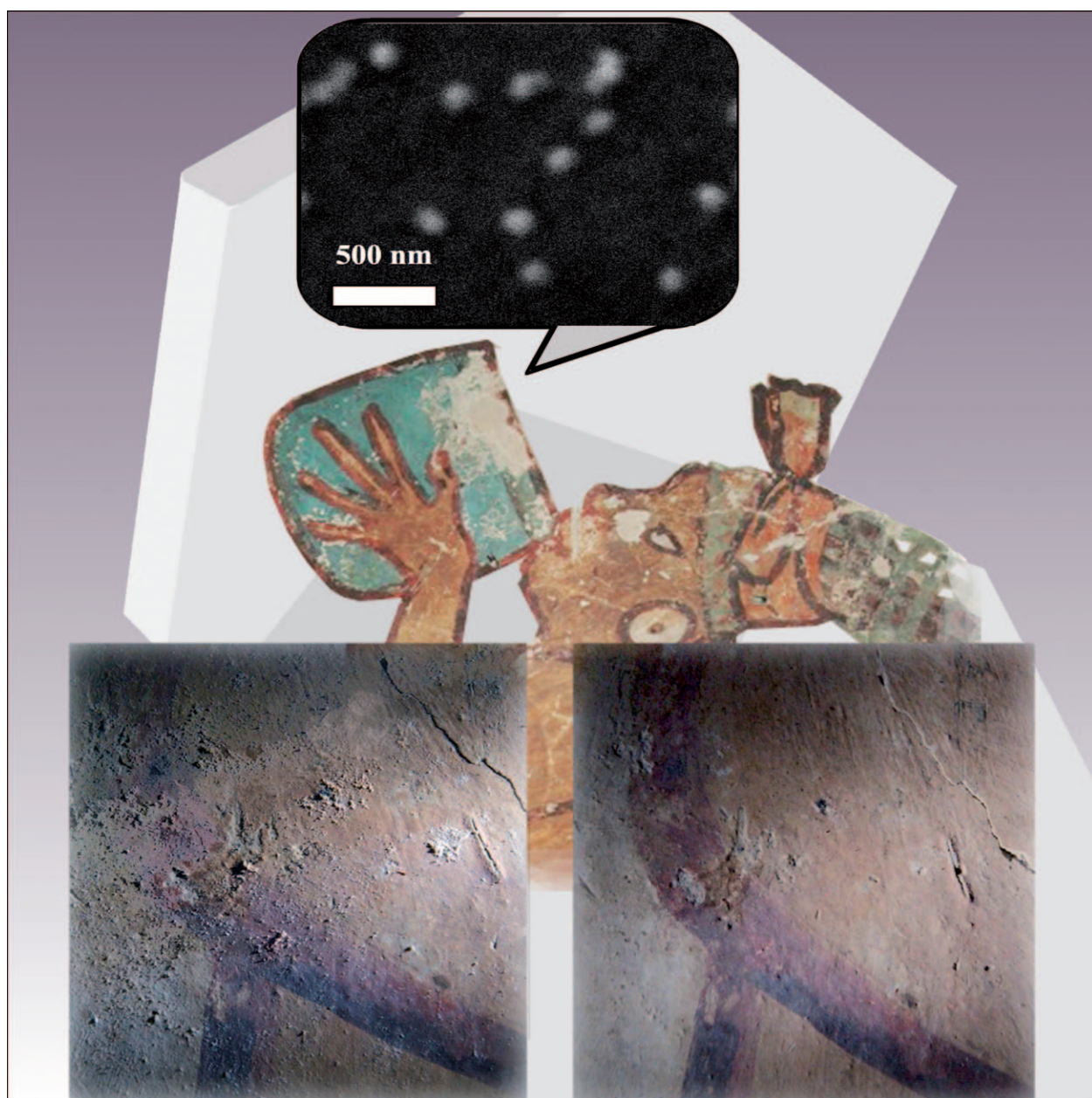




Nanoparticles for Cultural Heritage Conservation: Calcium and Barium Hydroxide Nanoparticles for Wall Painting Consolidation

Rodorigo Giorgi, Moira Ambrosi, Nicola Toccafondi, and Piero Baglioni*^[a]



Abstract: Nanotechnology provides new concepts and materials for the consolidation and protection of wall paintings. In particular, humble calcium and barium hydroxide nanoparticles offer a versatile and highly efficient tool to combat the main degradation processes altering wall paintings. Clear example of the efficacy and potentiality of nanotechnology is represented by the conservation in situ of Maya wall paintings in the archaeological area in Calakmul (Mexico).

Keywords: barium • calcium • conservation • hydroxides • nanoparticles • nanotechnology • restoration

Introduction

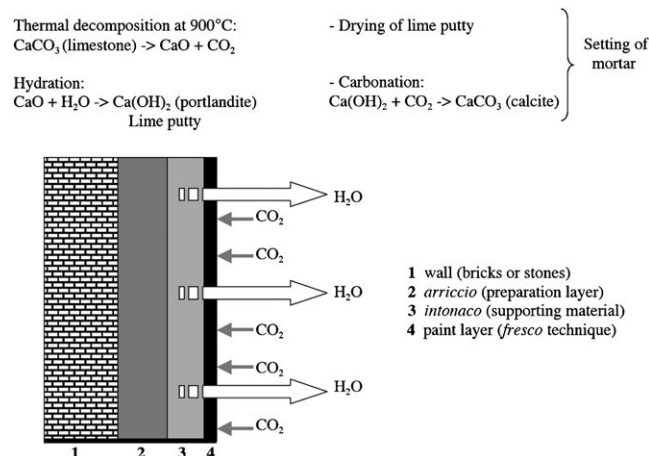
Historically, lime has been used by all the civilisations in every age and geographical area. Although it is not clear exactly when use of lime in mortars began, ancient examples have been found in the east Mediterranean area. One of the earliest documented uses of lime as a construction material dates back to 4000 BC, when Egyptians used it for plastering the pyramids.^[1] This technology was used in the classical age by Greeks and Romans (Vitruvius provided basic guidelines for lime mortar mixes in his treatise *De architectura*), by Mesoamericans in the Precolumbian age, and it was largely diffused in the Middle and Far East throughout the centuries.

The burning of limestone produces, through thermal decomposition of the material and elimination of carbon dioxide, porous lumps of calcium oxide known as quicklime. These lumps react with water to form calcium hydroxide (lime slaking) as dry lime powder or lime putty, depending on the amount of water used.^[2] The mixing of hydrated lime with an aggregate (usually sand) and more water forms mortar. The aggregate is necessary to avoid cracks that form upon drying; moreover, it imparts hardness to the mortar and favours the formation of porosity. The final hardening and mechanical strength of the mortar are due to the carbonation process of calcium hydroxide, which reacts with carbon dioxide dissolved in water to form calcium carbonate.

Hydraulic limes partly replaced ordinary lime mortars from the middle of the eighteenth century; the latter were completely abandoned with the development of Portland cement (patented by Joseph Aspdin, an English mason/builder, in 1824). This trend was certainly favoured by the

well-known difficulties associated with the use of lime mortars, such as the long setting times, particularly under very high relative humidity (RH) conditions. Moreover, because of their weak mechanical strength, lime mortars are prone to degradation due to salt crystallisation processes.^[3]

A large part of the artistic cultural heritage from the past is related to wall paintings performed on plaster (also named fresco paintings; Scheme 1). Salt contamination in



Scheme 1. Schematic representation of the stratigraphy of a wall painting executed by the fresco technique. Pigments are entrapped in the growing calcite originating from the carbonation of lime.

wall paintings is a challenge for their conservation. The paint layer is at the interface between the wall and the surrounding environment and it is strongly susceptible to degradation caused by the mechanical stresses that arise from salt crystallisation, usually occurring at the surface. Salt solutions eventually impregnate the porous network of the wall and move through by capillarity. Crystallisation takes place when the ions' concentration exceeds saturation, often as a result of water evaporation at the interface. This process is generally accompanied by volume expansion; the formation of new crystals inside the pores and/or at the interface between the paint layer and the plaster generates mechanical stresses and results in either lifting and detachment of the paint layer, or cracks and fissuring of the plaster.^[4] Sulfates are commonly found as contaminants of wall paintings, since they result from the chemical degradation of calcium carbonate due to acid pollutants. Thus, besides representing a symptom of an already happened chemical degradation process, sulfates favour further deterioration because of the aforementioned mechanical stresses.

The effects of salt crystallisation are usually strongly amplified if any protective coating, possibly applied in previous restoration treatments, is present. Polymers, mainly acrylic and vinyl resins, have been widely used to consolidate wall paintings and to confer protection and hydrorepellency to the painted layer.^[5] Formulations based on acrylate/meth-

[a] Dr. R. Giorgi, Dr. M. Ambrosi, Dr. N. Toccafondi, Prof. P. Baglioni
Department of Chemistry & CSGI
University of Florence
via della Lastruccia 3-50019 (Italy)
Fax: (+39)0554573032
E-mail: baglioni@csgi.unifi.it

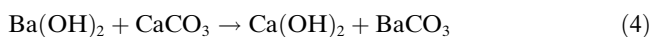
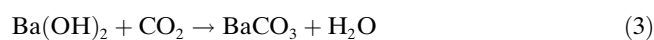
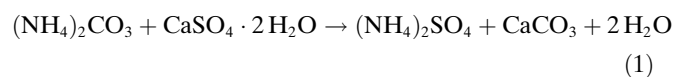
acrylate and acrylate/vinylacetate co-polymers have been extensively used for decades; unfortunately they threaten the survival itself of works of art and they can now be considered as one of the most dangerous sources of degradation. In the presence of polymer film, salt crystallisation processes involve deeper areas, with stronger de-cohesion until the complete powdering of the painting. The polymer closes the surface pores, generating mechanical stresses towards the paint layer. These polymers have been considered perfectly reversible materials for a long time. Unfortunately, their reversibility, that is, the possibility to solubilise them by the same solvent used for the application, has been proved to be a *chimera*. In fact, polymer resins degrade quickly with drastic variation of their physicochemical properties. In summary, contrary to the expectations, polymers used for the protection of wall paintings have induced further degradation of the works of art and their chemical modifications, such as cross-linking, strongly hampers their removal.^[6]

Concept

For the above reasons, the use of inorganic materials (possibly of the same materials used for the works of art), which are compatible with wall paintings, minimises the aforementioned risks and prevents unexpected side effects. Inorganic consolidants are highly chemically stable and preserve the wall painting porosity, so ensuring long-lasting consolidation effects.

With the aim of solving the problem of the degradation of wall paintings caused by the presence of sulfates and to achieve a good consolidation, in the mid-seventies Enzo Ferroni developed a conservation treatment based on the application of ammonium carbonate and barium hydroxide solutions. This methodology was used for the first time during the restoration of wall paintings by Beato Angelico in Florence.^[7]

The Ferroni method involves the application of ammonium carbonate and barium hydroxide in a two step procedure [Eq. (1)–(2)]. Ammonium carbonate changes gypsum into soluble ammonium sulfate, which is mostly absorbed by the cellulose poultice usually used for the application of the ammonium carbonate solution [Eq. (1)]. The subsequent application of an excess of barium hydroxide leads to a stable consolidation effect [Eq. (3)–(5)], thanks to the formation of barium carbonate [Eq. (3)] and the re-generation of calcium hydroxide [Eq. (4)], through a double-exchange reaction with calcium carbonate.



This “new” lime undergoes a slow carbonation reaction that enhances the mechanical strengthening of the paintings. Part of the applied barium hydroxide completes the transformation of gypsum, forming insoluble barium sulfate.

Unfortunately, at that time, the methodology was strongly averted by restorers who were confident of the use of polymer resins, mainly for the easy and fast application procedure. Indeed, this simple consolidation procedure, known as Ferroni or Florentine method, presents a twofold advantage, since it simultaneously provides the consolidation of wall paintings and a substantial removal of gypsum.

Although calcium hydroxide is one of the most ancient and widely used building materials, its application as consolidation agent of wall paintings is insignificant.^[8] There is no doubt that lime ensures the highest physicochemical compatibility with the work of art and it should be preferred when degradation results from loss of calcium carbonate. Nevertheless, the low solubility of calcium hydroxide in water (about 1 g L⁻¹) has hindered its use for years. Saturated solutions (lime-water) have been used only in a few specific cases. Alternatively, application of lime dispersions is hampered by the possible veil formation (due to the calcium hydroxide reaction with carbon dioxide) on the treated surfaces. Whitening could be overcome by using alcoholic dispersions of very tiny particles, with size lower than that of surface pores, which are in the range of micrometers.^[9]

Dry Hydrate Lime and Lime Putty

The slaking of quicklime (also known as hydration process) is the most common and cheapest method to prepare Ca(OH)₂ powder. By mixing one part by weight of CaO with about 0.5–0.75 part of water, a dry hydrate (i.e. Ca(OH)₂ powder) is obtained. Due to the high temperature developed during hydration, amounts of water slightly higher than the theoretical one are usually required to reach a complete hydration.^[1] On the other hand, the slaking with an excess of water produces a lime putty. The latter is characterised by finer particles and, therefore, a higher surface area, which confers a higher reactivity and plasticity to the putty than the dry hydrate. Lime putty contains chemically bound water and about 30–40% w/w of free water surrounding hydrate colloids.^[10] It has been shown that free water prevents particles' spontaneous aggregation, by acting as a lubricating agent.^[11]

It is not easy to define the best hydration parameters tailored to the final characteristics of powder and/or colloids. It is known that both large excess or insufficient amounts of water (lower than the stoichiometric ratio) produce very poor lime. In the first case, a fast hydration of quicklime lumps leads to the formation of a close surface calcium hydroxide layer, the low porosity of which inhibits further

water diffusion; in the second case, very high temperature is reached locally, which causes the burning of hydrate and its complete dehydration.^[12]

Classic historical sources by Plinius and Vitruvius, as well as the Renaissance treatise by Cennino Cennini, report recipes to enhance the slaked lime quality. In particular, a prolonged storage under pure water was recommended to reach a complete ripening of lime, which usually requires several months or even years. Practical experience has defined the best aging procedure to improve plasticity and workability of lime putties; however, little is known about mechanisms underlying the observed improvements.

The effect of prolonged storage of lime under water has been recently analysed by Rodriguez-Navarro et al.^[13] Crystal morphology and size of calcium hydroxide particles were shown to significantly change upon aging. Over time, prismatic crystals, present in fresh lime putty, undergo relevant size reduction and convert to sub-micrometer platelike crystals. The higher solubility of the prism faces compared to the basal faces of the hexagonal portlandite was hypothesised as an explanation for the observed prismatic-to-platelike transformation. Secondary nucleation of plate-like nano-sized portlandite crystals was also detected. The higher surface area and the changes in morphology account for the greater water adsorption capability and the resulting greater plasticity, water retention and workability of mortars prepared by aged lime putty.

The carbonation process of lime mortar proceeds through carbon dioxide diffusion followed by a chemical reaction to form calcium carbonate crystals. This process is influenced by several factors, the most important being the environmental humidity, the carbon dioxide concentration and the permeability of the mortar, which controls gas diffusion. The latter is also influenced by the carbonation reaction itself, since formation of calcium carbonate in the outer layer modifies the porosity of the mortar. Cazalla et al.^[14] demonstrated that mortars prepared with aged lime putties showed faster carbonation process compared to mortars containing fresh, commercially available, hydrate lime.

Interestingly, it was observed that once hydrate lime putty is dried, it does not recover its initial properties by re-dispersion in water.^[15] Many attempts have been carried out to better understand this irreversibility, due to its important scientific and technological implications, particularly in the field of cultural heritage conservation.

Short-range van der Waals forces are responsible for the attractive interactions that favour clustering of lime colloids. In principle, these forces are not strong enough to inhibit a complete re-dispersion of dry calcium hydroxide. Nevertheless, the original colloidal domain cannot be recovered even through vigorous stirring. This behaviour was elucidated by Rodriguez-Navarro et al.,^[13] who concluded that the irreversible colloidal behaviour of hydrate lime results from an aggregation mechanism involving an oriented (epitaxial) stacking of nano-sized platelike $\text{Ca}(\text{OH})_2$ particles.^[16] This aggregation process occurs already in diluted dispersion and, evidently, it becomes dominant during drying.

Therefore, we can conclude that slaked lime is probably one of the oldest nanomaterials known to mankind and that the ideal consolidating agent for wall paintings and limestone should be based on nano-sized crystals with a platelike shape. These characteristics provide a good consolidation and ensure a long-lasting effect.

We synthesised calcium hydroxide in a homogeneous-phase reaction, the simplest way to prepare nano-sized particles with the required platelike morphology.

Synthesis of Calcium Hydroxide Nanoparticles and Preparation of Alcohol Dispersion: An Overview

Nanoparticles of calcium hydroxide have represented a substantial improvement for the conservation of wall painting. The target was the synthesis of particles smaller than 300 nm and their proper dispersion in suitable solvents; thus particles could penetrate the thin painted layer carried by the dispersing solvent.

Calcium hydroxide nanoparticles were synthesised through homogeneous-phase reaction in water and other organic solvents. The size and shape of the particles could be tuned by proper selection of some reaction parameters, as the reaction temperature, the concentration of the reactants and their mole ratio.

Calcium hydroxide nanoparticles were prepared in water at about 90°C^[9] with concentration of the reactants in the range 0.10–0.75 M for Ca^{2+} salts and 0.18–1.50 M for OH^- , spanning molar ratios in the range 1.2–2.0 (cation:anion). This synthetic pathway was modified by Dei et al.^[17] using ethylene and propylene glycol as reaction solvents in order to reach higher temperatures (up to 175°C). Both synthetic routes produced nano-sized crystals of calcium hydroxide with a platelike shape. The average size and particle size distribution showed meaningful differences depending on the synthetic procedure. The synthesis at higher temperatures in glycol produced particles of 30–60 nm, while particles with an average size of 200–300 nm were usually obtained for reaction in water at 90°C (see Figure 1).

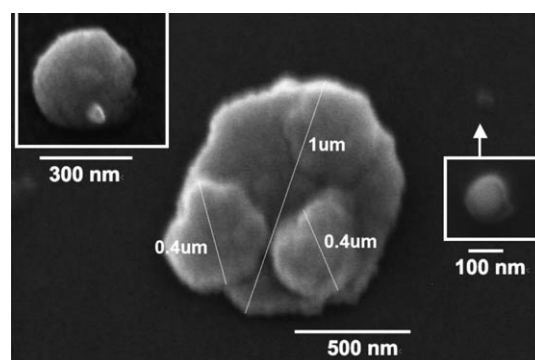


Figure 1. Clusters of calcium hydroxide nanoparticles prepared through a homogeneous phase reaction in water at 90°C, recorded by means of scanning electron microscopy (SEM).

Calcium hydroxide nanoparticle dispersions were also prepared starting from slaked lime. Heterogeneous-phase reaction of CaO with water produces, under specific conditions, lime putty, which usually has some unreacted CaO in the core of the particles. By using an autoclave system for the control of temperature and pressure, it is possible to force the hydration until a complete slaking of the lime is achieved. In this way, lime putty particles may undergo further fragmentation due to the volume expansion associated to the transformation of CaO to Ca(OH)₂, leading to the reduction of the particles size.

Although synthesised particles have both size and size distributions ideal for the application on wall paintings, they cannot be used as a dispersion in water, because of their tendency to aggregate in this solvent. A substantial improvement was achieved by using short chain alcohols as the dispersing media to produce kinetically stable dispersions. In particular, it was shown that 1-propanol and 2-propanol provide a good de-aggregation and stabilisation of the nanoparticles. It was hypothesised that this process occurs because of the physical absorption of alcohols onto the nanoparticles' surfaces, also favoured by the positive electro-kinetic potential of particles themselves. This will be further discussed in the following. Figure 2 shows the particle size distribution of calcium hydroxide nanoparticles' dispersions obtained by dynamic light scattering (DLS) measurements.^[18]

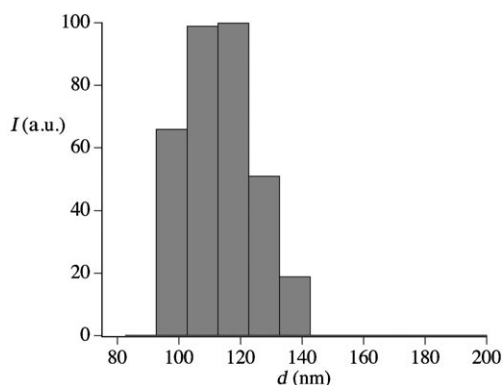


Figure 2. Particle size distribution of calcium hydroxide nanoparticles in 2-propanol, as obtained by DLS.

Co-precipitation reactions produce sodium chloride as a side-product and require time-consuming steps of purification. These are usually performed by dialysis against a lime-water solution. Purification from glycols is slightly more difficult, because of the adsorption of the solvent molecules on the nanoparticles surfaces. It was shown that this adsorption favours aggregation of the synthesised particles and produces micron-sized clusters. Glycol removal is usually achieved by peptisation treatment in an ultrasonic bath by using 2-propanol as washing medium.

The aggregation behaviour of nanoparticles in 2-propanol and ethylene glycol (EG) was investigated by using contrast-variation small-angle neutron scattering (SANS), and

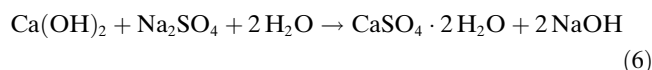
small- and wide-angle X-ray scattering (SAXS and WAXS). Nanoparticles aggregate into mass-fractal superstructures upon dispersion in 2-propanol; more compact and larger aggregates are formed when ethylene glycol is used as dispersing medium.

The specific surface area measured at the Porod limit is very high for nanoparticles in 2-propanol ($\approx 200 \text{ m}^2 \text{ g}^{-1}$), almost 30 times that determined in EG ($\approx 7 \text{ m}^2 \text{ g}^{-1}$). These differences depend on the relevant transformations of the surface at a microstructural level, which were demonstrated to arise from competitive solvent adsorption. Contrast-variation SANS analysis suggested that the composition of the first layer of solvent adsorbed onto the nanoparticles is determined by a thermodynamic equilibrium that favours ethylene glycol compared to 2-propanol by 1.4 kJ mol^{-1} with respect to the bulk solvent composition.^[19]

As mentioned above, nanoparticles prepared in glycols strongly aggregate to form micrometer-sized clusters, which can be peptised (de-aggregated) by washing with 2-propanol to yield individual nano-sized units. The hexagonal platelike nanoparticles form stacks, as evidenced by the increase of relative intensity of the peak ascribable to basal (001) crystallographic face present in the WAXS profile.^[17] SAXS and SANS investigations were also carried out in order to investigate the role of ethylene glycol and 2-propanol adsorption on the stability and compactness of calcium hydroxide nanoparticles' agglomerates. It was shown that de-aggregation actually proceeds through physisorption of 2-propanol molecules onto the particle surface. 2-Propanol and EG present a competitive adsorption on the nanoparticles' surface, showing opposite effects on the aggregation. In EG, nanocrystals are strongly aggregated, forming stacked plates and only micrometer-sized structures are observed. In 2-propanol the individual crystals are resolved by surface adsorption, leading to a stable dispersion; mixtures of the two solvents produce intermediate structures.

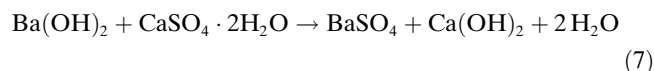
Nano-Sized Crystals of Barium Hydroxide as a New Tool for Consolidation of Wall Paintings

When large amounts of soluble sulfates (i.e., sodium or magnesium sulfates) are present in a wall painting, consolidation with calcium hydroxide nanoparticles might not produce durable results. In fact, sulfate ions can react with calcium hydroxide to give a double-exchange reaction [Eq. (6)], producing the slightly soluble gypsum (calcium sulfate dihydrate). The final result is the lack of the consolidation effect. Moreover, re-crystallisation of the newly formed gypsum leads to the formation of a white glaze on the painted surface.



Barium hydroxide nanoparticles represent a really useful alternative and a complementary tool to hinder this process.

In fact, BaSO_4 is totally insoluble and the aforementioned solubilisation–crystallisation cycles of sulfates are completely inhibited. Barium and calcium hydroxide can be used simultaneously and the thermodynamic equilibrium favours the formation of the less soluble barium sulfate [Eq. (7)].



Mixed formulations can be used for the pre-consolidation of surfaces largely contaminated by sulfates, the damage by which is so substantial that they cannot be cleaned without causing loss of material. Nowadays the common practice for the re-consolidation is the use of adhesives, such as calcium caseinate or acryl/vinyl polymers.

Synthesis of nano-sized barium hydroxide following a bottom-up approach is strongly hampered by its solubility in water. Better results were recently achieved through a top-down process. Micron-sized grains of barium hydroxide were dispersed in short-chain alcohols (1-propanol and 2-propanol) at high temperature and pressure, and milled to obtain a strong size reduction from several microns to about 100 nm^[20] (Figure 3). Dynamic light scattering shows particles size distributions similar to those obtained for calcium hydroxide (Figure 4).

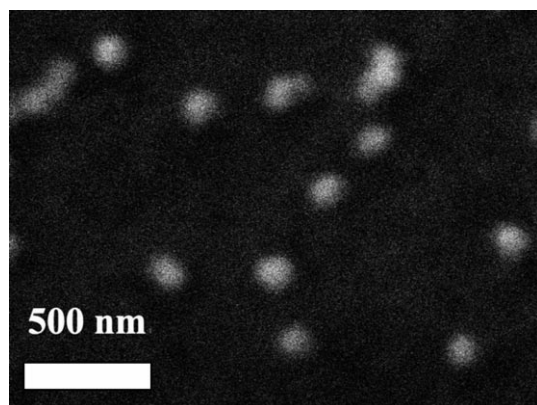


Figure 3. Barium hydroxide nanoparticles observed by means of scanning electron microscopy (SEM).

Both 1-propanol and 2-propanol present the appropriate features as dispersing media for application purposes: they are environmentally friendly, rather volatile and they show low surface tension. Despite their similarities, these solvents behave very differently; in fact, 1-propanol gives more stable dispersions and fast de-aggregation. Aggregation (and re-dispersion) phenomena cause quantifiable changes in particle size distribution, which affects the kinetic stability and other macroscopic properties of the colloidal dispersions.

It was observed that concentrated barium hydroxide dispersions (20–33.3 g L⁻¹) in 1-propanol spontaneously form supramolecular structures that show the typical characteristics of a thixotropic gel. Specific interactions of 1-propanol

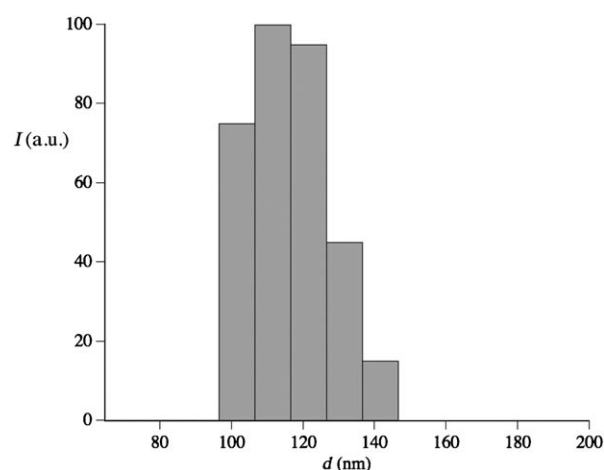


Figure 4. Particle size distribution of barium hydroxide nanoparticles in 1-propanol, as obtained by DLS.

with barium hydroxide nanoparticles were investigated by SAXS.^[20] Preliminary results seem to indicate that nanoparticles organise to form threads by stacking, which further assemble into bundles.^[20]

1-Propanol dispersions seem to lose their periodical organisation upon dilution and the nanoparticles are completely dispersed within the solvent. Dilute dispersions in 2-propanol are much less stable and particles have a high polydispersity.

It is worthwhile noting that dilution of a 1-propanol gel by 2-propanol does not induce any de-aggregation of the fibril structures previously mentioned, demonstrating the higher affinity of barium hydroxide towards 1-propanol compared to 2-propanol. Thus, unlike calcium hydroxide nanoparticles, which give very kinetically stable dispersions in both 1-propanol and 2-propanol, barium hydroxide shows a peculiar affinity with 1-propanol. This finding suggests that mixed barium and calcium hydroxide formulations in 1-propanol can be used for pre- and consolidation treatments.

An Example of the Nanoparticles Application for the Rescue of Mesoamerican Wall Paintings

La Antigua Ciudad Maya de Calakmul is located in the Campeche state (Mexico), inside the Calakmul Biosphere Reserve, which is an extensive protected area that preserves the typical tropical forest environment of Central America.^[21] The city of Calakmul, discovered in the jungle in 1931, was declared a UNESCO World Heritage Site in 2002. Calakmul was, together with Tikal in Guatemala, one of the most important cities of the Classic Maya period (AD 250–800). More than 6000 elements, including buildings, monuments, altars, and stelae (stone or wooden slabs erected for commemorative purposes), have been identified; in particular, the stelae (about 120) represent a precious witness of history, since all the main historical events were recorded as sculpted bas-relief.

Calakmul was inhabited for more than 12 centuries and was slowly abandoned towards the year AD 900 (Post-Classic period). Cyrus Lundell, the botanist who discovered the city, named it Calakmul, which translated from the Maya language means “two (Ca) close (lak) artificial hills or mounds (mul)”, taken from the presence of two big pyramids. The urban area of Calakmul occupies a natural dome covering about 25 km², surrounded by a lower area, or *bajo*, that collects water during rainy seasons.

The “Proyecto Arqueológico Calakmul” was established in 1993 and it is directed by the archaeologist Ramón Carrasco Vargas. This project involves archaeologists, architects, engineers, conservators and epigraphists, besides other specialists. The University of Florence (CSGI) has been an active partner since 2004, being involved in the study of the painting technique and in the development of nanotechnology for the consolidation and protection of the wall paintings and limestones.

In 2005 an extraordinary painting cycle was discovered inside the Structure I of the “Acropolis Chik Naab”^[22] (see Figure 5). These paintings constitute one of the most important documents of the pre-Columbian art history and a rare example of Maya painting from the Early Classic period

(250–600 BC). Wall paintings were intentionally entombed by Maya, who used specific materials (stones with a well-defined size and a great number of ceramic fragments) that were applied over a thick foundation layer, made of fine powder of stucco mortar and limestone, put in contact with the painting surfaces. After this step, a successive construction was built on top of the pre-existing building. The deliberate and careful burial of these paintings indicates the intention to preserve them, possibly for some religious reason. Inside Structure I, the mural paintings covered the walls (or steps) of a pyramidal substructure. The squared building has a 10 m base and is 5 m high; it is fully decorated with murals depicting scenes of daily life that can offer insight into Mayan social relationships. This archaeological discovery is extraordinary, because Mayan people, as well as many other civilisations, mostly depicted rulers, deities and religious authorities; paintings describing domestic and craft-made activities of the Maya people have only been found in Calakmul.^[22]

The subtropical climate of south Mexico presents a quite high and constant temperature (about 30°C), independent of the season. The seasons are characterised by a short but really intensive rainy period, with a relative humidity of about 99%. For the most part of the year, relative humidity inside Structure I is very close to saturation conditions; therefore, the surfaces of the paintings are usually slightly wet.

It is clear that excavation and recovery of the paintings led them to the exposure of new environmental conditions (light, temperature and humidity), presenting a real challenge for their conservation. To prevent degradation from these strong environmental variations, the paintings have been protected with the installation of a roof, and the presence of people was reduced to the minimum necessary to perform the delicate excavations and restoration work. Nevertheless, a consolidation treatment was necessary to conserve the paintings and we were involved in the formulation of systems respectful of the physicochemical characteristics of the paintings.

Recent history of conservation in Mexico has definitely shown that interventions based on polymer resins, largely used in the past by European and American conservators in Mexican archaeological sites, are not durable and are usually really detrimental for the survival of paintings (and limestones).^[23] These circumstances are common to most of the Mexican archaeological sites. There is evidence that clearly shows how degradation of wall paintings in Cholula, Caaxtla, Teotihuacan and Mayapan has been caused by the presence of polymer resin coatings.^[24] In the archaeological site of Kohunlich (Quintana Roo state), for example, the severe damage of modelled stucco polychrome masks (flaking and powdering of the surfaces) is the final result of polymers' degradation due to exposure to a tropical climate.^[25] Considering that the Biosphere of Calakmul has similar characteristics to that of Kohunlich, a different approach for the conservation of paintings and limestones has been undertaken.



Figure 5. Structure I in the Acropolis Chik-Naab in Calakmul (top); mural painting from the Early Classic Maya period, decorating the first step of sub-structure I in the south-east side of the building (bottom).

Thus, Mexican conservationists have decided on the use of inorganic materials compatible with the work of art to be preserved and, in particular, they opted for preventive treatments of the Calakmul paintings by nanoparticle dispersions in organic media.

Compatibility relies on the application of materials that possess physicochemical characteristics which are very similar, or possibly identical, to those of the original material. Hence, the effects of possible degradation processes can be homogeneously distributed throughout the whole material, without any localised stress. In other words, the restoration materials behave as the original, which ensures the lack of physicochemical and mechanical discontinuities between the layered structures of the wall painting.

In Calakmul, Maya paintings were treated by using a mixture of calcium and barium hydroxide nanoparticles. A blend of hydroxides was chosen and initially applied, because of the presence of sulfate salts. This formulation, used for consolidation of the wall paintings, was beneficial and led to a good consolidation effect even on wall paintings containing high amounts of salts. A dispersion of 5 g L^{-1} in 1-propanol was applied on the paintings by brushing. Barium hydroxide constituted 20 wt % of the total nanoparticle amount used. The consolidation effect was significant already after one week. Figure 6 shows the effect of the application procedure of nanoparticles on the painted surfaces. The size of the nanoparticles allowed a good penetration without white glaze formation and the results of application

are excellent: the paintings are stable and do not show ongoing degradation processes.

Summary and Outlook

Nanoscience and nanotechnology are revolutionising material science. The developments of novel tailored nanoparticle-based materials are creating new tools for Conservation Science and constitute the most advanced systems for consolidation of wall paintings.

Humble calcium hydroxide particles can be transformed into a noble material with excellent features as a consolidation agent, when synthesised as a nanomaterial. We have pioneered the use of calcium hydroxide nanoparticles to restore wall paintings, the degradation of which is basically due to the transformation of calcium carbonate into gypsum. Nanoparticles of calcium hydroxide efficiently interact with carbon dioxide to reform calcium carbonate and replace the degraded original ligand, leading to the re-cohesion of the paint layer.

In the presence of large amounts of sulfates, the consolidation effect of calcium hydroxide is boosted by the complementary use of barium hydroxide nanoparticles, which leads to the formation of the totally insoluble, and therefore inert, barium sulfate.

Each formulation requires specific procedures for the synthesis and this concept reports an overview for the preparation of inorganic consolidation materials, which ensure the safe and durable restoration of wall paintings. The application of mixtures of calcium and barium hydroxide nanoparticles to the recently discovered Maya paintings in Calakmul is illustrated.

The examples reported in this Concept article suggest the enormous possibilities that nanoscience opens up for Cultural Heritage conservation, due to the unique properties that the reduction in particle size confers to nanomaterials compared to their micrometric counterparts.

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Figure 6. Details of the mural paintings reported in Figure 5. Pictures on the left show the presence of sulfates over the surface and flaking phenomena damaging the paint layer; pictures on the right show the same detail six months after the application of a calcium/barium hydroxide nanoparticle mixture.

- [1] W. D. Kingery, P. B. Vandiver, M. Prickett, *J. Field Archaeol.* **1988**, 15, 219; S. Peroni, G. Tersigni, G. Torraca, S. Cerea, M. Forti, F. Guidobaldi, P. Rossi-Doria, A. De Rege, D. Picchi, F. J. Pietrafitta, G. Benedetti in *ICCROM—Cements and Grouts Used in the Conservation of Historic Buildings*, Rome, **1981**, p. 63; R. S. Boynton, *Chemistry and Technology of Lime and Limestone*, 2nd ed., Wiley, New York, **1980**.

- [2] K. Elert, C. Rodriguez-Navarro, E. S. Pardo, E. Hansen, O. Cazalla, *Stud. Conserv.* **2002**, 47, 62.
- [3] A. Arnold, K. Zehnder, *J. Cryst. Growth* **1989**, 97, 513; A. Arnold, K. Zehnder in *Proceedings of the 1st International Symposium on Conservation of Monuments in the Mediterranean Basin* (Ed.: F. Zezza), Frao, Brescia, **1989**, p. 31; L. Dei, M. Mauro, P. Baglioni, C. Manganelli Del Fà, F. Fratini, *Langmuir* **1999**, 15, 8915; G. W. Scherer, *Cem. Concr. Res.* **2003**, 34, 1613.
- [4] E. Ferroni, P. Baglioni in *Proceedings of the Symposium on Scientific Methodologies Applied to Works of Art—Florence 1984*, Montedison Progetto Cultura, Milano, **1986**, pp.108.
- [5] C. Horie in *Materials for Conservation: Organic Consolidants, Adhesives and Coatings*, Butterworth-Heinemann, London, **1987**; P. Mora, L. Mora, P. Philipot in *Conservation of Wall Painting*, Butterworths, London, **1984**.
- [6] R. Giorgi, M. Baglioni, D. Berti, P. Baglioni, *Acc. Chem. Res.* **2010**, 43, 695; P. Baglioni, R. Giorgi, L. Dei, *C. R. Chim.* **2009**, 12, 61.
- [7] P. Baglioni, E. Carretti, L. Dei, R. Giorgi, *Self-Assembly* (Ed.: B. H. Robinson), IOS, Amsterdam, **2003**, pp.32–41; E. Ferroni, V. Malaguzzi-Valerj, G. Rovida in *Proceedings of the ICOM Conference in Amsterdam*, ICOM Committee for Conservation, Paris, **1969**.
- [8] P. Baglioni, L. Dei, R. Giorgi, *Stud. Conserv.* **2000**, 45, 154; I. Brajer, N. Kalsbeek, *Stud. Conserv.* **1999**, 44, 145.
- [9] M. Ambrosi, L. Dei, R. Giorgi, C. Neto, P. Baglioni, *Langmuir* **2001**, 17, 4251; P. Baglioni, R. Giorgi, *Soft Matter* **2006**, 2, 293.
- [10] M. E. Holmes, G. J. Fink, F. C. Mathers, *Chem. Metal. Eng.* **1922**, 27, 1212; W. G. Whitman, G. H. B. Davis, *Ind. Eng. Chem.* **1926**, 18, 118.
- [11] D. G. R. Bonnell, *J. Soc. Chem. Ind. London Trans. Commun.* **1934**, 58, 279; C. R. Navarro, E. Hansen, W. S. Ginell, *J. Am. Ceram. Soc.* **1998**, 3032; D. R. Moorehead, *Cem. Concr. Res.* **1986**, 16, 700.
- [12] C. Rodriguez-Navarro, E. Ruiz-Agudo, M. Ortega-Huertas, E. Hansen, *Langmuir* **2005**, 21, 10948.
- [13] C. R. Rodriguez-Navarro, E. Hansen, S. W. Ginell, *J. Am. Ceram. Soc.* **1998**, 81, 3032.
- [14] O. Cazalla, C. Rodriguez-Navarro, E. Sebastian, G. Cultrone, M. J. De La Torre, *J. Am. Ceram. Soc.* **2000**, 83, 1070.
- [15] K. W. Ray, F. C. Mathers, *Ind. Eng. Chem.* **1928**, 20, 475.
- [16] R. L. Penn, J. F. Banfield, *Science* **1998**, 281, 969; R. L. Penn, G. Oskam, T. J. Strathamann, P. C. Searson, A. T. Stone, D. R. Veblen, *J. Phys. Chem. B* **2001**, 105, 2177.
- [17] B. Salvadori, L. Dei, *Langmuir* **2001**, 17, 2371.
- [18] E. Gabrowsky, I. Morrison in *Measurements of Suspended Particles by QELS*, Wiley-Interscience, New York, **1983**.
- [19] E. Fratini, M. G. Page, R. Giorgi, H. Cölfen, P. Baglioni, B. Demé, T. Zemb, *Langmuir* **2007**, 23, 2330.
- [20] N. Toccacchi, R. Giorgi, M. Ambrosi, E. Fratini, P. Baglioni, unpublished results.
- [21] R. Carrasco, *Maya* (Ed.: G. Orefici), Rizzoli, New York, **1998**, pp. 372–385; R. Carrasco, M. Colón, *Arquologia Mexicana XIII* **2005**, 75, 40; R. Carrasco Vargas in *The Metropolis of Calakmul, Campeche in Maya Civilization*, **1998**, Thames and Hudson, New York, pp. 372–385.
- [22] R. Carrasco Vargas, V. A. Vazquez Lopez, S. Martin, *Proc. Natl. Acad. Sci. USA* **2009**, 106, 19245.
- [23] H. Orea, V. Magar in *ICOM Committee for Conservation, 13th Triennial Meeting Rio de Janeiro* (Ed.: R. Vontobel), James & James, London, **2002**, pp. 176–182.
- [24] D. Magaloni, T. Falcon in *Temas y problemas—1 116 Coloquio del Seminario de Estudio del Patrimonio Artístico* (Eds.: A. T. Michua, E. X. de Anda Alanis), UNAM-IIE, Mexico City, **1997**, pp. 107–124; I. Torres, G. Pelaez, *Cacaxtla, Proyecto de Investigación y Conservación*, INAH, Gobierno del Estado de Tlaxcala, **1990**, pp. 77–87; T. López, V. M. Dávila, *33rd International Symposium on Archaeometry* (Eds.: H. Kars, E. Burke), Vrije Universiteit, Amsterdam, **2002**, p. 189; A. Espinosa, *In situ Archaeological Conservation* (Ed.: H. W. M. Hodges), INAH, Mexico City, **1987**, pp. 84–89.
- [25] J. Riederer in *ICOM Committee for Conservation, 7th Triennial Meeting, Copenhagen* (Ed.: D. de Froment), ICOM Committee for Conservation, Paris, **1984**, pp. 21–22.

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