

AN OVERVIEW OF NANOLIME AS A CONSOLIDATION METHOD FOR CALCAREOUS SUBSTRATES

Jorge Otero ^{a,b}, A Elena Charola ^b, Carol A. Grissom ^b, Vincenzo Starinieri ^a

*jorge.otero@student.shu.ac.uk

^a Materials and Engineering Research Institute, Sheffield Hallam University, UK

^b Museum Conservation Institute, Smithsonian Institution, Washington DC, USA.

ABSTRACT

Ca(OH)₂ particles with submicrometric dimensions (nanolimes) represent one of the most promising consolidants for the conservation of calcareous substrates. The nanolime treatment is similar to the limewater technique, traditionally used for its durability and high compatibility with the calcareous matrix but requiring a large number of applications and not always yielding a highly effective consolidation. Since 2001, alcohol-based dispersions of Ca(OH)₂ nanoparticles have been synthesised to overcome the limitations of the limewater treatment. Nanolimes present the same high compatibility and durability of the traditional technique but superior properties in terms of higher consolidation, penetration and reactivity, and fewer side effects. Since their discovery, nanolimes have been investigated by several research groups with the aim of refining their synthesis process, properties and applications. This paper presents an overview of the most relevant literature about nanolime as a consolidant for calcareous substrates.

Key words: Nanolime; Calcium hydroxide; Consolidation; Lime-water; Conservation; Nanoparticles; Synthesis; Calcareous substrates.

1. INTRODUCTION

The recent development of nanoscience and nanotechnology has opened the way to new applications in many scientific fields, including that of the conservation of cultural heritage. One example of a nanomaterial developed over the last decades is the so-called “nanolime”, nanoscale particles of Ca(OH)₂, with potentially superior consolidation properties compared to traditional lime-based treatments. So far, nanolime has been studied mainly within the built cultural heritage conservation field.

Scientific investigations on nanolime began around the year 2000 at the University of Florence [Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (CSGI) or Center for Colloid and Surface Science], in Italy, with the first results on its synthesis and application for the conservation of wall-paintings published in 2001 (Ambrosi et al. 2001). The researchers in Florence modified the synthesis methodology several times by reactions in diols (Salvadori and Dei 2001), aqueous solutions (Ambrosi et al. 2001) or water-in-oil (w/o) micro-emulsions (Nanni and Dei 2003). In 2003, other research group (Ziegenbalg 2003) prepared nanolime from a heterogeneous-phase reaction, which was patented under the brand name Calosil®. Calosil® was the first nanolime product introduced in the market in 2006 (IBZ-Salzchemie GmbH & Co. KG) followed by Nanorestore® (CSGI) in 2008. With these products made available to the scientific community, several research groups in Europe began investigating the properties and consolidation efficacy of nanolime. Three main EU research projects, STONECORE (2008 - 2011), NANOMATCH (2011 - 2014) and NanoforART (2012 - 2015) have made significant contributions to understanding the technologies and preparing the way for a range of applications of nanolime in the conservation field.

Nanolime is used mainly to recover the cohesion between particles in calcareous substrates such as wall-paintings, limestone, lime mortar, etc. For decades during the past, organic and inorganic consolidants have been used for the consolidation of these substrates. The use of organic consolidants such as acrylic, epoxy, or vinyl resins has been very common in restoration treatments since 1960 (Dei and Salvadori 2006). However, the low compatibility with the substrate and poor aging and durability of these treatments may cause unwanted degradation processes, including cracking and aesthetic changes, and may interfere with future treatments. In contrast, inorganic-based consolidants such as barium hydroxide and limewater have a high physico-chemical compatibility with the substrate and good durability, although their use requires a large number of applications and the consolidation is not always highly effective. The effectiveness of the traditional limewater technique, transmitted from generation to generation of practitioners, has been controversial. Price's research (Price et al. 1988) concluded that the limewater technique does not produce a noticeable consolidation as most of the lime is deposited within the outer

2mm and the low amount of particles does not produce consolidating effect. Nevertheless, another research (Brajer and Kalsbeek 1999) demonstrated that a prolonged and uninterrupted application of limewater over 80 days produces a positive consolidation effect. However, this treatment is tedious and has to be repeated up to 40 times due to the low solubility of calcium hydroxide in water (1.7 g/L^{-1} at 20°C). Other limitations are the reduced penetration depth of the lime size-particles and the possible decay processes associated with the use of large amounts of limewater solution (salt movement, etc.). The use of nanolime in alcohol allows incorporation of larger amounts of lime into the treated substrate with far less water, yielding better penetration and faster carbonation (Ambrosi et al. 2001). This paper expands on exiting work (Otero et al. 2017) and reviews the considerable literature produced.

2. SYNTHESIS

Nanoparticles can be produced through either the top-down or bottom-up processes. In the top-down method the nanoparticles are created by "breaking" a bulk micro-scale particle until fragments in the nanometer range are obtained. This normally involves using a source of high energy in processes such as laser ablation, thermal decomposition or mechanical milling. In the bottom-up method, the nanoparticles are built atom by atom by chemical precipitation using several techniques for the deposition and crystal growth from vapour (Chemical Vapour Condensation (CVC)) and hydrogen plasma-metal reaction (HPMR) and liquid phases (micro-emulsions, solvo-thermal, etc.). Most calcium hydroxide nanoparticles are synthesized through the bottom-up reaction by chemical precipitation from a liquid phase.

A survey of different synthesis methods from literature is summarized in Table 1. In 1997, colloidal dispersions of calcium hydroxide in organic solvents were obtained (Delfort 1997) and, in 2000, CSGI-group (Giorgi et al. 2000) also obtained stable alcohol dispersions of $\text{Ca}(\text{OH})_2$ particles. Both researchers found that dispersions in alcohol are much more stable and able to incorporate larger amounts of particles than limewater. With the aim of preparing stable nanoparticles of $\text{Ca}(\text{OH})_2$, the researchers at CSGI carried out a series of studies based on the works of Matijevic group (Pe et al. 1998) in the field of colloids synthesis. They reported that nucleation of nanoscale particles is affected by reaction time, high temperature (above 100°C) and high degree of super saturation, and it can be achieved with slow

synthesis and peptization processes. In 2001, CSGI group (Dei and Giorgi 2001) obtained Ca(OH)_2 particles (1-2 μm) by a hydrolytic method at medium-high temperature (60°C) and super-saturation. In order to reduce the size of particles, they synthesized calcium hydroxide nanoparticles (30-60 nm) from diols, which allowed higher temperatures to be reached during the process (Salvadori and Dei 2001). However, this synthesis method proved to be time consuming and produced a low quantity of nanoparticles. In the same year, they successfully obtained highly reactive and colloidal sub-micrometer Ca(OH)_2 particles ($\pm 300\text{nm}$) via an homogeneous phase following the aqueous reaction $\text{CaCl}_2 + 2\text{NaOH} \rightarrow \text{Ca(OH)}_2 + 2\text{NaCl}$, heated up to 90 °C under supersaturation conditions (Ambrosi et al. 2001). But, this process has drawbacks: 1) slow mixing rates; 2) the necessity of removing by-product NaCl by washing; 3) low yield of nanoparticles production. Ca(OH)_2 nanoparticles (2-10 nm) were also obtained using w/o micro-emulsions (Nanni and Dei 2003), but low yield and high production time make this method less practical. The synthesis method developed by CSGI (Dei and Giorgi 2001; Ambrosi et al. 2001; Dei and Salvadori 2006), which was commonly named "drop by drop method", was also adopted by several research groups with the aim of refining the synthesis process and properties (Sequeira et al. 2006; Daniele and Taglieri 2010; Daniele et al. 2008). In 2013, the Taglieri team (Daniele and Taglieri 2012) managed to reduce the synthesis time while decreasing the particle size (<50 nm) by adding a surfactant (Triton X-100) in the initial aqueous solution. In other synthesis pathways based on CSGI researches, Bhattacharya (Bhattacharya 2010) obtained nanolime by hydrolysing calcium nitrate tetrahydrate [$\text{Ca(NO}_3)_2 \cdot 4\text{H}_2\text{O}$] as a precursor in diols at a high temperature (175°C) and Samanta (Samanta et al. 2016) synthesized nanolime using calcium nitrate dihydrate [$(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$] as a precursor in an aqueous medium at room temperature without requiring purification, obtaining nanoparticles of about 250 nm.

Other approaches for obtaining nanosized Ca(OH)_2 use calcium alkoxides as precursors (Ziegenbalg 2003; Poggi et al. 2016; Rodriguez-Navarro et al. 2013). Nanolime has been developed from a hydrogen plasma-metal reaction method (HPMR), obtaining low cost, high purity and crystalline particles (10-100nm) (Liu et al. 2010), and recently the Taglieri team (Taglieri et al. 2015) synthesised nanolime by means of an anion-exchange process using an anion-exchange resin (OH^- group), obtaining nanoparticles

with better features in terms of size, morphology and reactivity, and reducing the synthesis time by eliminating purification processes.

3. APPLICATIONS

During the last two decades nanolimes have been tested as conservation treatments for various substrates. Most of these studies focused on the pre-consolidation of wall paintings, limestone, lime mortars, renders and plasters; and on the de-acidification of cellulose-based materials such as paper, canvas and wood (Poggi et al. 2016).

The first evaluation of the performance of nanolime in a practical application was carried out on wall paintings by the researchers at CSGI (Ambrosi et al. 2001; Dei and Giorgi 2001). The use of lime dispersions in alcohol was first reported by Giorgi et al. (Giorgi et al. 2000), who obtained higher consolidation effect than with aqueous solutions and less superficial white glazing. Later, Ambrosi and co-workers, (Ambrosi et al. 2001, Dei and Giorgi 2001) successfully tested the first synthesized $\text{Ca}(\text{OH})_2$ nanoparticles in lime mortar, limestone and wall-paintings, achieving good results and good re-adhesion of detached pigment flakes without side effects. After these preliminary works, the nanolime developed by the CSGI team was further tested on several Italian frescoes (Baglioni et al 2003, Baglioni and Giorgi 2006) as well as on limestone (Dei 2006) and on a wall-painting in the UNESCO World Heritage Archaeological Site of Calakmul (Baglioni et al. 2006) in Mexico, where a good degree of consolidation was achieved in few days under high relative humidity conditions. All work undertaken by CSGI between 2001 and 2006 reportedly achieved better superficial re-cohesion and quicker carbonation with fewer applications than traditional lime technique and without any aesthetic changes; thus demonstrating that nanolime is so far the best treatment for the consolidation of wall paintings.

The number of published reports on nanolime applications increased after 2008. Calosil® and Nanorestore® were tested by several research organizations and practitioners from various countries in Europe. One of the first studies about Calosil® (Drdácký et al. 2009) documented significant strength increase in lime mortar samples using many fewer applications than the traditional limewater method.

Other authors (Daniele et al. 2008; Campbell et al. 2011; Daniele and Taglieri 2011) investigated the consolidation and penetration of nanolime on limestones and lime mortars and found high superficial strengthening, although nanolime penetration only occurred within 200 μm -1 mm from the surface, depending on the porosity and degree of deterioration of the treated limestone (Ruffolo et al. 2014). These results highlight the importance of the material's pore structure in the effectiveness and penetration of the product. Other authors (Borsoi et al. 2012; Rodrigues 2012) observed insufficient nanolime penetration, no consolidation and nanolime migration back to the surface of the substrate in highly porous limestone, renders and very weak mortars. Afterwards, it was verified that this phenomenon occurs during evaporation of the solvent (Borsoi et al. 2015). The strength and penetrability of Calosil® products in plasters, lime mortars and wall paintings was also studied (Daehne and Herm 2013). It was found that the strength of lime mortar can be increased up to seven times when Calosil® E-25 is applied with cellulose ether gels (hydroxypropylcellulose gel) and that the addition of a low amount of Calosil®-Micro (contains calcium hydroxide particles with a size of 1-3 μm) enhances penetration and reduces back migration.

Treatments combining nanolime and other products were also studied. Based on the Ferroni-Dini method, the CSGI-team (Baglioni et al. 2003; Baglioni et al. 2006) used a combined treatment of barium hydroxide and nanolime for the treatment (desulphation and consolidation) of wall paintings affected by large amounts of sulphates. This combined application was improved later in 2010 (Giorgi et al. 2010) with nanoparticles of barium and calcium hydroxides. The combination of nanolime dispersions (CaLoSiL®) with silicic acid esters (SAE) can be used to enhance the affinity of SAE to a calcareous matrix (Piaszczyński and Wolf 2011). Photo-catalytic nanolime (Nuño et al. 2015) has been successfully used for self-cleaning coatings and environmental pollution control.

4. FACTORS INFLUENCING NANOLIME PERFORMANCE

There are several factors influencing the effectiveness of the application of nanolime for consolidation purposes: nanolime characteristics (concentration and type of solvent, particle size, morphology and

specific surface area), physical and mechanical characteristics of the substrate, extrinsic factors (RH, temperature, exposure time, CO₂ available) and the application method. Some of the published literature explains its efficacy as a consolidant.

It has been shown that nanolimes have superior consolidation properties to limewater, including higher, faster carbonation and greater penetration (Ambrosi et al. 2001; Dei and Giorgi 2001; Dei and Salvadori 2006). A short-chain alcohol dispersion provides the following benefits: 1) greater colloidal stability than suspensions in water (Dei and Giorgi 2001); 2) solvent evaporation so that higher concentrations of Ca(OH)₂ are attained (Giorgi et al. 2000); 3) higher amounts of lime (up to 30 times higher), result in an increased lime incorporation into the treated substrate, hence reducing the number of applications (Dei and Salvadori 2006); 4) enhancement of carbonation kinetics and CaCO₃ polymorph nucleation (Rodriguez-Navarro et al. 2013); 5) significant reduction of the amount of water introduced into the treated material, associated with undesirable effects, such as swelling clays, salt movement, etc. Nanoparticles in an alcohol dispersion penetrate better in porous structures and carbonate faster due to their higher specific surface area (Sequeira et al. 2006).

The role of the solvent for in-depth consolidation was studied recently (Borsoi et al. 2016). It was found that solvents with high boiling points improve the depth of nanolime deposition in stones with large pores (35–40 μm), while solvents with lower boiling points perform better in materials with finer pores (0.5–2 μm), which reduces nanolime migration back to the surface during the solvent drying. Comparison of different concentrations (5 and 25 g/L in isopropanol) of different products (Calosil®, Nanorestore® and Merck®) for the consolidation of lime mortars found that lower concentrations (Calosil® 5 g/L) yield the most significant improvement in the degree of carbonation in the pores (Arizzi et al. 2015). A percentage of residual water content in the alcohol medium (1:10 w/a ratio) clearly enhanced the carbonation process (Dei and Salvadori 2006; Daniele and Taglieri 2010). The colloidal behaviour of Ca(OH)₂ nanoparticles in alcohol was studied (Rodriguez-Navarro et al. 2013; Rodriguez-Navarro et al. 2016) and showed that, upon contact with alcohol, Ca(OH)₂ nanoparticles partially transform into Ca-

alkoxides via the reaction $\text{Ca(OH)}_2 + 2\text{ROH} \rightleftharpoons \text{Ca(OR)}_2 + 2\text{H}_2\text{O}$. The Ca-alkoxide conversion is time-dependent; therefore a long period of storage will produce higher conversion. The rate of carbonation of Ca(OH)_2 particles is reduced by such conversion, so that a freshly prepared alcohol dispersion should be preferred for a fast and effective consolidation. The influence of repeated applications (1 to 6) of Calosil® with different concentrations on high porosity stone showed that the appropriate amount of consolidant has to be chosen in relation to the stone porosity; the optimal treatment for stones with large pores ($\pm 48 \mu\text{m}$) seems to be 2 applications of Calosil® at 25 g/L concentration (Slizkova et al. 2012).

The mechanism of carbonation of nano-dispersions depends on extrinsic factors. Relative humidity, temperature, and exposure time strongly influence the carbonation kinetics and the precipitation of CaCO_3 polymorphs (López-Arce et al. 2010). It was shown that the nucleation of polymorphs varies as a function of RH and time, and the optimum carbonation rate is achieved at high RH (75-90% RH). The full carbonation may be achieved in 9-10 days at room temperature, ambient CO_2 concentration and high RH values (75%) (Baglioni et al. 2014). An important factor in the consolidation of porous substrates using nanolime is the availability of sufficient CO_2 in the pores of the treated material for the calcium hydroxide to fully carbonate. Some research groups investigated the possibility of increasing the amount of CO_2 in the pores of treated substrates. For example, the Taglieri team (Daniele et al. 2008) achieved full and faster carbonation by adding sodium bicarbonate (NaHCO_3) to the alcohol solution. However, the addition of NaHCO_3 may induce processes such as the formation of salt efflorescence. Other researchers (Lopez-Arce and Zornoza-Indart 2015) obtained good results and a full conversion in 21 days by creating a CO_2 -rich atmosphere in a yeast-sugar environment.

5. CONCLUSIONS

This paper gives an overview of the available literature about nanolime as a consolidant for calcareous substrates. From it there is no question that nanolime represents one of the most promising materials for the conservation of calcareous substrates because of its compatibility and minimal side effects. However, despite many years of research, it is clear that more technical and practical knowledge needs to be

acquired. The main conclusion is that whilst nanolime appears to be an effective consolidation treatment for superficial consolidation, when an in-depth consolidation is needed, as in the case of large portions of weathered porous substrates, the results vary significantly between materials. In-depth consolidation is influenced by several factors such as substrates' porous structure and nature, nanolime concentration, nature of solvent, RH, time, CO₂ exposure, additives, storage, application method, and number of applications. The interaction between all of these factors requires further study. Furthermore, the literature lacks data on the long-term performance of nanolime treated materials. The popularity of nanolime is growing and future investigations will hopefully contribute to addressing its current limitations.

6. AUTHOR'S CV

Jorge Otero is a PhD student at the Materials and Engineering Research Institute at Sheffield Hallam University, UK. He received his Master's degree in technologies for the conservation of unmovable heritage from the University of Vigo, Spain.

***corresponding author:** Tel+44 (0)1142253500, Postal address: Materials and Engineering Research Institute, Sheffield Hallam University - City Campus, Sheffield, S1 1WB, GB.

E-mail(s): jorge.otero@student.shu.ac.uk (Jorge Otero), CharolaA@si.edu (A. Elena Charola), GrissomC@si.edu (Carol A. Grissom), v.starinieri@shu.ac.uk (Vincenzo Starinieri)

7. BIBLIOGRAPHY

- Ambrosi, M., et al., (2001), "Colloidal particles of Ca(OH)₂: Properties and applications to restoration of frescoes", *Langmuir*, 17(14), pp.4251–4255.
- Arizzi, A., et al., (2015), "Lime mortar consolidation with nanostructured calcium hydroxide dispersions: the efficacy of different consolidating products for heritage conservation". *European Journal of Mineralogy*, 27(3), pp.311–323.
- Baglioni, P., Carretti, E., Dei, L., et al., (2003), "Nanotechnology in wall painting conservation". *Self-Assembly*, ed.

- B.H. Robinson, (IOS-Press), pp.32–41.
- Baglioni, P., et al., (2014), "Commercial $\text{Ca}(\text{OH})_2$ nanoparticles for the consolidation of immovable works of art". *Applied physics. A, Materials science & Processing*, 114(3), pp.723–732.
- Baglioni, P., et al., (2006), "The Maya site of Calakmul: In situ preservation of wall paintings and limestone using nanotechnology". IIC Congress, the object in context: Crossing conservation boundaries: Contributions to the Munich, Munich, pp.162–169.
- Baglioni, P., Giorgi, R., (2006), "Soft and hard nanomaterials for restoration and conservation of cultural heritage". *Soft Matter Journal*, Royal Society of Chemistry, pp.293–303.
- Borsoi, G., et al., (2016), "Effect of solvent on nanolime transport within limestone: How to improve in-depth deposition". *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 497, pp.171–181.
- Borsoi, G., et al., (2012), "Microstructural characterization of consolidant products for historical renders: an innovative nanostructured lime dispersion and a more traditional ethyl silicate limewater solution". *Journal of Microscopy Society of America*, 18(5), pp.1181–9.
- Borsoi, G., et al., (2015), "Understanding the transport of nanolime consolidants within Maastricht limestone". *Journal of Cultural Heritage*, pp.1–8.
- Brajer, I., Kalsbeek, N. (1999), "Limewater absorption and calcite crystal formation on a limewater-impregnated secco wall-painting". *IIC Studies in Conservation* 44(3), pp.145–156.
- Campbell, A., et al., (2011), "Calcium hydroxide nanoparticles for limestone conservation: Imbibition and adhesion". *Proceedings of symposium, adhesives and consolidants for conservation*, Ottawa, pp.1–16.
- Daehne, A., et al., (2013), "Calcium hydroxide nanosols for the consolidation of porous building materials". *Heritage Science*, 1(1), p.1-9.
- Daniele, V., Taglieri, G., (2011), " $\text{Ca}(\text{OH})_2$ nanoparticle characterization: microscopic investigation of their application on natural stones". *Materials Characterisation*, 72, pp.55–66.
- Daniele, V., Taglieri, G., (2010), "Nanolime suspensions applied on natural lithotypes: The influence of concentration and residual water content on carbonatation process and on treatment effectiveness". *Journal of Cultural Heritage*, 11(1), pp.102–106.
- Daniele, V., Taglieri, G., (2012), "Synthesis of $\text{Ca}(\text{OH})_2$ nanoparticles with the addition of Triton X-100. Protective treatments on natural stones: Preliminary results". *Journal of Cultural Heritage*, 13(1), pp.40–46.
- Daniele, V., Taglieri, G., et al., (2008), "The nanolimes in cultural heritage conservation: Characterisation and analysis of the carbonatation process". *Journal of Cultural Heritage*, 9(3), pp.294–301.
- Dei, L., Salvadori, B., (2006), "Nanotechnology in cultural heritage conservation: nanometric slaked lime saves

- architectonic and artistic surfaces from decay". *Journal of Cultural Heritage*, 7(2), pp.110–115.
- Dei, L., Giorgi, R., (2001), "Stable dispersions of $\text{Ca}(\text{OH})_2$ in aliphatic alcohols: properties and application in cultural heritage conservation". *Progress in Colloid and Polymer Science*, 118, pp.68–72.
- Delfort, B., et al., (1997), "Colloidal calcium hydroxide in organic medium: Synthesis and analysis". *J Colloid Interface Science*, 157(189), pp.151–157.
- Drdácký, M., et al., (2009), "A Nano approach to consolidation of degraded historic lime mortars". *Journal of Nano Research*, 8, pp. 13-22.
- Giorgi, R., et al., (2010), "Nanoparticles for cultural heritage conservation: Calcium and barium hydroxide nanoparticles for wall painting consolidation". *Chemistry - A European Journal*, 16(31), pp.9374–9382.
- Giorgi, R., Dei, L., Baglioni, P., (2000), "A new method for consolidating wall paintings based on dispersions of lime in alcohol". *Studies in Conservation*, 45(3), pp.154–161.
- Liu, T., et al., (2010), "Synthesis and characterization of calcium hydroxide nanoparticles by hydrogen plasma-metal reaction method". *Materials Letters*, 64(23), pp.2575–2577.
- López-Arce, P., et al., (2010), "Influence of porosity and relative humidity on consolidation of dolostone with calcium hydroxide nanoparticles: Effectiveness assessment with non-destructive techniques". *Materials Characterization*, 61(2), pp.168–184.
- Lopez-Arce, P., Zornoza-Indart, A., (2015), "Carbonation acceleration of calcium hydroxide nanoparticles: induced by yeast fermentation". *Applied Physics A*, 120(4), pp.1475–1495.
- Nanni, A., Dei, L., (2003), " $\text{Ca}(\text{OH})_2$ nanoparticles from W/O microemulsions". *Langmuir*, 19(13), pp.933–938.
- Nuño, M., et al., (2015), "Environmental performance of nano-structured $\text{Ca}(\text{OH})_2/\text{TiO}_2$ photocatalytic coatings for buildings". *Building and Environment*, 92, pp.734–742.
- Otero, J., Charola, A. E., Grissom, C., Starinieri, V., (2017), "An overview of nanolime as a consolidant for calcareous substrates". Submitted to *Proceedings of the 5th International Conference Youth in Conservation of Cultural Heritage*, Museo Nacional Centro de Arte Reina Sofia.
- Pe, L.A., Wang, L., Matijevic, E., et al., (1998), "Nanosize indium hydroxide by peptization of colloidal precipitates". *Langmuir*, 14(8), pp.4397–4401.
- Poggi, G., et al., (2016), "Calcium hydroxide nanoparticles from solvothermal reaction for the deacidification of degraded waterlogged wood". *Journal of Colloid and Interface Science*, 473, pp.1–8.
- Piaszczyński, E., Wolf, V. (2011), "The combination of nano-lime and silicic acid ester for stone conservation". *Proceedings of the European Workshop on Cultural Heritage Preservation, Berlin 2011*, Fraunhofer IRB:Verlag, 254.

- Price, C., et al., (1988), "A further appraisal of the 'lime technique' for limestone consolidation, using a radioactive tracer. *Studies in Conservation*, 33(4), pp.178–186.
- Rodrigues, J. D., (2012), "Consolidation of a porous limestone with nanolime". *Proceedings of the 12th International Congress on the Deterioration and Conservation of Stone*, New York, pp. 17–21.
- Rodriguez-Navarro, C., et al., (2013), "Alcohol dispersions of calcium hydroxide nanoparticles for stone conservation". *Langmuir*, 29(36), pp.11457–11470.
- Rodriguez-Navarro, C., et al., (2016), "Kinetics and mechanism of calcium hydroxide conversion into calcium alkoxides: Implications in heritage conservation using nanolimes". *Langmuir*, 32(20), pp. 5183-5194.
- Roy, A., Bhattacharya, J., (2010). "Synthesis of $\text{Ca}(\text{OH})_2$ nanoparticles by wet chemical method". *Micro & Nano letters*,(3), pp.131–134.
- Ruffolo, S., et al., (2014), "Efficacy of nanolime in restoration procedures of salt weathered limestone rock". *Applied Physics A: Materials Science and Processing*, 114, pp.753–758.
- Salvadori, B., Dei, L., (2001), "Synthesis of $\text{Ca}(\text{OH})_2$ nanoparticles from diols". *Langmuir*, 17(8), pp.2371–2374.
- Samanta, A., et al., (2016), "Synthesis of nano calcium hydroxide in aqueous medium". *Journal American Ceramic Society*, 795(37004), pp.787–795.
- Sequeira, S., et al., (2006), "Deacidification of paper using dispersions of $\text{Ca}(\text{OH})_2$ nanoparticles in isopropanol". *Journal Cultural Heritage*, 7, pp.264–272.
- Slizkova Z., et al., (2012), "Consolidation of a porous limestone with nanolime". *Proceedings of the 12th International Congress on the Deterioration and Conservation of Stone*, New York.
- Taglieri, G., et al., (2015), "A new and original method to produce $\text{Ca}(\text{OH})_2$ nanoparticles by using an anion exchange resin". *Advances in Nanoparticles*, 4, pp.17–24.
- Ziegenbalg, G., (2003). *Verfahren zur verfestigenden Behandlung von mineralischen anorganischen Baustoffen*, Patent number: DE:10327514 B3.

Table 1. Brief summary of literature on the synthesis of nanolime

Year	Research group	Synthesis route	Inorganic precursor(s)	Synthesis media	Processing	T (°C)	PS (nm)
2001	CSGI group	CP-HS	CaCl ₂ and NaOH	aqueous	high T, wash. and pept.	60	1-2 (µm)
2001	CSGI group	CP-HS	CaCl ₂ ·2H ₂ O and NaOH	diols	high T, filtration, wash. and pept.	195	30-150
2001	CSGI group	CP-HS	CaCl ₂ ·2H ₂ O and NaOH	aqueous	high T, wash. and pept.	90	300
2003	CSGI group	CP-HS	CaCl ₂ ·2H ₂ O and NaOH	w/o microemulsions	wash. and pept.	≤ 15	2-10
2010	Bhattacharya et al.	CP-HS	Ca(NO ₃) ₂ ·4H ₂ O and NaOH	diol (1,2-ethanediol)	hot vacuum filtration and pept.	115	35
2010	Liu et al.	CP-HPMR	melted Ca ingot and H ₂ O	H plasma	Ca vapour reacts O, CaO reacts with H ₂ O	room T	10-100
2012	Taglieri et al.	CP-HS	CaCl ₂ and NaOH	aqueous & Triton-X100	wash. and pept.	90	<100
2015	Taglieri et al.	CP-HS	CaCl ₂ ·2H ₂ O and AER (OH)	aqueous	pept.	room T	<100
2016	Samanta et al.	CP-HS	Ca(NO ₃) ₂ ·2H ₂ O and NaOH	aqueous	pept.	room T	350
2016	CSGI group	CP-HPS	calcium metal	alcohol and H ₂ O (high P & T)	high P reactor (High P & T)	65-130	200

CP (chemical precipitation), HS (homogeneous synthesis), HPS (heterogeneous phase synthesis), HPMR (hydrogen plasma metal reaction), H (hydrogen), Ca (calcium), CaCl₂ (calcium chloride), NaOH (sodium hydroxide), w/o (water in oil), Ca(NO₃)₂·4H₂O (calcium nitrate tetrahydrate), CaO (calcium oxide), w/o (water in oil), P (pressure), T (temperature), PS (particle size), AER (anion exchange resin), wash (washing with deionized water), pept (peptization process)

