicate minor interactions between the healing agent and the encapsulation material, which may warrant further investigation to ensure long-term stability.

| Clear PLA capsules | Test duration (days) | | | |
|---|---|---|---|---|
| | 7 | 14 | 21 | 28 |
| Adv-NL | I/B | I/B | I/B | I/B |

Tabel 1. Longevity test of Adv-NL in clear PLA.

## 4. Conclusion

From the analysis of the results presented in this paper, the following main conclusions can be drawn:

-Advanced nanolime, combined with silicic acid esters (Adv-NL), demonstrates strong potential as a healing agent for self-healing technologies that rely on encapsulation, including vascular and mini-vascular networks.

-Adv-NL meets the essential criteria for these technologies, including maintaining low viscosity over time when encapsulated in PLA polymer capsules, without inducing any significant changes in the polymer. A slight volume reduction has been observed, suggesting partial evaporation/absorption.

**Acknowledgments**
This research was funded by the Leverhulme Trust ECF-2022-235.

**References**

Valluzzi MR, Casarin F, Garbin E, Da Porto F, Modena C. 2005, Long-term damage on masonry towers case studies and intervention strategies. In: 11th International Conference on Fracture ICF11. 5, 3253-3256.

Harding P . 2010, The Limits of Lime, Repointing a damp church tower in the Hebrides. Historic Churches.

Vučetić S, Čjepa D, Miljević B, Bergh J, Šovljanski O, Tomić A, Nikolić E, Markov S, Hiršenberger H, Ranogajec J. 2023. Bio-Stimulated Surface Healing of Historical and Compatible Conservation Mortars. Materials. 16(2).

De Nardi C, Gardner D, Jefferson T. 2024, Biomimicry in Built heritage: Mini Vascular Networks for Self-healing Lime-based Mortars. In: SUBLime Conference 2024 Towards the next Generation of Sustainable Masonry Systems: Mortars, Renders, Plasters and Other Challenges,152-153.

De Nardi C, Bullo S, Ferrara L, Ronchin L, Vavasori A. 2017, Effectiveness of crystalline admixtures and lime/cement coated granules in engineered self-healing capacity of lime mortars. Materials and Structures/Materiaux et Constructions, 50(4).

Rodriguez-Navarro C, Ruiz-Agudo E. 2018. Nanolimes: from synthesis to application. Pure and Applied Chemistry. 90(3).523-550.

Ziegenbal G. 2024. Nanolime State of the Art and Recent Developments. In: Towards the next Generation of Sustainable Masonry Systems: Mortars, Renders, Plasters and Other Challenges, 144-145.

Cristina De Nardi
Cardiff University, Queen’s Building, Cardiff CF24 3AA, United Kingdom
denardic@cardiff.ac.uk

Gerald Ziegenbal G
IBZ-Salzchemie GmbH&Co.KG, Schwarze Kiefern 4, 09633 Halsbruecke, Germany
info@ibz-freibereg.de