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AN OVERVIEW OF NANOLIME AS A CONSOLIDATION METHOD FOR CALCAREOUS SUBSTRATES

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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.

RESUMEN

Partículas de nanocal, $Ca(OH)_2$ con dimensiones sub-micrométricas, es uno de los principales consolidantes emergentes dentro de la conservación de sustratos calcáreos. La nanocal se basa en la técnica de agua de cal, utilizada tradicionalmente por su alta compatibilidad y durabilidad con el substrato calcáreo; pero su aplicación requiere de un gran número de aplicaciones y la consolidación no siempre es muy eficaz. Desde 2001, dispersiones alcohólicas de nanopartículas de $Ca(OH)_2$ se han sintetizado para obviar las limitaciones de los tratamientos tradicionales. La nanocal presenta la misma alta compatibilidad y durabilidad del método tradicional y propiedades

superiores en términos de mayor consolidación, penetración, reactividad y menores efectos secundarios. Desde su creación, estas formulaciones han sido estudiadas por varios grupos de investigación con el objetivo de perfeccionar su proceso de síntesis, propiedades y aplicaciones. Esta publicación revisa la bibliografía más relevante para identificar áreas donde un mayor estudio es necesario.

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 CSGI -, 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, another 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 to the market in 2006 (IBZ-Salzchemie GmbH & Co. KG) followed by Nanorestore® (CSGI) in 2008. With these products made available to the scientific community, European researchers 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 recuperate the cohesion between particles in calcareous substrates such as wall-paintings, limestone, lime mortar, etc. In 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 were 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 has been controversial. Price (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 existing 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 through 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 $Ca(OH)_2$ particles. Both researchers found that dispersions in alcohol are far more stable and able to incorporate larger amounts of lime than limewater. With the aim of preparing stable nanoparticles of $Ca(OH)_2$, 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 colloid 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 (1-2μm) 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 (±300nm) via an homogeneous phase following the aqueous reaction $CaCl_2 + 2NaOH \rightarrow Ca(OH)_2 + 2NaCl$, 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 the produced NaCl by washing; and, 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 [$Ca(NO_3)_2 \cdot 4H_2O$] as a precursor in diols at a high temperature (175°C) and Samanta (Samanta et al. 2016) synthesized nanolime using calcium nitrate dihydrate [$(NO_3)_2 \cdot 2H_2O$] 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 also 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 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 $Ca(OH)_2$ nanoparticles in lime mortar, limestone and wall-paintings, achieving good results and good re-adhesion of detached pigment flakes without side effects. The nanolime developed by CSGI was further tested on several Italian frescoes (Baglioni et al 2003, Baglioni and Giorgi 2006), limestone (Dei 2006) and a wall-painting in the archaeological site of Calakmul (Baglioni et al. 2006) in Mexico, achieving a good degree of consolidation. All work undertaken by CSGI between 2001 and 2006 achieved

better superficial re-cohesion and quicker carbonation with fewer applications than limewater and without any aesthetic changes; thus demonstrating that nanolime is so far the best treatment for the consolidation of wall paintings.

Calosil® and Nanorestore® were tested by several authors in Europe since 2008. Using Calosil®, Drdácký (Drdácký et al. 2009) documented significant strength increase in lime mortars with far fewer applications than with limewater. Other authors (Daniele et al. 2008; Campbell et al. 2011; Daniele and Taglieri 2011) studied the consolidation and penetration of nanolime on limestone(s) 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 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 1-3 μm calcium hydroxide particles) enhances penetration and reduces back-migration.

Treatments combining nanolime and other products were also studied. 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. This combined application was improved later in 2010 (Giorgi et al. 2010) with nanoparticles of both 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 (Piaszczynski 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 nanolime as a consolidant: 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, CO_2 available) and application method. Some of the published literature explains its effectiveness as a consolidant.

It has been shown that nanolimes have superior consolidation properties to limewater, including both higher and faster carbonation with 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 (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), resulting in an increased lime incorporation into the treated substrate and lower number of applications (Dei and Salvadori 2006); 4) enhancement of carbonation kinetics and $CaCO_3$ polymorph nucleation (Rodriguez-Navarro et al. 2013); 5) significant reduction of the amount of water introduced into the treated material. 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 $Ca(OH)_2 + 2ROH \rightleftarrows Ca(OR)_2 + 2H_2O$. 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 this conversion, so that a freshly prepared alcohol dispersion should be preferred. 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 (±48 μm) seems to be 2 applications of Calosil® at 25 g/L concentration (Slizkova et al. 2012).

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 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

The paper gives an overview of the available literature about nanolime as a consolidant for calcareous substrates. 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, 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, CO_2 exposure, additives, storage and application method. 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 Vice Chancellor's 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 (2011), Spain. He was Icon Intern in Preventive Conservation at the National Trust for Scotland, UK (2014-15) and MCI intern at the Museum Conservation Institute of the Smithsonian Institution, USA (2016).

Dr. A. Elena Charola obtained her doctorate in Chemistry from the Universidad Nacional de La Plata, Argentina. After having served at the Metropolitan Museum of Art, New York City (1981-85) and at ICCROM, Rome (1986-87), she has been in private practice, working mainly for World Monuments Fund and its Portuguese affiliate WMF-Portugal as Scientific Advisor and Program Coordinator (2005-08). For over 15 years, she was Lecturer at the Graduate Program of Historic Preservation at the University of Pennsylvania and a Guest Lecturer at the Katholieke Universiteit Leuven in Belgium. At the Museum Conservation Institute of the Smithsonian Institution in Washington, DC, she was a Visiting Scientist (2008-2010) and is currently a Research Scientist since 2011. She has published extensively in the field of stone conservation.

Carol Grissom has been Senior Objects Conservator at the Smithsonian's Museum Conservation Institute since 1984. She obtained a master's degree in art conservation from Oberlin College and gained further training at the

national conservation institutes of Belgium and Italy. Her special interests include stone and metals conservation, notably of nineteenth-century zinc sculpture.

Vincenzo Starinieri is a Research Fellow in the Materials and Engineering Research Institute at Sheffield Hallam University. He holds a PhD in Science for Conservation of Cultural Heritage from the University of Bologna and a Master's Degree in Geology from the University of Chieti - Pescara. He specialises in the characterisation of masonry materials, the investigation of their degradation phenomena and the development of materials and technologies for their conservation and repair.

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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	$CaCl2{\cdot}2H_2O$ and NaOH	diols	high T, filtration, wash. and pept.	195	30-150
2001	CSGI group	CP-HS	$CaCl2{\cdot}2H_2O$ and NaOH	aqueous	high T, wash. and pept.	90	300
2003	CSGI group	CP-HS	$CaCl2{\cdot}2H_2O$ and NaOH	w/o microemulsions	wash. and pept.	≤ 15	2-10
2010	Bhattacharya et al.	CP-HS	$Ca(NO_3)_2{\cdot}4H_2O$ and NaOH	diol (1,2-ethanediol)	hot vacuum filtration and pept.	115	35
2010	Liu et al.	CP-HPMR	melted Ca ingot and H_2O	H plasma	Ca vapour reacts O, CaO reacts with H_2O	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	$CaCl_2{\cdot}2H_2O$ and AER (OH)	aqueous	pept.	room T	<100
2016	Samanta et al.	CP-HS	$Ca(NO_3)_2{\cdot}2H_2O$ and NaOH	aqueous	pept.	room T	350
2016	CSGI group	CP-HPS	calcium metal	alcohol and H2O (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), $CaCl_2$ (calcium chloride), NaOH (sodium hydroxide), w/o (water in oil), $Ca(NO_3)_2 \cdot 4H_2O$ (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)