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Inorganic Nanomaterials for Restoration of Cultural Heritage: Synthesis Approaches towards Nanoconsolidants for Stone and Wall Paintings

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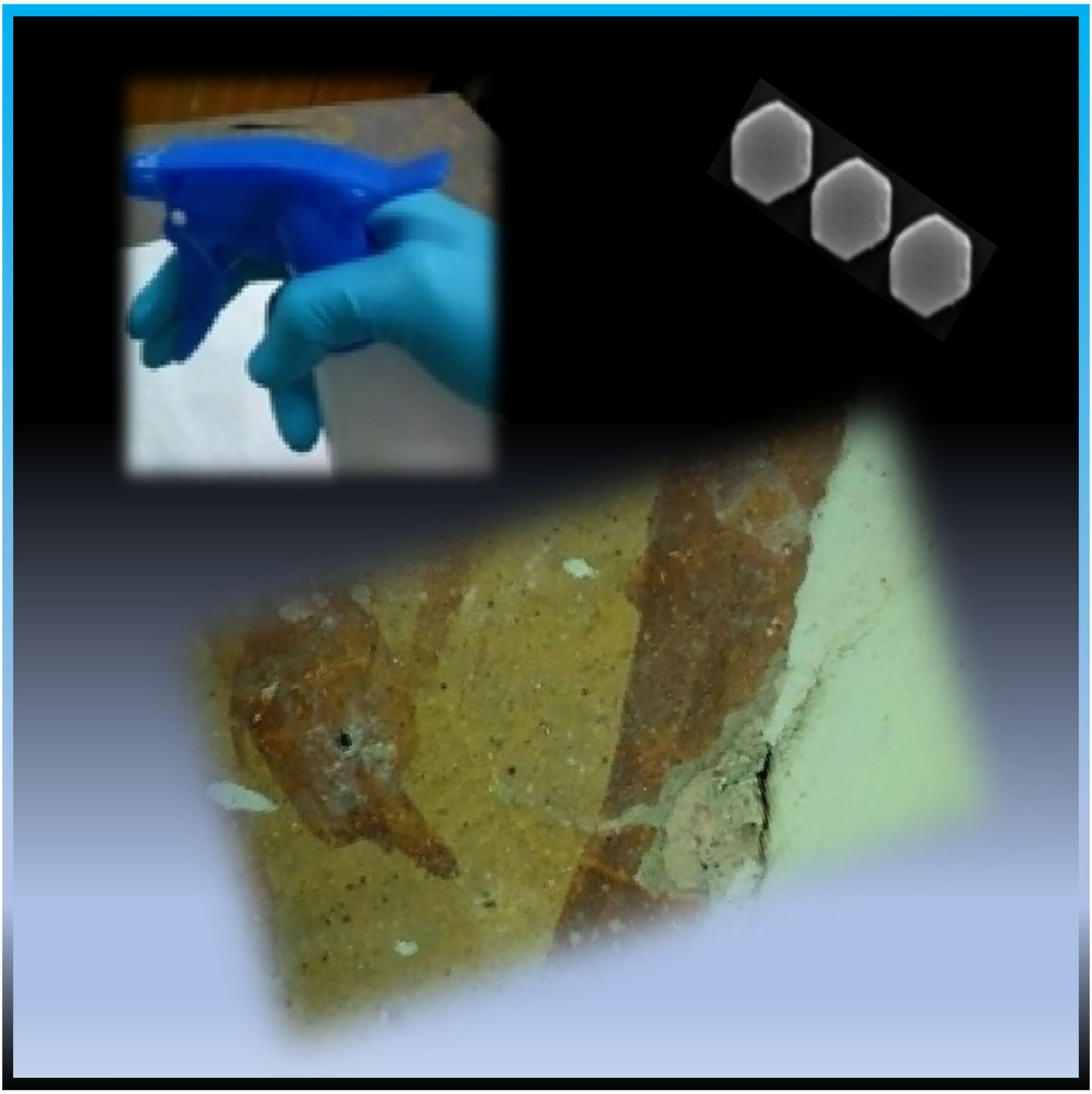

The synthesis of inorganic nanostructured materials for the consolidation of stone and wall paintings is reviewed. To begin, a description of the methods most commonly used to prepare nanoconsolidants is provided, particularly in the frame of colloid chemistry. Some concepts of the carbonation mechanism as well as the transport properties of some of these materials are addressed. An overview of the synthesis methods together with some of the application particularities of the distinct consolidants are presented thereafter. Furthermore, the requisites for efficient consolidants and some drawbacks of the nanoconsolidants are discussed.

1. Introduction

The main challenge in materials science and nanotechnology is to tailor classical materials with controlled properties for specific uses. Most manufacturers are interested in the possibility of controlling particle size, particle shape, particle-size distribution, particle composition, and the degree of agglomeration. This can be achieved by paying special attention to the preparation methods that allow the synthesis of particles with uniform size distributions (in the range of 1–100 nm) and shapes (e.g., nanosized tubes, spheres, wires, rods, fibers, pyramids).

The self-assembly of nanoparticles (NPs) can be achieved by different approaches, either from bottom-up techniques (by assembling particles synthesized mostly in solution; the main chemical approaches are based on colloidal process) or from top-down techniques (different lithographic methods, grinding of bulk materials, thermal decomposition). The main difference between the two approaches is the starting materials from which the particles are obtained. In the bottom-up synthesis approach, the NPs are built atom by atom or molecule by molecule. In the top-down (or break-down) process, the starting materials are reduced from the bulk size to the nanoscale by using different forms of energy, such as mechanical, chemical, and thermal energy.

Several aspects must be considered in the consolidation of artwork mortars. The consolidant must have similar or, preferentially, the same chemical composition as the decayed substrate and must cover its mineralogical phases. Moreover, it is necessary to manifest good chemical and physical compatibility with the mortar. The physical and mechanical properties must be improved, whereas the esthetical appearance must not be altered. Good consolidants are characterized by good penetration from the surface to the interior.[1]

1.1. Most common synthesis approaches to inorganic nanoparticles for consolidation of cultural heritage

A variety of methods for the synthesis of inorganic nanomaterials have been used, including co-precipitation, microemulsions, precipitation from solution, high-temperature decomposition of organic precursors, and sol–gel, among others.

A common synthesis route for inorganic NPs is precipitation from solution under controlled conditions with respect to thermodynamics and the principles of colloidal chemistry. A dispersion of narrow-sized particles (smaller than 1 μm) or a two-phase heterogeneous system consists of a dispersed phase and the dispersion medium, that is, a phase of one material in another form a colloid. The dispersed phase in a colloidal system is uniformly distributed in the dispersion medium that makes the colloid particle, and this colloid particle is formed by clusters of atoms and molecules and is undetectable by conventional optical microscopy. Colloidal particles are characterized by high area-to-volume ratios as a result of their small sizes, and this predetermines their specific properties and behavior. Sometimes, surface-active substances are added to a colloid to modify its properties. Inorganic colloids are usually prepared by precipitation reactions, which involve two steps: nucleation and growth of nuclei. To achieve monodispersity, the two steps must be separated and must not happen at the same time. The kinetics of these reactions for the synthesis of monodispersed colloidal particles were studied by LaMer, who investigated the formation of sulfur colloids from thiosulfate solutions.[2]

In 1968, Stöber and Fink applied a procedure based on LaMer's theory in different systems to prepare monodispersed silica colloids.[3] The basis of this method was the hydrolysis of a dilute solution of tetraethylorthosilicate (TEOS) in ethanol at a high pH value. They obtained uniform spheres of amorphous silica with sizes between 50 nm and 2 mm by changing the concentrations of the reactants. This method was improved later and has been modified and used by many other researchers. For example, Matijević improved and applied the Stöber strategy to many different materials (cubes, colloidal spheres, rods, and others).[4] A very common method for the synthesis of metal powders, alloys, and metal oxide NPs is the polyol method. Its mechanism is realized with respect of LaMer's theory and can be seen as a sol–gel process at high temperatures. The basis of this method is the reduction of metal precursors by high-boiling alcohols (polyols, such as glycerol, glycol, and ethylene glycol) to micron, submicron, and nanosized metal particles.[5] Besides acting as high-boiling solvents and reducing agents, polyols are seen as stabilizers to control particle growth. The reaction in solution occurs over four

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steps: 1) dissolution of the solid precursor, 2) reduction in solution, 3) homogeneous nucleation, and 4) growth of the metallic phase from solution.[5a]

In a typical sol–gel process, the inorganic networks are built through the formation of a colloidal suspension (sol) and further gelation of the sol to form a network in a continuous liquid phase (gel).

1.2. Wall paintings: composition and common damage

Calcium carbonate ($CaCO_3$) is the main component of the majority of wall paintings and different stones (e.g., limestone, marble) that are used in creating artworks such as sculptures and architectural works. Classical wall paintings such as frescoes are commonly composed of three layers. The inner layer that is in contact with the wall structure is the richest in sand, and it is called arriccio. The intermediate layer, called intonaco, represents a plaster composed of a mixture with a higher lime content and finer sand than that found in arriccio. The paint layer of a buon fresco is executed on the freshly prepared and wet intonaco. The pigments, usually of mineral origin, are applied dispersed in water. In some cases, the base for the paint is another thinner layer, the lime-rich intonachino. The pigments are fixed in the crystalline carbonate network during carbonation. In the secco painting technique, pigments are applied on the dried intonaco layer by using organic binders (egg, milk, oil, gums) or by mixing with lime water.

Both carbonate stone and wall paintings, as an irremovable part of architectural heritage, are subject to constant attack by soluble salts and pollutants. They can undergo different kinds of degradation, including corrosion by acid rain, physical erosion, crystallization/solubilization cycles of salts (e.g., sulfates, nitrates, and chlorides), and biodegradation due to bacteria, fungi, or lichens. Very common damage to renders and plasters results in a change in the mechanical and hydric properties of the mortar, the formation of shrinkage cracks, lime leaching, powdering, and loss of material caused by the loss of cohesion between the matrix, aggregate grains, and rendering layers. The deterioration rate of stone materials is strictly related to porosity features, which affect interaction of the surface with all damaging environmental agents, including water.

Often, past treatments have tended to cause additional substrate damage. For instance, synthetic polymeric materials (e.g., acrylic and vinyl copolymers) applied as consolidants, protectives, adhesives, and cleaning agents for work-of-art restoration were initially seen as good treatment alternatives. However, upon aging they are subject to degradation; this results in cross-linking or chain scission, which consequently alters their own initial properties on the one hand and accelerates the decay of the work of art by changing its physicochemical properties on the other hand.[6]

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1.3. Nanoconsolidants as good alternatives to common bulk materials

A highly efficient nanoconsolidant must meet a large list of requisites; for example, it must be effective for long-term use, be compatible with the damaged substrate, mechanically improve and protect the material from weathering, and show the capacity to penetrate homogenously at a certain depth depending on the material that is to be consolidated. For consolidation purposes, the particles should not form clusters so that stable dispersions are obtained (at least during the application time, usually a few hours). Consolidation with bulk materials or NPs with the same chemical composition as that of the substrate to be consolidated is often an effective solution to increase the compactness of a decaying mortar.

These consolidants act as binders by providing a cohesive capacity to the damaged material and are expected to retain strong long-term consolidating properties. In frescos, nanolime increases cohesion between the paint layer and the pigment particles from the substrate.[7] With low-porosity stone, at a superficial level, the consolidating effect of nanolime consists of reinforcing the structure and reaggregating the powdering surfaces.[7b] At a deeper level, nanolime consolidants can decrease the tendency of the matrix to absorb liquid water.[7b]

The application of inorganic nanoparticles, in particular those based on lime, in the conservation and consolidation of calcareous building materials and other artistic heritage has increased in the last decades. In this respect, alcohol dispersions of alkaline earth hydroxide NPs, in particular those of $Ca(OH)_2$, have shown high efficiency as consolidants for various types of artwork, building stone, mortars, and plasters present in old masonry and are an excellent alternative to synthetic polymers.

Recent research has focused on developing coupling agents for limestone consolidation, treatment for clay swelling of stone, nanoparticle-modified silane consolidants, and calcium alkoxide, phosphate, or oxalate treatment.

Other advanced nanostructured systems include complex fluids such as micelles and microemulsions, superhydrophilic coatings that are activated by solar light, and innovative nanostructured gels and gel-like systems, including rheoreversible gels and nanomagnetic sponges. However, they are mostly used in the conservation field for their cleaning performance and their ability to remove synthetic materials selectively from stone,[8] marble,[9] and artwork surfaces;[6c,10] thus, they are beyond the scope of this Review.

2. Alkaline Earth Metal Hydroxide NP Dispersions

2.1. Lime, nanolime, and other alkaline earth metals hydroxide NP dispersions: nature and consolidation mechanism

The use of lime in cultural heritage and building conservation is based on the carbonation reaction and on the characteristics of obtained $CaCO_3$. The compatibility between lime and the material substrates makes it excellent for conservation treatment. However, its effectiveness as a consolidant of largely used limewater is limited because of the low solubility of $Ca(OH)_2$ in water (1.7 $g\,L^{-1}$ at 20 °C), which limits the amounts of the consolidant that can enter the porous system of the treated material and, therefore, may cause chromatic alteration to stone surfaces. The use of large quantities of water can cause additional damage, such as substrate dissolution, freeze–thaw deterioration, weathering by the activity of the salts formed, and swelling clays.

These limitations of limewater treatment have been overcome with the use of nanolime–aliphatic alcohol dispersions of $Ca(OH)_2$ NPs for the consolidation of limestone and wall paintings. These dispersions have a huge impact upon application in the conservation and consolidation of building and artistic heritage.[7a,10d,11] $Ca(OH)_2$ NP dispersions are compatible with the original materials constituting the works of art and have shown high efficiency as consolidants for various types of artwork, including frescoes and/or wall paintings,[7a,b,12] building stone,[7c,11e,13] and mortars and plasters present in old masonry.[14] They are more reactive in porous media and have very different transport properties in these media. The high surface area of the NPs influences their chemical reactivity, and they produce a consistent consolidation of the treated surfaces only a few days after the application owing to the reaction of the hydroxide with carbon dioxide (CO_2) in air to give crystalline $CaCO_3$.

If applied to frescoes and stones, nanolime can enhance the strength and the cohesion in the porous decayed material. The replacement of the lost blocks from the deteriorated network consists of the carbonation of the $Ca(OH)_2$ NPs. Although the alcohol evaporates, these NPs penetrate to different depths inside the treated substrate, in which they react with CO_2 from the atmosphere and in the presence of water to form $CaCO_3$. The overall carbonation process is represented by the following reaction [Eq. (1)]:

$$Ca(OH)_2 + (H_2O + CO_2) \rightarrow CaCO_3 + 2\,H_2O \qquad (1)$$

The water necessary for the process can be provided from the atmosphere, from the treated material, or by additional spray application. It can also be added to the nanolime before application.[15] If water is added to nanolime to increase its reactivity, the resultant formation of a $Ca(OH)_2$ gel may affect the particle penetration by reducing it[15] or optimizing it.[16]

In addition, nanosized barium, strontium, and magnesium hydroxides have emerged as efficient consolidants for porous stone and frescoes.[11d,13c,17] Depending on the characteristics of their colloids and the nature of the dispersion alcohol, similar to the $Ca(OH)_2$ dispersion, strontium hydroxide [$Sr(OH)_2$] and magnesium hydroxide [$Mg(OH)_2$] dispersions can produce the respective carbonates. A possible application of $Sr(OH)_2$ NPs as a potential desulfating agent by reaction with gypsum has been anticipated.[17]

Barium hydroxide [$Ba(OH)_2$] has been used as a consolidant for carbonaceous materials since the end of the 19th century. Ferroni-Dini's method was proposed for the use of aqueous solutions of $Ba(OH)_2$ in the consolidation of frescoes seriously damaged in the Florence flood of 1966.[11d] This method is particularly recommended for wall paintings containing large amounts of undesired sulfates. The procedure consists of two steps:

Step 1: Desulfation with ammonium carbonate solution [Eq. (2)]:

$$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3 \qquad (2)$$

Step 2: Application of $Ba(OH)_2$ solution, which transforms the residual soluble sulfates into $BaSO_4$ (insoluble) [Eq. (3)]:

$$Ba(OH)_2 + (NH_4)_2SO_4 \rightarrow BaSO_4 + 2\,NH_3 + 2\,H_2O \qquad (3)$$

The excess amount of $Ba(OH)_2$ converts $CaCO_3$ formed in the first step into $Ca(OH)_2$, which finally carbonates to $CaCO_3$.

Nanolime particles dispersed in alcohol with a homogeneous size and shape distribution provide good penetration in treated lime mortar substrates. However, there are several factors influencing the effectiveness of the application of hydroxide NPs for consolidation purposes:[18] temperature, relative humidity, amount of free water within the pores of the substrate, particle crystallinity, crystal orientation, crystal size, crystal surface area, and nature of the solvent.

Notably, nanoconsolidants for artwork, in particular nanolime, are not equally effective if applied to distinct materials or under different conditions.[19] Renders and plasters suffer the same decay problems as wall paintings, but in terms of open porosity and pore-size distribution, the renders have different textural characteristics. This affects the penetration of the nanoconsolidant, which influences the carbonation process. The degree of carbonation of nanolime consolidants in lime-based mortars, for instance, depends on the size and homogeneity of the colloidal particles, traits that are strongly related to the degree of dispersion. Lower concentrated dispersions of $Ca(OH)_2$ NPs with a smaller size and higher homogeneity may correspond to a stronger consolidation effect.[19b] Lime mortars of reduced loss of cohesion can be treated only with nanolime or in combination with other consolidation products.[19a] In other cases, a larger number of applications or more concentrated dispersions is/are required. The mortars, as heterogeneous materials, may change their characteristics over time. Owing to uncontrolled water circulation (groundwater capillary uptake, moisture condensation) in the mortar under treatment, the small amount of non-carbonated binder in the matrix can carbonate or dissolve in water and reprecipitate within the pores during the drying process. This must be taken into account if in situ consolidation is performed.

Besides the characteristics of the substrate, the consolidant, and the nature of the solvent, the effectiveness of the consolidation treatment depends on the whole application process, including the dispersion concentration, number of applications, time interval between applications/time for solvent carrier evaporation, amount of product applied, ambient conditions during and after treatment, indication of limiting conditions (e.g., temperature and relative humidity ranges), and so on.[20]

2.1.1. Nanolime: transport mechanism

Nanolime transport is strictly related to the properties of the dispersing solvent, the environmental conditions, and the pore size and pore character of the surface treated (e.g., until 80 μm depth in low-porosity substrates[7b]). For good application, the degraded zone should be saturated with the consolidant, and the treatment is usually repeated after evaporation of the solvent.

The nature of the consolidant and its surface tension, viscosity, and volatility are important factors for the speed of impregnation and for the quantity of the consolidant (some of it may be lost by evaporation).[15] The rate of diffusion of nanolime is lower than that of its alcohol dispersant, and the rate of diffusion of the alcohol dispersant is lower than that of water or limewater.[15] Alcohols diffuse less into porous materials than water owing to their diffusion limitations.

Nanolime shows some limitations as a consolidant with respect to its transport mechanism into a stone matrix. NPs can accumulate at or just under the surface of the treated material. Studies on the consolidation/transport mechanism of commercial hexagonal platelike nanolimes with sizes in the range of 50 and 250 nm were performed on Maastricht limestone, a high-porosity yellowish limestone known as a traditional building material in the Netherlands and Belgium.[16,21] The dispersion may be partially back-transported to the surface during drying owing to the high volatility of the solvent and the high stability of the dispersion. More recently, Borsoi et al.[16,22] suggested that it was possible to avoid the migration of NPs back to the surface during drying by choosing the dispersive media as a function of the porosity of the substrate to be consolidated. Solvents providing higher kinetic stability (e.g., ethanol and 2-propanol) are more suitable for fine porous substrates.[22] A mixture of ethanol and a low amount of water (5%) can be a solution for good in-depth consolidation treatment, as it partially prevents back-transport.[16] Back-migration can also be avoided if water is applied immediately after treatment with nanolime.[21b]

2.1.2. Nanolimes: carbonation mechanism

The carbonation mechanism and kinetics of $Ca(OH)_2$ NPs on both wall paintings and stone can be achieved within days or weeks and have been reported in several papers.[12b,13a,23] The precipitation of $CaCO_3$ polymorphs (calcite, aragonite, and vaterite) and hydrated calcium carbonates (amorphous and monohydrocalcite), phase transformations, and mineral morphological and structural variations depend on the pH, temperature, saturation, conductivity or impurities, and additives. The relative humidity (RH) and exposure times in the environment are other important variables for the speed by which nanolime undergoes carbonation and for the nature of the mineral phases resulting from the carbonation (vaterite and aragonite are less stable than calcite).[13a,23b,24]

The carbonation of nanolime to the stable polymorph calcite $CaCO_3$ is reached directly or indirectly. These two pathways consist of: 1) direct nucleation in solution and subsequent growth after dissolution of amorphous calcium carbonate and/or vaterite (and aragonite) and 2) nucleation on vaterite (or aragonite) and grow either by a particle-mediated (aggregation) mechanism or an ion-mediated mechanism.[23c]

Nanolime treatment of magnesian limestone (dolostone) at low RH (33%) favors calcite recrystallization, in contrast to the consolidation at high RH (75%). However, dissolution and fracture of dolomite crystals [$CaMg(CO_3)_2$] can occur at low humidity, but this is not observed at 75% RH.[7c]

The solvent can strongly affect the kinetics of carbonation and influences $CaCO_3$ polymorph formation.[11e,23b,c] $Ca(OH)_2$ NPs may react with ethanol and 2-propanol and can also partially transform into calcium ethoxide and calcium isopropoxide, respectively, by pseudomorphic replacement of $Ca(OH)_2$ particles by calcium alkoxides. The yield of the Ca alkoxide depends on the reactivity of the $Ca(OH)_2$ particles (surface area and lattice defects) and their exposure time to the alcohol. Such a conversion of consolidant NPs into Ca alkoxides may induce the formation of metastable vaterite instead of stable calcite.[25] This effect has been observed not only in larger particles with low surface area but also in nanolime with a smaller size and higher surface area. Therefore, to avoid partial conversion of nanolime into a Ca alkoxide and to achieve fast and effective consolidation, freshly prepared alcohol dispersions are preferred. Moreover, if storage of nanolime dispersions prior to application is required, they must be kept at a low temperature.

The carbonation process of nanolime may be accelerated or even completed by the addition of a source of CO_2: baking soda ($NaHCO_3$)[11c] or yeast–sugar solutions.[26] Upon adding an external CO_2 source, that is, a solution of $NaHCO_3$, a conversion factor of 95% can be reached.[11c] However, the authors do not specify in which polymorph forms $CaCO_3$ precipitates. Under anaerobic conditions, yeast (strains of *saccharomyces cerevisiae*, baker's yeast) can provide a saturated atmosphere with CO_2, water vapor, and ethanol. Under such an atmosphere, assured by yeast fermentation, and a high-humidity environment, nanolime (60–130 nm NPs in 2-propanol) can completely transform $CaCO_3$ (aragonite and calcite) in 28 days. In a high-humidity environment and without the favorable effect of the addition of CO_2, conversion of 95% to the same mineral phases (aragonite and calcite) for the same number of days can be achieved. Samples exposed to lower humidity (laboratory room conditions) display much lower rates of carbonation of the initial portlandite NPs and yield 85 % portlandite and 15 % calcite in 28 days.[26] In the three different environments (with and without yeast at high humidity and without yeast under ambient conditions), all limestone specimens consolidated with these NPs show an increase in their mechanical properties. However, the NPs and the mixture of amorphous, nanocrystals and microcrystals of $CaCO_3$ cause the formation of a white crust and glazing on the treated stone surface.[26]

2.2. Nanolime and other alkaline earth metal hydroxide NP dispersions: synthesis and application particularities

2.2.1. Calcium hydroxide nanoparticles

The synthesis of $Ca(OH)_2$ NPs (as the mineral portlandite) within the range of 50 to 300 nm has been improved to tune the size and shape of the NPs and to make them suitable for application and penetration in the consolidated layer as a dispersion in a suitable solvent.

The top-down method for obtaining $Ca(OH)_2$ NPs is based on the thermomechanical treatment of slaked lime, for which the complete slaking of lime is obtained.[27] The particle-size distribution and polydispersity can be tuned by adjusting the temperature and pressure.[7c] A heterogeneous-phase reaction of CaO with water produces lime putty, which usually has some unreacted CaO in the core of the particles. If hydration is forced by adjusting the specific conditions until complete slaking of lime, the lime putty particles may suffer further fragmentation. This fragmentation is due to volume expansion associated with the transformation of CaO into $Ca(OH)_2$, which leads to a reduction in the particles size. Large quantities of highly crystalline hexagonal portlandite NPs with an average size of 150–300 nm[27] may form a stable dispersion in 2-propanol without further purification or additional treatments.

A common method for the synthesis of $Ca(OH)_2$ NPs consists of a homogeneous-phase reaction in water or organic solvents, during which some of the reaction parameters, such as temperature, concentration of the reactants, and the molar ratio of the reactants, are varied to give different sizes and morphologies. The obtained nanolime particles exhibit different morphologies and particle sizes, and they are applied by using various dispersing solvents such as ethanol, 1-propanol, and 2-propanol. The reaction consists of the precipitation of particles from the liquid phase.

Dei and Salvadori[23a] have elaborated a synthesis pathway based on the polyol method in high-boiling solvents (1,2-ethanediol and 1,2-propanediol) that allows a temperature above 100 °C. The authors have studied the reaction at various temperatures ($T = 115$, 150, and 175 °C) by adding aqueous NaOH to a hot hydrolyzed solution of calcium chloride in diols. This synthesis route gives highly crystalline nanoparticles and submicroparticles of hexagonal and spherical shapes with unit sizes in the ranges of 30–60, 50–100, and 60–150 nm depending on the experimental conditions but mainly depending on the molar ratio of the reactants and on the aging time. A decrease in the aging time of the solution after the reaction between NaOH and $CaCl_2$ causes a decrease in the average dimensions of the NPs and/or a change in the shape from hexagonal to almost spherical.[23a] However, these particles may consist of agglomerates of nanometric units owing to the diols, which remain adsorbed on the NPs. This issue can be overcome by further NP peptization in a suitable solvent.

This pathway has been adopted for the synthesis of nanosized crystal, hexagonal platelets of $Ca(OH)_2$ in water. Preparation of the NPs is performed in the temperature range of 60 to 90 °C from equal volumes of NaOH and $CaCl_2$ solutions with different degrees of supersaturation (from 2 to 10).[7a, 11c, 28] This method requires special attention to the entire removal of undesirable sodium chloride (NaCl) formed during the reaction, as it can damage the treated mortar substrates. The particles usually obtained by this method are hexagonally shaped with sides in the range of 50 to 300 nm and a thickness of 2 to 40 nm. The formation of less agglomerated smaller NPs may eventually be achieved by adding a surfactant to the reaction with a reduced preparation time.[28b]

Alternatively, $Ca(OH)_2$ NPs can be obtained by a two-step solvothermal reaction in the temperature range of 65 to 130 °C.[29] Initially, metallic calcium (Ca) is oxidized by ethanol or *n*-propanol, and then in a subsequent step, the formed Ca alkoxide is hydrolyzed as a hydrothermal reaction. This method results in the formation of pure-phase $Ca(OH)_2$ hexagonal platelets with a mean diameter of approximately 170–206 nm (oxidized by propanol) or approximately 80 nm (oxidized by ethanol).

Nanoparticles of $Ca(OH)_2$ (2–10 nm) with a highly active surface can be obtained by using water-in-oil microemulsions formed from a nonionic surfactant acting as a template.[30] These nanoparticles are highly reactive towards atmospheric CO_2. For comparison, colloidal $Ca(OH)_2$ particles with a greater average size show partial carbonation, even after long exposure to the atmosphere. However, this method is not feasible owing to low yields and because it is time consuming.

Alcohol dispersions of nanolime have been successfully applied in situ on wall painting surfaces and on limestones as a consolidant agent to stop the damage processes affecting artwork exposed to natural weathering (mainly powdering and flaking).[7b, 12a, 15] Case studies have been performed on lime-based wall paintings in Florence, Italy;[7a, 12a] on deteriorated frescoes (13th century) in San Zeno Church, Verona (Italy);[7b] and on medieval wall paintings at All Saints' Church, Little Kimble, Buckinghamshire.[15] The damaged surfaces/cracks are first protected by Japanese paper and are then treated by brush[7b, 12a] or by syringe and brush[15] until saturation. The reported results show evidence for effective consolidating action.

Pure and crystalline $Ca(OH)_2$ NPs have been obtained by ion exchange in water at room temperature and ambient pressure without undesired byproducts.[31] The reversible process occurs between aqueous $CaCl_2$ solution and anionic-exchange resin, Dowex Monosphere 550A (R–OH), with substitution of the resin hydroxy groups by chloride anions from the solution [Eq. (4)]:

$$2\,R{-}OH + CaCl_2 \rightarrow 2\,R{-}Cl + CaOH_2 \qquad (4)$$

Importantly, it is possible to regenerate the resin and to reuse it for a new synthesis. The resulting portlandite nanocrystals are very reactive, with complete carbonation. Depending on the solvent, the environmental RH, and the concentration, they form pure calcite in a few hours or up to 7 days. NPs prepared by this method and dispersed in water/2-propanol (1:2; 5 and 10 $g L^{-1}$) and water/1-butanol (1:20; 5 $g L^{-1}$) have been applied as consolidants by brushing on decayed biocalcarenite stones until saturation.[32] These stones were used as building materials for most buildings of the "Valley of the Temples" in Agrigento, Sicily, Italy. A complete carbonation process occurs in the first 30 min and leads to the formation of calcite as a pure and unique phase that is fundamental for assuring compatibility with the treated surface. Treatment of the stone surface three times with 10 $g L^{-1}$ nanolime in water/2-propanol (W/A = 50 %) is reported to be the most efficient formulation acting as a superficial consolidant, and it increases the superficial cohesion, reduces porosity, and enhances the mechanical properties in the first 10 mm beneath the surface.[32]

In 2017, Bastone et al. reported the application of an insolubilization–precipitation method upon the formation of nanolime after the addition of 2-propanol to an aqueous solution of calcium hydroxide at the solubility limit.[33] The kinetic stability increases as the alcohol content increases. The NPs obtained have been used for paper deacidification.

2.2.2. Magnesium hydroxide nanoparticles

Magnesium hydroxide [$Mg(OH)_2$] occurs naturally as the mineral brucite and is characterized by very low solubility in water (0.009 $g L^{-1}$ at 18 °C). In the field of conservation science, $Mg(OH)_2$ NPs are usually applied for the deacidification and pH control of cellulose-based artworks, such as paper, canvas, and wood.[7c,34] In particular, small particles are preferred for the treatment of low-porosity materials. In terms of consolidation, the application of $Mg(OH)_2$ dispersions is mostly related to the preservation of calcium–magnesium carbonate substrates, for example, dolomite stones, and requires particles with an average size of about 250 nm. For consolidation purposes, mixed systems consisting of calcium and magnesium hydroxide NPs are preferred.

$Mg(OH)_2$ nanocrystals with different morphologies have been prepared, including hexagonal nanoplates, nanosheets, nanotubes, and nanorods, often with surfactants and templating agents. However, the use of surfactants or non-aqueous solvents is not environmentally sustainable and novel approaches without them are under study.

Nanosized $Mg(OH)_2$ particles are usually obtained by chemical precipitation in supersaturated aqueous solutions of the reactants[34] at temperatures from ambient temperature up to 90 °C; these conditions are similar to those used in the synthesis of $Ca(OH)_2$ NPs. By this homogeneous-phase reaction, the size can be controlled mainly by the reaction temperature, concentration of the ions, and the type of counterions.

The counterions of magnesium salts affect the morphology of the crystallites. The particle size increases from about 50 nm (from a magnesium sulfate solution) to 200 nm (particles obtained from a magnesium perchlorate solution) and follows the series: sulfate < chloride < nitrate and perchlorate (Hofmeister anion series).[34a] The surface charge of the particles, the ionic adsorption on the surfaces, and the chemical nature of the ions present in the solution play fundamental roles during crystal growth. Each counterion from the different magnesium salts acts as a surface modifier, so that the nucleation and growth of crystal seeds are consistently and systematically influenced. For instance, precipitation of the nitrate, chloride, and bromide salts of magnesium with NaOH at 30 °C leads to the formation of nanoflowers composed of self-assembled nanoplatelets derived from the chloride and nitrate starting salts and to the formation of nanocapsules derived from the bromide starting salt.[35]

Particles with a mean diameter of 314 nm can be prepared at room temperature by a direct precipitation method that involves the addition of ammonia to an aqueous solution of $MgCl_2$.[36] Smaller particles can be synthesized through aging with the cationic surfactant cetyltrimethylammonium bromide (CTAB). This synthesis gives rise to small platelet-shaped particles with a thickness of about 80 nm.[37] In this case, CTAB acts as a crystal-modifying agent by arranging the $Mg(OH)_2$ NPs in a preferential orientation without the formation of a chemical bond to the hydroxide. The need for aging should be underlined, as once the NPs are synthesized, without aging they tend to form clusters.

Hexagonal $Mg(OH)_2$ nanoflakes with a thickness of 40 nm can be obtained from magnesium nitrate [$Mg(NO_3)_2$] and hydrazine at 150 °C by a hydrothermal route.[38] The hydrazine/nitrate content and the time of heating during the synthesis can modify the dimensions of the unit cell and the crystal orientation.[39] A hydrothermal reaction at a temperature of 180 °C yields larger crystals of brucite with bigger unit-cell parameters if the reagent concentrations are high (hydrazine/ nitrate: 0.14 M/0.24 g) instead of low (0.0002 M/0.12 g). The unit-cell parameters are smaller at shorter reaction times (4 h) than at longer reaction times (e.g., 6 and 12 h).[39]

A water-in-oil microemulsion can be applied to synthesize nanoplatelets of $Mg(OH)_2$ with a mean crystallite size of 12–17 nm depending on the micelle size, which controls the nucleation, growth, and crystallization of the particles.[40] NP nucleation and growth are performed in a microemulsion of Triton X-100/cyclohexane/*n*-hexanol/water by the reaction between the magnesium cations provided by a solution of $MgCl_2$ and gaseous ammonia, which flows into the reverse micelles.

Considering that dolomite stones are composed of magnesium and calcium carbonate, a compatible consolidation treatment may be achieved by the application of mixed calcium and magnesium hydroxides. Such an approach was used in the consolidation of the historical building "Collegio Ghislieri" in Pavia funded in 1567 by Pope Pius V with $Ca(OH)_2$ NPs prepared by thermomechanical treatment of lime and $Mg(OH)_2$ obtained by a homogenous-phase reaction (in excess of Mg^{2+}).[7c]

"Collegio Ghislieri" is mainly a dolomite stone characterized by fine grains and high porosity, both of which increase as a result of the cutting and curving processes. Usually, it suffers from exfoliation and detachment of the outermost layers caused by water freeze–thaw cycles and acid rain. NPs dispersed in alcohol were applied onto the stones with a brush by using Japanese paper to protect the degraded surface. This treatment was reported to be efficient for the durable preservation of dolomite stone surfaces.

Pure $Mg(OH)_2$ NPs with a lamellar morphology have been obtained by ion exchange in water at room temperature without the need for future purification.[41] The process is reversible and occurs between aqueous $MgCl_2$ solution and anionic-exchange resin, Dowex Monosphere 550A (R–OH), with substitution of the hydroxy groups of the resin by the chloride anions from the solution [Eq. (5)]:

$$2\,R{-}OH + MgCl_2 \rightarrow 2\,R{-}Cl + Mg(OH)_2 \qquad (5)$$

This mechanism provides platelike NPs with dimensions ranging from 20 to 80 nm. The NPs are formed by oriented aggregation of $Mg(OH)_2$ primary hexagonal particles (singlets), which are crystalline, regularly shaped, and homodisperse, with dimensions between 2 and 3 nm. It is possible to regenerate the resin and to reuse it for a new synthesis. The same ion exchange mechanism was used later on also for the preparation of $Ca(OH)_2$ NPs.[31]

2.2.3. Barium hydroxide nanoparticles

Owing to the fact that $Ba(OH)_2$ is highly soluble, it is very difficult to achieve saturation in water. This fact is an issue for the synthesis of $Ba(OH)_2$ NPs from an aqueous, homogeneous-phase reaction. A heterogeneous approach based on the breakdown of $Ba(OH)_2$ macrocrystals was reported by the Baglioni group.[7c,27a]

The milling of commercial $Ba(OH)_2$ in 1- or 2-propanol at high temperature and pressure leads to stable dispersions in the alcohol for NPs with a size of 100[27a] or 270 nm.[7c] $Ba(OH)_2$ synthesized by this top-down method can be used together with dispersions of $Ca(OH)_2$ NPs in 1-propanol for the consolidation of wall paintings that are strongly degraded and affected by gypsum [5 $g\,L^{-1}$; the $Ba(OH)_2$ NPs represent 20 wt% of the total NP amount].[27a] The authors show high efficiency in the consolidation of wall paintings contaminated by salts (mainly sulfates and chlorides) in the Mesoamerican area.[7c,27a] Mixed $Ca(OH)_2$ and $Ba(OH)_2$ NP alcohol dispersions are preferred over one-component $Ca(OH)_2$ NP or $Ba(OH)_2$ NP dispersions to compensate for the partial transformation of $Ca(OH)_2$ into more stable $CaSO_4$ and to increase its consolidation efficiency.

A significant consolidation effect of the application of NPs (5 $g\,L^{-1}$) was achieved on detached samples of Mesoamerican wall paintings belonging to the pre-Columbian archaeological sites of Ixcaquixtla and Calakmul (Mexico).[12b,27a,42] The wall paintings are elaborated on a carbonate substrate with a lime-based technique, and polysaccharide additives were added to the lime. The paintings show severe degradation (flaking and powdering of the pictorial layer) owing to processes such as biodegradation, salt crystallization, and swelling of the polysaccharide additives caused by high RH values (between ≈70 and 98%). The dispersions were applied by brushing on the painted layer. A significant consolidating effect with no change in the esthetical properties (in the first case[27a]) and only minimally affected (in the second case[12b]) esthetical properties was detected in 1 week to 10 days.

2.2.4. Strontium hydroxide nanoparticles

The potential use of strontium hydroxide [$Sr(OH)_2$] NPs as an alternative to $Ba(OH)_2$ solutions for the protection and consolidation of wall paintings, paper, stone, wood, and other artistic artifacts, mainly as a desulfating agent, has been reported. However, in comparison to $Ba(OH)_2$, the application of $Sr(OH)_2$ as a consolidant is undesirable because of the high solubility of $SrSO_4$ [$K_{sp,Sr(OH)_2}=3.2\times10^{-4}$ at 25 °C[17]].

Well-defined $Sr(OH)_2$ NPs with a crystallite size of 25 nm are often synthesized by the homogeneous precipitation of supersaturated solutions of $Sr(NO_3)_2$ and NaOH, similar to other alkali earth hydroxides,[7a,17] and are usually dispersed in 1- and 2-propanol.

2-Propanol dispersions of $Ca(OH)_2$ (5 $g\,L^{-1}$) and $Sr(OH)_2$ (3 $g\,L^{-1}$) NPs can be considered as promising strengthening agents for very porous biocalcarenite substrates, such as Lecce Stone, and as alternatives to alkoxysilane as consolidating treatments for calcareous substrates, particularly if applied by brushing.[13c,17] This kind of stone easily undergoes weathering and is characterized by a high content of calcite and high porosity. Spherically shaped $Ca(OH)_2$ particles with sizes ranging from 25 to 150 nm can be synthesized in 1,2-ethanediol,[13c,23a] whereas $Sr(OH)_2$ particles with sizes ranging from 80 to 300 nm are produced in water.[17] Vapor permeability after complete carbonation of the applied $Ca(OH)_2$ and $Sr(OH)_2$ NPs does not drastically affect the "transpiration" of the original material.

3. Inorganic Nanocomposites based on Silica

The potential of SiO_2 NPs has recently been studied for the conservation treatment of different stone substrates.[13c,43] The efficacy of SiO_2 nanoparticles as a consolidating product of stone depends on the relative humidity of the exposure environment.[43a]

The treatment of Lecce stone with silica NPs (15%, *w/w* in water; 15–20 nm) is less effective than treatment with the above-described $Ca(OH)_2$ and $Sr(OH)_2$ NPs, probably because of the lower chemical affinity of silica NPs for carbonate substrates. The smaller silica NPs are absorbed to a much lower extent than the hydroxide NPs.[13c] Treatment by brushing induces the formation of a thick and cracked silica (SiO_2) layer covering the stone surface. As a result, the resistance to salt crystallization weathering is considerably lower than that obtained through hydroxide treatment.

The consolidation treatment of chert samples, composed of quartz (SiO_2), moganite (SiO_2 polymorph), and calcite ($CaCO_3$), with a mixture containing SiO_2 and $Ca(OH)_2$ NPs may become ineffective after aging. This is the case for variations in relative humidity, as they can cause a loss of the consolidating product surface layer.[44]

4. Calcium Alkoxides [Ca(OR)$_2$]

4.1. Nature and consolidation mechanism

Calcium alkoxides (Ca alkoxides) have been studied mostly as suitable consolidating agents for carbonate stones, plasters, and wall paintings in solution and as NP inorganic sols.[45]

Under atmospheric conditions, Ca alkoxides undergo hydrolysis and carbonation inside the porous structure of the substrate, whereas the solvent evaporates, and this leads to the formation of calcium carbonates. This process strongly depends on the atmospheric conditions, particularly on the humidity of the air and the nature of the solvent. Their application in hot geographic areas with low humidity may be limited.

The possibility to form a stable M–O(R)–M bridge as a result of the high donor activity of the oxygen atom from the OR groups is another limitation for the application of alkoxides as consolidants. This can cause oligomerization of the monomeric alkoxide groups.[45c,46] The formation of oligomers reduces the solubility and volatility of the alkoxides. Oligomerization can be limited with the use of an appropriate ligand.[45c]

The carbonation mechanism of Ca alkoxides is complex and may occur through two possible paths[45a,b,e] lasting from a few minutes up to 6 h:[47]

1) Insertion of CO_2 into the Ca–O bond of the alkoxide [Ca(OR)$_2$]. The elimination of ROH from the formed alkylcarbonate derivative results in the formation of $CaCO_3$
2) Hydrolysis of Ca(OR)$_2$ leading to the formation of Ca(OH)$_2$, which carbonates afterwards

Both processes for the formation of the polymorph crystalline form of $CaCO_3$ are competitive, appear to be independent of the alkoxide structure, and depend on the relative humidity, the pathway used for the synthesis of the alkoxides, the solvent carrier, and the temperature.[45b,c,e] The final product, $CaCO_3$, is mostly a mixture of vaterite/calcite in variable ratios. Variation of the ratio depends on the solvent/dispersion agent and on the nature of the substrate.

The suitability of Ca alkoxides for stone consolidation was anticipated by Favaro et al.,[45a] who evidenced the carbonation of alkoxides exposed to atmospheric CO_2 and moisture, that is, commercially available Ca(OCHMe$_2$)$_2$ and two species, Ca(OMe)$_2$ (**1**) and Ca(OEt)$_2$(EtOH)$_4$ (**2**), synthesized in a glove box from metallic Ca granules cleaned in dry diethyl ether and the respective alcohol, methanol and ethanol. White precipitate **1** was obtained after stirring overnight and **2** was obtained after heating at reflux for 6 h. After exposure to air, different phases of $CaCO_3$ were formed, and complete carbonation was achieved from 2–4 to 35–45 days. The low solubility of the alkoxide in methanol, causing the formation of a low amount of $CaCO_3$, implied many consecutive application procedures.

A thermodynamically stable calcite is formed from the transformation of vaterite by the addition of water and with a high relative humidity.[45e] Slow carbonation (influenced by the solvent carrier) favors its formation. A higher solvent vapor pressure corresponds to a fast evaporation rate and faster carbonation. In the frame of the EC NANOMATCH Project,[48] an approach to test the durability under environmental conditions has been elaborated.

4.2. Syntheses and application particularities

Favaro et al.[45c] have explored five synthesis pathways and have obtained Ca alkoxides (Ca content $>40\ g\,L^{-1}$) soluble in common organic solvents with good penetration depths that are suitable for application as consolidants after carbonation:

1) Direct reaction between alcohol and metallic Ca
2) Alcoholysis reaction with the formation of a new Ca(OR)$_2$ by heating a solution of Ca(OEt)$_2$ in the appropriate alcohol at reflux with or without a co-solvent
3) Rieke calcium: preparation of Rieke metals by reduction of a tetrahydrofuran suspension of an anhydrous metal chloride with an alkali metal, eventually with a catalytic amount of an organic electron carrier
4) Ammonia method: dissolution of metallic Ca in anhydrous solvent at temperatures of -45 to $-60\,^{\circ}C$ with gaseous ammonia bubbled during the process and with the addition of the desired alcohol once the metal is dissolved
5) Synthesis from Ca(OH)$_2$: formation of alkoxide derivatives by removal of water with a Dean–Stark apparatus in high-boiling point alcohols

The ammonia method has been identified as the most suitable one. If exposed to air at a temperature of 25 °C and a RH$>$50%, a conversion of the Ca alkoxides to $CaCO_3$ takes place with formation of vaterite as a predominant phase and calcite as a minor phase.

It is relevant to consider the importance of the solvent carrier of the alkoxide that carries it in the deteriorated stone. Before carbonation, interchange of the alkoxy groups between the alcohol and the alkoxide may occur. This phenomenon has not been reported upon replacing methanol with 2-propanol.[45b] Hence, 2-propanol is the solvent carrier if new liquid Ca alkoxide are applied to marble specimens. Three new Ca alkoxides have been synthesized with ammonium-activated calcium and triethylene glycol monomethyl ether {[Ca(O(CH$_2$CH$_2$O)$_3$Me)$_2$]}, triethylene glycol monoethyl ether {[Ca(O(CH$_2$CH$_2$O)$_3$Et)$_2$]}, and 2,2-dimethyl-1-propanol [Ca(OCH$_2$CMe$_3$)$_2$] in toluene. The starting alcohols are selected according to the increasing solubility of the Ca alkoxide.

Two more Ca alkoxides prepared by the ammonia method were tested as consolidants: Ca(OEt)$_2$ and Ca(OTHF)$_2$ (THF = tetrahydrofurfuryl). Carrara marble, Savonnières limestone (nummulitic limestone), Laspra dolostone, and Albeşti (nummulitic limestone) in field lithotypes and representative of the Santa Croce Basilica in Florence, Cologne Cathedral, Oviedo Cathedral, and Stavropoleos Monastery, respectively, were treated.[45e,48] The best results were obtained with a solution of alkoxides at a concentration of 20 g L^{-1} in ethanol/ligroin = 1:1 applied twice by brush. Treatment with the alkoxide materials led to the formation of a layer of $CaCO_3$ microcrystals. Observations indicated that this $CaCO_3$ layer was less compact than the one formed by commercial Ca-containing consolidant NPs in the size range of 50 to 150 nm. However, the consolidant remained mainly on the surface or in the first micrometers of the surface of the decayed stone.[49] In fact, the authors anticipated the possibility of the formation of a xerogel with a cracked surface after complete evaporation of the solvent, although evidence of copolymerization or a sol–gel was not obtained.

The alkoxide does not affect the appearance of the stone if appropriately applied. A good surface cohesive effect can be achieved in a short time after its application on stone owing to fast reaction of the alkoxide with atmospheric H_2O and CO_2. This leads to the formation of microcrystalline aggregates on the surfaces of porous limestones. On low-porosity stones and on microporous stones (e.g., Carrara marble), the alkoxide-based consolidant forms a discontinuous microcrystalline surface layer.[45e]

Another alkoxide, calcium triethylene glycol monoethyl ether $[Ca(TEGmEE)_2]$, can be used as a calcite precursor in a porous material.[50] It has high solubility in polar protic solvents and has relatively good workability and penetration if brushed on powdery surfaces. These nanomaterials were tested as consolidants on carbonaceous substrates: marble and wall paintings. Two types of substrates were consolidated: weathered Carrara marble and wall painting specimens of frescoes and a secco technique with a mixture of green earth, yellow ochre, azurite, lead-tin yellow, and cinnabar-white lead. $Ca(TEGmEE)_2$ gave the best results in butanol for wall paintings and good results for consolidation specifications in 2-propanol for marble specimens.[50]

There has so far not been any convincible data that suggests the suitability of magnesium alkoxides for the conservation of built heritage.[45c]

5. In Situ Formed Hydroxyapatite (HA)

The mechanical properties of limestone can be significantly improved by in situ formed hydroxyapatite. Furthermore, in its various applications in materials science, medicine, and archaeology, this calcium-containing compound is seen as a good inorganic consolidant for carbonate stones. An aqueous phosphate solution (diammonium hydrogen phosphate, DAP) reacts with calcite in stone, which leads to the formation of hydroxyapatite[51] and byproducts that are not harmful for the stone [Eq. (6)]:[51a,c,e]

$$\begin{aligned}10\,CaCO_3 + 5\,(NH_4)_2HPO_4 \rightarrow {} & Ca_{10}(PO_4,CO_3)_6(OH,CO_3)_2 \\ & +5\,(NH_4)_2CO_3 + 3\,CO_2 + 2\,H_2O\end{aligned} \tag{6}$$

The aqueous phosphate solution is able to penetrate deeply into the stone (>2 cm) and bring significant strengthening in a few days,[51c,d] depending on the application technique.[51a] A nanolime dispersion in 2-propanol (≈86 nm, 10 g L^{-1}), synthesized at 90 °C from NaOH and $CaCl_2$,[7a] can be used as a Ca source, and it mineralizes with ammonium phosphate $[(NH_4)_3PO_4]$ into a weathered stone.[52] This leads to the formation of hydroxyapatite and isolated rhombohedral crystalline grains of calcite. During the mineralization process at ambient temperature, a porous and interlinked apatite phase is formed, and it can bind the $CaCO_3$ particles together with weathered stone blocks.[52]

The addition of CTAB to DAP affects the crystallinity of HA and the surface area of HA formed upon their reduction, that is, the crystal size of HA increases.[53] CTAB molecules form positively charged micelles that attract HPO_4^{2-} anions owing to strong electrostatic attraction. After calcite dissolution, calcium cations (Ca^{2+}) combine with hydrogen phosphate dianion (HPO_4^{2-}). However, the formation of HA remains unclear, as the presence of PO_4^{3-} ions is fundamental.[54] The addition of CTAB to the DAP solution leads to improvement of the consolidation effectiveness of the HA. The addition of a TEOS-based consolidant to the surface coated with HA improves cohesion with the stone. The CTAB/DAP/TEOS-based consolidant solution has better acid rain resistance than DAP and CTAB/DAP solutions.[53]

Phosphate compounds have been studied as consolidants of limestone and as coupling agents for silicate consolidants. Phosphate treatment has been studied for consolidation, protection from dissolution in rain, prevention of bowing, and functionalization to provide self-cleaning ability, antifungal ability, and desulfation. All of these functions are discussed in detail by Sassoni.[54]

6. Organic–Inorganic Nanostructured Materials: Alkoxysilanes

The suitability of alkoxysilanes and their gels for stone consolidation is determined by their low viscosity and by their ability to form siloxane (Si–O–Si) bonds. As a result of their first property, they can easily penetrate into an intergranular stone substrate, at which point, owing to their second property, they polymerize and through a sol–gel process form stable siloxane bonds. In this way, cohesion of the grains of the stone is improved.[55]

Two main reactions take place when the sol–gel transition occurs: first, hydrolysis of the alkoxy groups to create silanols; second, polymerization by condensation of the silanol groups of the products. In addition, condensation occurs between the silanol groups of the products and those present in the siliceous mineral surface of the stone. Tri- and tetrafunctional alkoxysilanes are characterized with low toxicity. Ambient relative humidity contributes to the relatively low rate of the reaction, which implies the necessity of adding water to increase the rate. Although water and alkoxysilanes are immiscible, a solvent such as ethanol is necessary to form a homogeneous solution.

Besides the choice of the alkoxysilane and the addition of water, the rate of hydrolysis can be influenced by acid or base catalysts.[55] The nature of the resulting gel depends on the catalyst type.[55] Acid and base catalysts promote the rapid and complete hydrolysis more so than neutral conditions.

Alkoxysilane solutions based on TEOS and methyltrimethoxysilane (MTMOS) have been widely used for the consolidation of decaying heritage stone surfaces.

Along with a time-consuming TEOS curing reaction, the lack of efficiency in bonding to calcite, and the risk of biodeterioration, one of the main issues in the application of alkoxysilanes is shrinking and cracking of the gel during the drying process. The gel can suffer crack formation during the drying phase owing to the developing capillary pressure and dense gel fractures left inside the stone.[56] The smaller the pore radius, the higher the capillary pressure. The capillary pressure can be reduced by the coarsening of the pores within the gels, which limits the shrinking and cracking of the gel. Two approaches can be applied to achieve this purpose: modification of the polymer with inorganic nanoparticles and addition of a surfactant.[56]

The addition of NPs (mostly titania, alumina, and silica) is expected to coarsen the pores and, thus, causes a lower capillary pressure, but the addition also improves the physical properties of the polymer (i.e., stiffness, porosity, thermal expansion coefficient), which has a positive effect on the consolidation. These two- or three-component formulations are known as particle–modified consolidants (PMCs).

In a previous report, a TEOS-based matrix is loaded with 2-propanol dispersions of silica (10–20 nm), alumina, and titania (average particle sizes of alumina and titania are 200 and 300 nm), and the last two are coated with silica.[20b] The consolidation capacity of the distinct xerogels does not differ in a significant way, except that the salt resistance is lower for the silica-loaded compound. The particles do not change significantly the viscosity of the sol. Their inclusion into the matrix enhances the elastic modulus and decreases the thermal expansion. The reduced thermal expansion coefficient is closer but yet much higher than that of stone. The composites exhibit a strong reduction in the shrinkage of the silicate's network and a lower risk of cracking during and after solvent evaporation.[20b]

It is also possible to increase the porosity of the TEOS matrix by loading it with colloidal silica (SiO_2) nanoparticles and titania oxide (TiO_2) particles. The addition of the particles increases the porosity of the gel and decreases the capillary pressure. Hence, the three-component formulation is the most effective. The higher ratio of TiO_2/SiO_2 (1:1) in the TEOS matrix causes the formation of coarser pores in the microstructure, which results in an improvement in the permeability of the material. This results in a reduction in the cracking and shrinking of the dried material.[20c]

It is possible to reduce the capillary pressure with the addition of GPTMS [3-glycidoxypropyl)trimethoxysilane] and silica NPs to TEOS by forming a TEOS/GPTMS/SiO_2 composite solution.[57] The product reduces water absorption inside the stone. The SiO_2 NPs are 7, 16, and 40 nm in size and are smaller than the pore size of the tested sandstones (with porosity of 18.06 % and an average pore diameter of 68.8 nm).

A derivative structure containing polyhedral cluster-like oligomeric silsesquioxane (POSS) [of the type $(RSiO_{1.5})_n$] instead of silica with nanometer-sized pores has been tested on Korean granite stone.[58] The addition of nanometer-sized POSS (silica NPs with inner voids) and/or GPTMS that have a flexible segment reduces the capillary force developed during solvent evaporation; they should also improve the transport of water vapor. The consolidants have been applied on decayed granite located in Namsan, Korea; this is a major stone material of the Korean cultural heritage built during the Silla Dynasty (BC 57 to AD 935). The composite solution prevents the stone from secondary deterioration. The addition of POSS and GPTMS provide a crack-free gel after drying with increased surface hydrophobicity of the treated decayed Namsan granite.[58]

The other alternative to decrease the capillary pressure by pore coarsening in the gel network and with an additional decrease in the surface tension is the addition of a surfactant, which acts as a template for the gel pores to the formulation. The Mosquera group has explored surfactant-templated synthesis to obtain a crack-free xerogel with respect to the following prerequisites: the sol must have low viscosity to penetrate into the stone, the gelation in situ must occur in a few hours, and the surfactant must be spontaneously removed. The authors contemplate the use of a small amount of a neutral primary amine (*n*-octylamine) and controlled ethanol contents to avoid instantaneous gelation of TEOS.[59] The surfactant modifies the hydrolysis/condensation process of TEOS by accelerating the rate of hydrolysis. It leads to increased pH to the sol, and under basic conditions, water dissociates to produce nucleophilic hydroxy anions that can displace the ethoxy groups from TEOS.[59a,60] In the recent reports of the Mosquera group, the need to heat a mixture of TEOS in hydrochloric acid at reflux to induce hydrolysis does not arise; the acid catalyst is extremely hazardous to the stone.

The primary amine surfactant, *n*-octylamine, plays a significant role in enhancing the consolidant effectiveness of siloxane. If its concentration is above its critical micellar concentration, it acts as a structure-directing agent during polymerization. There are two possible strategies for the preparation of hybrid inorganic–organic frameworks with *n*-octylamine micelles.[61] Each of them includes hydrolysis and surfactant extraction with ethanol. Upon considering that silica interacts with the surfactant by means of hydrogen bonding, the surfactant can be removed by slow evaporation instead of by impracticable in situ calcination or extraction.[59a,61]

According to Facio et al.,[62] who studied the mechanism for consolidation, the mesoporous xerogel is composed of packed silica particles, the size of which depends on the nature of the surfactant and the water content. The silica particles are formed by a sol–gel reaction occurring with the formation of a water-in-oil microemulsion of alkoxysilane/water, stabilized by *n*-octylamine inverse micelles. The aliphatic chains of the surfactant face the alkoxysilane molecules, whereas the amino groups are in the inner side of the inverse micelles enclosing water. The micelles act as nanoreactors for the formation of the silica particles, which grow at first within the micelles and thereafter outside of the micelles until they become part of the xerogel. The mesoporosity represents the interparticle space between the silica.

This method can be applied for the synthesis of alkoxysilane-based xerogels with the aim to improve the mechanical strength of granite[63] and the robustness, hydrophobicity, water repellence, and stain resistance of carbonate stones.[64] The sol composed of silica oligomers and NPs polymerizes in situ under outdoor conditions with a surfactant once it is applied to the stone by spraying. The formed crack-free coating fills the pores of the decayed stone.[65]

With the objective to attribute both consolidation and hydrophobic properties to the mesoporous framework, the possibility of adding reagents has been explored. The new nanostructured organic–inorganic hybrid mesoporous silica gels consist of organically modified silicate (ormosil), which is synthesized by the co-condensation of TEOS and hydroxy-terminated polydimethylsiloxane (PDMS-OH) in the presence of di-*n*-butyltin dilaurate (DBTL)[66] or *n*-octylamine.[59,60,64] The organotin compound DBTL is a neutral polycondensation catalytic component that is used instead of strong acids or bases as catalysts in the hydrolysis of TEOS and it participates in the formation of siloxane bonds. The resulting xerogels are characterized by very low porosity, and in particular, these xerogels have porosity that is lower than that of xerogels prepared with acid or base catalysts.[67] DBTL may accelerate the gelation time.[20c] PDMS-OH enhances the flexibility and gives toughness to the material, which increases shrinkage and subsequently prevents cracking; furthermore, it brings useful hydrophobic properties. Both formulations allow the formation of a more elastic consolidant phase inside the porous stones treated in one step. The xerogels increase the mechanical resistance of the stone and create a hydrophobic coating without any negative effects on the treated stone. As an alternative, this silica nanocomposite can combine with a fluorinated alkoxysilane hydrophobic layer, which, once applied after polymerization of the xerogel, creates a chemical bond between them.[65]

Liu and Liu have developed a TEOS/PDMS-OH/CTAB composite coating material.[68] The composite has good hydrophobic properties, crack-free surface homogeneity, acid resistance, and salt crystallization resistance abilities.

TEOS-based consolidants are efficient for the consolidation of silicate stones and are not chemically compatible with carbonate stones.[55] *n*-Octylamine can additionally facilitate interaction between the siloxane and carbonate stone (pure and dolostone) and, in this way, enhances the nanocomposite consolidation efficiency of a silica nanocomposite with self-cleaning properties owing to the incorporation of TiO_2 NPs.[69]

The addition of a bioactive copper(II) oxide nanopowder (<50 nm) component in the same silica-based nanocomposite can lead to the formation of a promising multifunctional consolidant that results in a hydrophobic and biocidal CuO/SiO_2 coating for natural limestone.[70]

Electrochemically synthesized zinc oxide (ZnO) NPs, incorporated in commercial consolidant/water repellent TEOS-based products, form a material that is expected to display long-term biocide activity. Nevertheless, chromatic changes, although reduced, still remain as the main issue for application of this nanocomposite.[71]

6.1. Silica and calcium oxalate-based nanocomposites

Hybrid nanocomposites based on silica and calcium oxalate improve the tensile strength of the treated stone, enhance the chemical and physical affinities for natural stone, and exhibit a partial protective effect without altering the microstructure of the treated stone.

A mesoporous xerogel with an average pore radius of approximately 15 nm and tested at porous limestone can be obtained by following a two-step synthesis route consisting of mixing a colloidal solution of nanocalcium oxalate in 2-propanol with TEOS.[72] During the first phase, a colloidal solution of calcium oxalate monohydrate NPs ($CaC_2O_4{\cdot}H_2O$) is synthesized from $Ca(OH)_2$ and oxalic acid in stoichiometric proportions in 2-propanol [Eq. (7)]:

$$Ca(OH)_2 + H_2C_2O_4 \rightarrow CaC_2O_4 \cdot H_2O + 3\,H_2O \tag{7}$$

The next step is the addition of TEOS and *n*-octylamine into the colloidal solution, which gives rise to the formation of calcium oxalate. Calcium oxalate is composed of aggregates consisting of rod-shaped crystals, and the majority of the crystals exhibit a width of approximately 30–35 nm and a length of 70–170 nm. The formation of a network between TEOS and calcium oxalate reduces water absorption.[72]

The method has been modified to a one-pot synthesis by a sol–gel method without a surfactant.[73] Nanocalcium oxalate is formed simultaneously with the polymerization of TEOS, and oxalic acid acts as a catalyst for the hydrolysis of TEOS. The addition of $Ca(OH)_2$ and oxalic acid to TEOS produces $CaC_2O_4{\cdot}H_2O$, which is then incorporated into the silica matrix. The crack-free nanocomposite has a uniform microstructure with an average pore diameter of 2.73 nm and particles that are approximately 7–15 nm in size. Amorphous nanocalcium oxalate incorporated into the silica matrix confers chemical affinity and good interfacial compatibility between the nanocomposite and the building materials (e.g., calcareous stones and cement mortars) and improves the mechanical properties owing to its crack-free microstructure. The hybrid nanocomposite can penetrate inside the stone substrate and acts as a strengthening agent with a protective effect against environmental loading.[73] Experiments suggest that the solution penetrates deeply into the building material substrate without blocking the pores, which thus prevents moisture entrapment. The derived hybrid nanocomposite is stable in humid environments and under UV light.

Treatment with a layer of TEOS/nanocalcium oxalate can be combined with treatment with a hydrophobic layer of copolymerized TEOS and PDMS and a self-cleaning layer of TiO_2 NPs from titanium tetraisopropoxide (TTIP) with oxalic acid.[74]

Besides producing hydrophobic and crack-free gels, PDMS is important to prevent the penetration of TiO_2 NPs into the stone and mortars. Otherwise, photoactivation may be compromised. In addition, chemical compatibility among TEOS, PDMS, and TTIP enables TiO_2 to be anchored in the silica matrix, which thus prevents its leaching.

7. Outlook

Undoubtedly, nanomaterials are good alternatives to commonly used organic consolidants. Their complete carbonation and polymerization inside/onto the treated substrate are complex processes and occur in connection with a variety of factors that can affect the consolidation process. To achieve good results, often they must be applied in combination with more products or the substrate must be pre-consolidated. Optimization of the penetration depth and homogeneous application of nanoconsolidants remain some of the most important requirements, together with avoiding modification of the breathability of the substrate and flaking of the surface or detachment, among others. At the same time, chromatic changes caused by either nanolime concentrations or by the inclusion of NPs in the silica matrices have been reduced but not overcome.[43b,71,75] Moreover, the solvents and surfactants are potentially hazardous for living organisms and the environment.

Much work on inorganic nanomaterials for the consolidation of artwork has been published in the last two decades. A reduced size will facilitate the penetration and interaction of a dispersion and will achieve better stability and adhesion with the artwork, while preserving its original appearance. Stable alcohol dispersions of alkaline earth metal hydroxides and alkoxides, nanocomposites with oxides or NPs incorporated in silica/silicate matrix, and alkoxides and TEOS-based consolidants have been explored. The synthesis methods have been adopted and studied to obtain morphologies that correspond to the nature of the decayed substrate and meet the requisites for efficient consolidants. The most commonly used methods for the synthesis of nanostructured consolidants are the sol–gel and co-precipitation techniques. Studies on preparative strategies are focused on the economically sustainable preparation of long-term, highly efficient, compatible, easy-to-apply pure phase materials with controlled sizes and in a stable dispersion. Secondary effects must be carefully studied to overcome the eventual disadvantages of inorganic nanoconsolidants: toxicity or alteration of the esthetical properties of the consolidated substrate. Besides the alternative of incorporating NPs in inorganic or organic–inorganic matrices, there is another possibility to achieve good products, and this is to provide the NPs with multifunctionality and use them for more than one purpose.

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Conflict of interest

The authors declare no conflict of interest.

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