

A review of selected inorganic consolidants and protective treatments for porous calcareous materials

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Abstract

Incorporating the results of a meeting held in London in December 2000, sponsored by English Heritage and The Getty Conservation Institute, this article reviews both consolidants and protective treatments for the conservation of deteriorated limestone and lime plaster. Carbonate deposition (including both inorganic solutions and biomineralization), barium hydroxide treatment, ammonium oxalate and tartaric acid treatments are covered. The article reviews selected literature, identifies open questions and promotes discussion of a range of issues, encompassing application techniques, performance, compatibility and retreatability. While many questions concerning these important systems have been addressed in published sources, there are significant opportunities for new research.

Introduction

Conservators today employ a limited array of consolidating and protective methods and materials to treat critically weakened surfaces. While the use of polymer and silica gel consolidants for friable limestone and wall paintings is well documented in the conservation literature, the materials and methods discussed here - both old and new - are not as well represented, despite their past use and potential usefulness.

The authors assembled for a meeting of experts, held in London in December 2000, with the hope that a greater understanding of the merits and appropriateness of selected consolidants and protective treatments for limestone and lime plaster could be established. This paper has evolved from that meeting and looks at several treatment processes: carbonate deposition (including both inorganic solutions and biomineralization), barium hydroxide treatment, ammonium oxalate treatment and tartaric acid treatment. Open questions identified during the meeting and since have been presented, which, along with the review of selected literature, aim to promote discussion of a range of issues, encompassing application techniques, performance, compatibility and retreatability. By delineating questions and by identifying the potential for scientific research, the authors hope that the understanding of methods for consolidating and protecting limestone and lime plaster can be clarified and enhanced.

The treatments reviewed in this paper may be used for remedial purposes or for preventive conservation. Some treatments have specific consolidating effects for limestone and lime plaster, while others have more protective and

sacrificial qualities, especially if combined with ancillary supportive works such as grouting, filleting and mortar repairs. For example, natural oxalate patinas on marble have long been noted for their apparently protective properties in a range of environments and a protective treatment may seek to recreate the properties of these patinas. Patinas may reduce the reactivity of fresh stone surfaces, providing a passivating barrier as well as a sacrificial surface. Lime shelter coating is a common treatment that produces a thin sacrificial layer on the surface.

To provide a realistic evaluation of conservation treatments one must be careful to note what is responsible for the observed effects, whether it is the parameters of the consolidation procedure or the substrate itself. Stone and plaster of different coherence and porosity will respond differently and thus should be appropriately characterized before comparisons can be made. For example, a small amount of a well-distributed consolidant may have a significant cementing effect on an extremely friable or powdery substrate, while a greater amount of consolidant might have little effect upon a more coherent material. Similarly, a change in the application method may be as important, if not more important, than a change in the chemistry of the treatment solution.

In order to evaluate fully the effects of the application of any consolidant system, changes in the chemical and physical properties (e.g. strength, porosity, liquid-water and water-vapor transport, and hygroscopicity) of the substrate must be determined. This includes determining the effects of the solvent itself, which may dissolve or otherwise modify the substrate, along with the depth of penetration, material-strength profile and the concentration profile of the consolidant. Changes in appearance (e.g. whitening and added gloss) should also be quantified. Unfortunately, convincing examples of quantitative data that document the fine-scale distribution and material property changes that are caused or affected by a consolidation treatment are the exception, not the rule (see Table 1).

Table I Consolidant properties II, p. 341 to be considered when evaluating a consolidant system

consolidating value
depth of penetration
effect on appearance
compatibility of consolidant with substrate
durability of treatment
effect on liquid water and vapor permeability
biological resistance
ease of application
health and safety issues

Table 2 Basic chemical reactions

calcium compounds		
$\text{Ca(OH)}_2 + \text{CO}_2$ calcium hydroxide	—————	$\text{CaCO}_3 + \text{H}_2\text{O}$ calcium carbonate consolidating action
barium compounds		
$\text{Ba(OH)}_2 + \text{CO}_2$ barium hydroxide	—————	$\text{BaCO}_3 + \text{H}_2\text{O}$ barium carbonate consolidating action
$\text{Ba(OH)}_2 + \text{CaCO}_3$	—————	$\text{BaCO}_3 + \text{Ca(OH)}_2$ consolidating action
$\text{Ba(OH)}_2 + \text{CaSO}_4$ calcium sulfate	—————	$\text{BaSO}_4 + \text{Ca(OH)}_2$ barium sulfate desulfating action
ammonium oxalate		
$\text{CaCO}_3 + (\text{NH}_4)_2\text{C}_2\text{O}_{4\text{aq}}$		$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + 2\text{NH}_3 + \text{CO}_2$ calcium oxalate dihydrate passivating action and consolidating action
$\text{CaSO}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{C}_2\text{O}_{4\text{aq}}$	>	$\text{CaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O} + (\text{NH}_4)_2\text{SO}_4 + \text{H}_2\text{O}$ desulfating action

The treatments discussed here have in common a reliance on reaction chemistry, wherein material is precipitated from solution, some minerals are dissolved and others are precipitated in their place (see Table 2). One broad advantage of this group of consolidants is their reliance on environmentally friendly water-based systems, rather than on organic solvents. However, water is often considered the most important activator of long-term deterioration processes in stone and plaster. Over time the infiltration of moisture may introduce dangerous soluble salts or mobilize those inherent in the stone. Nevertheless, some treatments can facilitate the conversion of salts such as gypsum into more stable forms such as calcite.

It should be noted that these treatments embody complex methodologies, not merely simple chemical reactions. The method of application is a critical part of the treatment, apart from the chemistry of the treatment and the attributes of the substrate. Accordingly, each of these methods constitutes a process and a methodological approach.

Calcium carbonate: chemical and physical deposition

General premise

The belief that calcium carbonate represents the preferred consolidant for objects that are themselves composed of calcium carbonate is based on the concept of compatibility: materials with the same chemical composition would tend to possess similar physical properties and chemical reactivity. Theoretically, the problems often associated with some polymeric treatments that introduce organic materials into inorganic materials should be reduced.

However, while treatment of limestone or lime renders with solutions of calcium hydroxide - producing calcium carbonate through *in situ* carbonation - appears to represent an ideal for compatibility, some differences between the deposited calcium carbonate and the substrate could still exist, such as grain size, crystal habit and crystal-aggregate texture. These differences may result in different dissolution rates, which would affect the longevity of the treatment. In addition, the formation of a texturally non-coherent surface aggregate of poorly cemented, newly

formed calcite might lead to powdering and a lack of consolidation efficacy. Also, the process of carbonation of calcium hydroxide may alter the pore properties of the material, thus creating a surface layer with somewhat different characteristics than the untreated substrate.

Historically, limestone objects, lime-based renders and wall paintings have been treated with solutions that resulted ultimately in the deposition of calcium carbonate. A saturated solution of calcium hydroxide in water (often referred to as 'limewater') was one of the earliest treatments for building materials and was well documented in the classical literature by authors such as Vitruvius (c. 70-25 BC) [2].

Calcium hydroxide readily reacts to form calcium carbonate when exposed to atmospheric carbon dioxide under moist conditions. The rate and extent of carbonation may vary, prompting attempts to hasten or supplement the transformation of the calcium hydroxide. Due to the slowness of the reaction and difficulties relating to the introduction of carbon dioxide in the interior of an object, other systems for introducing carbon dioxide have been tested. Such systems include application in carbonated water, exposure to CO_2 gas and the introduction of carbamates that produce carbon dioxide through chemical means [3].

Because of the very low solubility of calcium carbonate (see Table 3), direct precipitation from a saturated solution of calcium carbonate has only recently been considered as a consolidation treatment. Various methods to increase the concentration in solution of either calcium hydroxide or calcium carbonate itself are now being investigated, such as the addition of small amounts of crystallization inhibitors to an aqueous solution. This work is discussed in more detail below.

Evaluations of the effectiveness of consolidants include the determination of the depth of penetration as well as strength and concentration profiles of the consolidant. Additionally, the bonding between different grains of calcite (varying in crystal morphology, size and size distribution) in both the friable substrate and the consolidating mass must be taken into account.

Table 3 Solubility in water 141

compound	g/100 cc x 10 ⁻⁴
barium sulfate	2
calcium oxalate	7
calcium carbonate	14
barium carbonate	22
calcium tartrate	270
calcium hydroxide	1,850
calcium sulfate di-hydrate	2,410
barium hydroxide octa-hydrate	56,000

Note: temperatures vary (all at or below 25°C)

Consolidating action

The consolidant effect of a saturated solution of calcium hydroxide has been attested to empirically and has been reported in the conservation literature. For example, limewater was used extensively as a treatment for friable wall paintings in England [5] and Scandinavia [6, 7] during the twentieth century. Treatment systems where limewater application is just one step, such as the 'lime treatment' developed by Baker for Wells Cathedral, have been widely used on stone with perceived satisfactory results according to the practitioners. However, scientific doubts have been expressed by other observers and experimenters [8-13]. ('Lime treatment' is described as cleaning and removal of old fillings; consolidation by limewater; and/or surface repair with lime mortar and lime shelter coating [8].) As noted by Quayle: 'Frequently, however, perhaps more often than not, limewater consolidation appears to have no effect at all' [12, p. 681. He quotes Ashurst and Ashurst who state that '...attempts to record or quantify the phenomenon have met with a disappointing lack of success' [13, p. 63]. Attempts to resolve this question have focused on two effects:

- 1) a consideration of the application methods and the effects of solution application on a friable surface; and
- 2) laboratory efforts to quantify the effect of adding limewater to friable materials and testing the degree (or lack) of consolidation.

With regard to solution application, the effects are debatable. For example, opponents of the method suggest that application with a brush or by other means involving surface contact removes friable material, leaving only intact material behind. In other words, there is no consolidation but rather the removal of the friable surface, giving the appearance of consolidation. On the other hand, proponents of limewater claim that the treatment consolidates the weak material. It should be clear that the treatment is not a deliberate attempt to remove weak material, although if it does, even inadvertently, this may create difficulties for an evaluation of the treatment. Laboratory tests, though few, have demonstrated the negligible cementing action of limewater [14].

Depth of penetration and dissolution of salts or substrate

Tests conducted by Price *et al.* [15] show only a limited depth of penetration of an aqueous solution of limewater

to approximately 1mm. Quayle [12] has therefore suggested that, at best, only a thin surface shell of harder calcium carbonate surrounds a soft inner core of more porous, friable stone. Additionally, due to the size and morphology of deposited crystals from an aqueous solution, this surface shell may in itself possess limited durability.

Because of the limited solubility of calcium hydroxide (see Table 3) a solution of limewater must be applied in successive coatings to result in any appreciable deposition of portlandite [16]. Multiple applications in a wet state are used in response to concerns that pores may be blocked by deposition of portlandite, which would subsequently reduce the penetration of additional applications. There are some dangers endemic to this treatment, which include:

- 1) large amounts of water, which may pose a risk to the substrate through the mobilization of soluble salts and additional stress from the weight of the water.
- 2) the pH of the solution, which is quite high. This may affect pigments sensitive to an alkaline medium.
- 3) dissolution and recrystallization of carbonates through the chemical and physical action of water.

The last may lead to substrate dissolution and reprecipitation at the point of evaporation, resulting in case-hardening.

Other means for introducing an increased amount of calcium hydroxide - over that which can be added from an aqueous solution - include the dispersion of calcium hydroxide particles in ethanol. Ethanol promotes a slower sedimentation rate than water [17]. Alternatively, a dispersion in water can be achieved through the application of shear forces, breaking up aggregates of calcium hydrates into smaller ones, thus reducing the particle size [18]. A similar effect can be achieved more naturally following long-term aging of hydrated lime (lime putty) that has been stored under water [19]. Difficulties inherent in these methods include the complex inter-relationship of viscosity and maximum particle size, along with the surface-wetting characteristics and pore-size diameter distribution of the substrate. When ethanol is used as a solvent, dispersions of lime particles showed a slower rate of agglomeration (and therefore slower sedimentation rates) in comparison to an aqueous medium. This reduces the tendency for a white film to form on surfaces to be consolidated. In the case where mechanical stress is applied to break up larger calcium hydroxide aggregates into smaller ones, an increased setting rate (faster carbonation than non-dispersed lime) has been observed.

A new method that both increases the amount of calcite deposited in a porous substrate and uses the cementing action of the portlandite carbonation is that suggested by Larson *et al.* [20] (see also Madden [16]) which involves the direct deposition of synthetically precipitated calcite in a dispersion. Cementing of small calcite particles *in situ* is achieved by the further application of a saturated solution of calcium hydroxide in a 100% carbon dioxide environment. This method has been used to consolidate deteriorated, porous marble. Larson and colleagues performed extensive modelling and characterization of:

- 1) the porosity of the substrate
- 2) the size of the synthetic calcite particles in relation to the porous substrate (in order to get penetration and prevent filling or blockage of pores)
- 3) the dynamics of crystallization of calcium carbonate (possible oriented crystal growth) under an atmosphere of CO₂

A depth of penetration up to 1 cm has been measured and this method has also been used to fill voids behind gypsum crusts.

Another issue of particular importance to conservation treatments based on aqueous solutions is that of soluble salts. The application of water to salt-laden materials will result in the redistribution of the more soluble salts. In some cases salts might be mobilized and could cause an increase in damage as the result of the treatment; in other cases the salts might cement grains together and their removal could further weaken the substrate. It has been postulated, for example, that limewater treatments simply redistribute gypsum crusts.

Concentration of consolidant

For calcium hydroxide, the concentration of the solid decreases at higher temperatures (the solubility is inversely proportional to temperature) and thus, to maximize the concentration in solution, colder temperatures need to be used. Because of the limited solubility in water of calcium hydroxide, several means have been suggested to increase the concentration of a calcium hydroxide solution. These include the addition of sugars, carbohydrates and other organic materials [21, 22] to aqueous solutions of calcium hydroxide. The advantage of an increase in the concentration of a solution is that the number of applications needed to deliver the required amount of hydroxide might be reduced.

It has been noted that low concentrations of crystallization inhibitors used to prevent scale formation might dramatically increase the concentration of a solution of calcium carbonate in water [23]. For example, polyaminopolyethylenephosphonic acid (PAPEMP, Calgon Corp., Pittsburgh, PA, USA), a sodium salt, appears to hold calcium carbonate in solution at up to 200 times its normal saturation point. Further testing of these and other additives is needed.

Parameters of carbonation and crystallization (morphology and size)

In order to discuss the possible cementing effects that result from the carbonation of calcium hydroxide (see Table 2) the dynamics of the diffusion of carbon dioxide must be considered. Carbonation takes place in solution as a result of the reaction of carbonate ions (formed from atmospheric CO₂ dissolved in pore water) with calcium ions to form calcium carbonate. It is not a direct reaction of carbon dioxide gas with solid calcium hydroxide to form calcium carbonate and water. Thus, the dynamics of the diffusion of carbonate ions in water create an optimal thickness of the water layer on a crystal surface necessary for carbonation. Therefore, the reaction rate is lower at both low and high relative humidities [24]. Sufficient porosity must be sustained in the substrate to allow

diffusion of carbon dioxide into the interior of the substrate. Deposition of portlandite in pores may block further inner diffusion of carbon dioxide due to the volume expansion that accompanies the formation of calcite. Pores must remain sufficiently open to allow the reaction to proceed. (According to Van Balen [24] the volume expansion is of little concern because only the very small pores are blocked and the overall porosity reduction is minimal. Papayianni and Stefanidou [25] report the opposite effect, however, noting a decrease of up to 25% in the porosity of lime-based mortars upon carbonation.)

Crystals of calcium hydroxide [26, 27] and calcium carbonate [28], which differ in morphology and size, may be precipitated from aqueous solutions or deposited from suspensions, depending on variables such as the starting material, solution pH and the presence of additives. Yamada [28] investigated the effects of the concentration of dissolved calcium hydroxide and additives such as saccharose and glutamic acid on the crystallization of amorphous calcium carbonate and on conditions for the synthesis of different forms of crystals.

Areas for future research

The important questions are:

What are the parameters of a fragile material to be treated (e.g. porosity, grain size, mineralogy) and how can these be measured? There are many methods to monitor consolidation efficacy in porous materials, including but not limited to ultrasound, drill resistance, bi-axial flexural strength, pull-off strength and abrasive strength as a profile. Other parameters that are important for compatibility are water transport (liquid and vapor) and storage characteristics.

Having determined what concentrations and distributions of consolidant are necessary, how is it possible to achieve these?

What are the parameters of calcium carbonate formation, resulting from the carbonation of calcium hydroxide, that are important factors in controlling added strength?

For limewater, specifically, a greater understanding of the following issues is needed and could be provided through laboratory studies:

- crystallization parameters, the required morphology and size
- carbonation, the rate and effect on crystal growth
- depth of penetration and what controls it
- how to enhance solution concentrations, e.g. organic additives, crystallization inhibitors and/or alternative solvents
- solubility issues of substrate and consolidant solutions

Calcium carbonate: biological deposition

General premise

Building materials may be cemented through the biological deposition of a wide range of different substances, such as calcium oxalates, silica, calcite and apatite. However, applied research into cementing agents

has historically focused on the enhancement of the deposition of calcium carbonate (calcite), in part because many microbes naturally precipitate calcite [29]. The introduction of calcium carbonate into weakened carbonate-based building materials, through the action of bacteria and other biomineralization processes, has long been viewed positively due to several promising conservation treatments [30-33]. The technique has seen wide application as a method to produce sacrificial coatings on limestone [34, 35].

History of development and application

The biomineralization method of limestone protection has several variants. Foremost among them is a patented technique, CALCIN, developed at Université Pierre et Marie Curie in Paris, which involves the application of calcite-forming bacteria [36]. A number of large-scale buildings have been treated with this method in France, including the cathedral at Bordeaux and a chateau at Chateaudun (Eure-et-Loir) [37]. More recent research at Université de Nantes has explored the use of crushed stone and bacteria as a grouting material [38].

Applied research on biomineralization, emphasizing applications for conservation purposes, is being undertaken in a number of laboratories around the world [29, 39]. Recent work at Universidad de Granada has focused on the use of soil bacteria to precipitate calcite on limestone [33, 40] with encouraging results. The bacteria, *Mycrococcus xanthus*, induced the precipitation of both fibrous vaterite (a calcite polymorph) and rhombohedral calcite cement. The newly formed coherent carbonate cement uniformly blanketed the accessible stone pores without reducing the pore connectivity and bulk porosity, thereby ensuring appropriate permeability of the treated limestones. Calcite growth is apparently confined to larger pores because of the size of the bacteria. The depth of penetration of the cementing carbonate is often limited to less than a millimeter.

In addition to bacteria, yeasts and algal organisms, some organic materials have also been found to enhance calcite precipitation. For example, certain proteins from the organic matrix of seashells have been found to enhance strongly calcite precipitation from solution [41]. Tiano and others [32, 42] have developed a consolidant method based on the use of such organic matrix macromolecules to enhance calcite precipitation in stone. Biomineralization processes may encompass a range of source material (both living and nonliving) and methods of application, and are no longer reliant solely on microbiological activity to cause mineralization.

Enhanced deposition of calcium carbonate

Calcite precipitation is generally enhanced through the addition of calcium ions or of carbonate, or through an increase in pH of the solution. Such chemical modifications to microenvironments are thought to be accomplished during the biomineralization process through three pathways: active, passive and via ion exchanges on cell membranes [29].

Specific bacterial species are well-documented agents of biomineralization of calcite [43]. Active sites on cell walls

act as templates for crystal nucleation and growth. This was demonstrated by carbonate precipitation on the external cell wall of dead bacteria [44]. A number of normal microbiological activities acting through different pathways, such as the ammonification of amino acids, often result in an increase in pH, calcium or bicarbonate. These increases are generally characterized by the normal responses of bacterial communities in organic-rich environments [37]. Spherules of crystal aggregates are among the most commonly observed; different bacteria may produce different polymorphs of calcium carbonate (aragonite, vaterite or calcite, which is the most stable phase). A comprehensive discussion of the different factors involved in microbiological CaCO_3 precipitation is given by Stocks-Fischer *et al.* [45].

Significant materials-science research continues to focus on understanding and mimicking the structure of calcite in seashells and skeletal material [46-48]. Both represent nanocomposites (e.g. comprising nanometer-scale crystals and organic macromolecules, or composites) and possess great resistance to fracture. Such research has defined the influence of shell-material macromolecules upon the geometry and crystal structures of carbonate formation. This fruitful line of research is expected to engender a greater understanding of biomineralization and improvements to existing treatments.

Consolidation and protection of stone

The *in situ* precipitation of calcite in stone or plaster depends upon the bacteria used, the environmental conditions (e.g. temperature, humidity and solution ion content), the type and abundance of nutrients and the reaction kinetics. Bacteria multiply rapidly in suitable environments and the reaction curve often exhibits an 'S' shape, with a latency period followed by rapid reaction and subsequent leveling off [37]. The amount of calcite produced varies, but one researcher found that for a nutritive input of 4.0 g.L^{-1} , the calcite output was 2.40 g.L^{-1} , a yield of 0.6 [49].

When applied to deteriorated limestone, a suspension of the appropriate bacteria is sprayed onto the surface. The bacteria are typically nourished with a nutrient spray either daily or every two days; practical considerations such as cost generally limit applications to five. This practice creates a superficial calcareous scale that is several microns thick. The calcite layer substantially reduces water absorption (~80%) while remaining permeable to water vapor. Three to six years of outdoor testing in a range of environments has resulted in little alteration of the calcite in limestone building blocks and moderate erosion of the layer on treated sculpture. Other observations indicate that the absorption (as measured with a Karsten tube) is continuously increasing over time and that the treatment has little consolidating effect [50]. The method has been improved by attempting to find more efficient bacteria (to provide a better yield), less expensive nutrients and a better match between the type of limestone, the feeding schedule and the strain of bacteria [37].

The method of using live bacteria to precipitate calcite (the French method) has been criticized by Perito *et al.*

[51] who replicated it and found that reference stones treated with growth medium "...but without bacteria showed biological growth due to development of airborne contaminants and a noticeable decrease in water uptake. For this reason the decrease in the amount of absorbed water measured in the treated samples must be attributed, for at least 50%, to the fact that the stone porosity was physically obstructed by the presence of a consistent layer of biological mat' or biofilm [51, p. 221]. They go on to suggest that other negative consequences may occur such as 'deposition of new products, due to chemical reactions between the stone minerals and by-products, originating from the bacterial metabolism; and stained patches, due to the growth of air-borne fungi and related to the presence of organic nutrients, necessary for bacterial development' [51, p. 221]. The general advantages and disadvantages of the biological deposition of carbonate are summarized in Table 4.

Table 4 Advantages and disadvantages of biomineralization treatment

advantages

- environmentally and physically compatible with limestone and plaster
- takes advantage of biological process to enhance the chemistry of precipitation at the nanoscale
- forms a coherent, well-cemented, newly-formed calcium carbonate structure strongly adhered to the substrate
- the cement type as well as cement texture can be tailored by selection of the appropriate bacteria (or organic precursor) and the culture media

disadvantages

- works best on newly cleaned stone
- depth of penetration is limited
- some treatments create a sacrificial layer rather than substantial penetration and bonding of the newly formed calcite
- may promote further types of biological growth on surfaces
- biofilm formed on surface reduces water permeability

Areas for future research

The important questions are:

What is the distribution and fate of the organic material associated with the biomineralization (dried media, dead bacteria) and what happens following a treatment when it undergoes humidity cycling or microbial decay?

Where does the calcium incorporated into the calcite come from? Possibilities include calcium acetate and calcium phosphate from the media used to nourish the bacteria. The formation of calcite by specific species of bacteria has been observed to occur in the absence of limestone, suggesting an alternative source for the calcium.

Has an even application of calcite been demonstrated? Because bacteria normally have a patchy or irregular distribution due to nutrient needs and microbial colony growth patterns [52], obtaining a relatively even distribution of precipitated calcite is likely to be difficult to accomplish in practice.

How is the reaction rate of the bacteria controlled? The reaction rate is partially controlled by the media composition and the rate of media application.

What are the application methods for biomineralization treatments? How specific to a given area is the treatment? What is the experience with these methods in museums versus outdoor environments? What are the climate limitations for application?

What is the surface area of the calcite deposited by biomineralization methods and how does this affect its properties? What is the efficiency of the biomineralization treatment (typical volume of calcite deposited per day per m²) and how does it vary with the substrate? In general, the efficiency seems to be fairly low, but can continue for an extended period of time if the nutrient conditions are appropriate, typically four to five days for the French method.

Barium compounds: consolidating, desulfating and indirectly protective

General premise

The review of a consolidant system has to be seen not simply as the evaluation of the materials but of the processes, such as the variations of treatment possibilities and their ramifications using particular materials [1]. Barium hydroxide treatments involve a more complex set of processes than the previously discussed calcium hydroxide treatments.

Barium carbonate, deposited from barium hydroxide, has been considered as an alternative consolidant to calcium carbonate because barium hydroxide is more soluble in water than calcium hydroxide (see Table 3). Barium carbonate is considered a somewhat similar material to calcium carbonate, both being alkaline-earth carbonates with relatively low solubilities.

Barium hydroxide solutions have also been given preference in certain situations because gypsum can be converted into barium sulfate when treated with ammonium carbonate followed by barium hydroxide [53], often referred to as 'the Florentine method'. Compared to calcium carbonate, barium sulfate is a compound of very low solubility, even in acidic environments (see Table 2).

Theoretically, determining the depth of penetration and distribution of barium compounds within a calcareous substrate should be more easily accomplished than determining the introduction of calcium compounds into a calcium carbonate substrate. This is because barium as an element is easily distinguished from calcium by a variety of analytical methods, most notably backscattered scanning electron microscopy (SEM) and elemental mapping of sections with energy dispersive spectrometry (SEM-EDS). In practice, the concentration of barium may be so low or the barium so unevenly distributed that definitive detection of its presence is difficult. Recently, a new and simple method for monitoring the presence and distribution of barium carbonate (formed from barium hydroxide) in cross-section was developed by Matteini and Scuto [54]. An aqueous solution of sodium rhodizonate stains barium carbonate dark red, clearly

indicating its location. A number of stone and plaster samples were treated with barium hydroxide and exposed to spontaneous carbonation. Cross-sections of each sample were then examined with, first, SEM-EDS and then with the sodium rhodizonate staining method. Comparison clearly showed a definitely higher sensitivity of the rhodizonate staining method in detecting barium carbonate presence and distribution in the cross-sections.

Consolidation of stone: barium hydroxide and urea

The introduction of barium hydroxide (baryta water) was considered for the consolidation of stone in the nineteenth century [55]. However, the initial consolidation that was achieved eventually led to negative effects, primarily the exfoliation of the surface-hardened layer of barium carbonate and/or barium sulfate [56].

Different methods for applying barium-based consolidants to severely disaggregated limestone [57] include those based on the precipitation of barium carbonate [58] and highly insoluble sulfates [59]. In the method tested by Lewin [58], barium carbonate is precipitated from an aqueous solution of barium hydroxide and urea. The urea hydrolyzes to produce ammonium carbonate (or ammonia and carbon dioxide) and the carbonate ions in solution react with the barium ions. The reaction rate can be controlled so that this 'precipitation from a homogenous solution' can take place over a number of days, thus possibly increasing the depth of penetration [56, p. 297]. Schnabel [60] suggests that the barium hydroxide-urea consolidation method is inappropriate due to the uneven distribution of the deposited barium carbonate. However, Matteini and Moles [61, 62] attribute this to the typically uneven distribution of gypsum inside pores and micro-cracks, based upon an examination of cross-sections obtained from mural paintings and stone objects. Barium carbonate partially saturates the micro-discontinuities and rebuilds the local coherence where it was lost.

Conversion of barium hydroxide and barium carbonate

When gypsum is present (calcium sulfate dihydrate) a reaction occurs where the combination of barium hydroxide and gypsum forms barium sulfate and calcium hydroxide [63, 64]. The calcium hydroxide obtained from this reaction with excess barium hydroxide upon carbonation converts to calcium carbonate and barium carbonate. The result is a consolidating action (see Table 2).

Matteini [53] has suggested a further consolidating action from the reaction of barium hydroxide with calcium carbonate, a heterogeneous reaction that converts the outer shell of the grains of calcium carbonate into calcium hydroxide. This reaction is little known in the literature; and the kinetics and favorable conditions (e.g. time, concentration and types of grains) are not yet sufficiently understood.

Consolidation of wall paintings

Barium hydroxide has been extensively used for the consolidation of wall paintings in Italy with the so-called 'Florentine method' described by Matteini [53]. It has

been suggested that in this two-step method, gypsum is first transformed with a solution of ammonium carbonate that converts the gypsum into calcium carbonate and soluble ammonium sulfate. In a subsequent treatment with a barium hydroxide solution, the ammonium sulfate is converted to barium sulfate, which is an inert and insoluble substance. In this way, existing sulfation is arrested. Ferroni and Dini [65] proposed a combined method based on ammonium hydroxide poultices to desulfate mural paintings affected by gypsum crystallization and to consolidate incoherent plasters and paint layers.

Theoretically, no preventive action is assured against new sulfation caused by SO_2 corrosion or by dry gypsum deposition. However, the surface-paint layer exhibits lower porosity and reduced roughness due to the formation of both barium carbonate and barium sulfate. The specific surface of the physical system is decreased to some extent, which may lower exposure to environmental pollutants. The risk of both acid attack and penetration of soluble salts would thus be reduced. When appropriate application procedures are not followed, precipitates can form on the surface causing notable whitening or 'bloom'. Therefore, careful removal by swabbing of freshly precipitated calcium carbonate is an indispensable part of a successful treatment.

As noted above, two consolidating mechanisms are then possible: 1) the carbonation of barium hydroxide, and 2) the reaction of barium hydroxide with calcium carbonate to produce barium carbonate and calcium hydroxide, the latter then converting upon carbonation to calcium carbonate. There are several reasons why barium compounds, which include barium aluminates [66, 67], are considered desirable consolidants. These include high durability; compatibility with the substrate; minimal effect on appearance; preservation of the original hydrophilic properties; compatibility with other consolidants; and effectiveness in transforming gypsum, thereby providing indirect protective action (e.g. formation of insoluble barium sulfate). It has been noted that barium treatments are not appropriate for substrates rich in magnesium carbonates (e.g. plaster made with dolomitic lime) due to the formation of highly soluble magnesium sulfate.

Areas for future research

The important questions are:

To what extent are barium carbonate and barium sulfate compatible with the substrate and are effects such as anisotropic crystal growth and differential volume changes upon crystal growth important negative factors? Lewin and Baer [68] suggest that the formation of a layer composed of a solid solution of barium calcium carbonate will increase the compatibility of the deposited barium carbonate with a calcite substrate.

Barium hydroxide solutions have been known to penetrate further than the detected barium carbonate. Does surface barium carbonate limit further carbonation of interior barium hydroxide?

To what extent does barium hydroxide promote consolidation through the formation of calcium hydroxide upon reaction with calcium carbonate?

What parameters (e.g. temperature, humidity and porosity of substrate) control the carbonation of barium hydroxide?

Although appearance changes seem to be minimal (if calcite gels are removed before drying) yellowish or brownish tones in paintings have sometimes been affected. Why? Is this due to the solubilization of organic impurities caused by the strongly alkaline barium hydroxide water solution and are these later removable?

Questions specifically related to application procedures include:

- What are the parameters and case-specific factors affecting poultice time?
- How can the problem of bloom be mitigated?
- Can the addition of anion exchange resins reduce partial desulfation and excess surface calcium hydroxide? To what extent would the addition of anion-exchange resins allow the application of the 'barium method' to be extended to more delicate substrates such as proteinaceous tempera-based mural paintings, or areas painted with copper-based pigments?
- How can the reaction with nitrates be inhibited and what would the impact of such treatments be? Tributyl phosphate has been suggested as a possible solution.

Artificial calcium oxalate and tartrate: protective methods

Two treatments - using artificial calcium oxalate and tartrate - are relatively new to conservation. The artificial oxalate treatment was developed over a decade by Matteini and published in 1994 [69, 70]; the tartrate conversion method was only introduced in 2000 [71]. Nevertheless, each method responds to specific needs: the oxalate treatment is for limestone objects that are subject to an unavoidably acidic environment while the tartrate method has been seen, initially, as a way to improve bonding of calcite with silica gel consolidants.

Artificial calcium oxalate

A moderate transformation of calcite into calcium oxalate can be produced on the surface of carbonate stone and plaster by its reaction with a dilute solution of ammonium oxalate, $(\text{NH}_4)_2\text{C}_2\text{O}_4$. This is primarily considered to be a protective treatment for outdoor sculpture and structures composed of carbonate stone that are exposed to acidic environments, rather than as a conventional consolidant. The treatment builds on many observations of natural oxalate patinas on stone that appear to have a clear protective effect. Oxalate minerals are a common but irregularly distributed component of patinas on monuments [70, 72]. The protective nature of some natural patinas has been attributed to the much lower solubility of components such as calcium oxalate and calcium phosphate as compared to calcium carbonate stone [73, 74].

While oxalic acid has been used to treat stone since the nineteenth century and oxalate solutions have been used to treat sulfated marble [75], it is significant that natural

calcium oxalate films on stone or plaster were once regarded as a rarity, if they were noted at all. This has changed dramatically in the past 15 years, however. Two scientific congresses held in Milan in 1989 and 1996 have addressed this topic and it is now widely appreciated that natural oxalate films exist on a wide range of materials and works of art, often as thin layers on carved stone [76, 77]. Well-known examples include the Parthenon in Athens [73] and Trajan's Column in Rome [78].

The idea of producing artificial oxalate - either as a conversion coating to provide an acid-resistant and compatible treatment for weak stone and plaster, or as a consolidant similar to barium hydroxide or calcium hydroxide - originated in the mid 1980s and continued through the 1990s [62-64, 69, 79, 80]. For the oxalate method, laboratory tests were carried out for about five years in the scientific laboratories of Opificio delle Pietre Dure in Florence. Later, *in situ* tests on small areas of monuments were carried out.

Standard ammonium oxalate treatment method

A standard treatment has been developed, using ammonium oxalate in solution to react with calcite to form calcium oxalate and ammonium carbonate. Together these spontaneously decompose to ammonia and carbon dioxide gas (leaving behind the calcium oxalate) (see Table 2).

Typically, a 5 to 7% solution of ammonium oxalate (pH 7) is dispersed in a cellulose paste on the surface to be treated for a period between several hours and a few days. Decisions regarding concentrations and duration of application are largely based on empirical experience. Most of the reaction appears to take place in the upper 2 mm of the treated surface, with the uppermost surface being most affected. *In situ* analysis of the calcium oxalate is difficult and the depth of penetration is not easily measured because of the similarity of oxalate and carbonate [81]. The use of micro-Raman spectroscopy has been helpful in positively identifying oxalate distributions [82]. In addition to calcite, gypsum is also partially converted by the ammonium oxalate solution into solid calcium oxalate hydrate, water and ammonium sulfate (see Table 2).

The reaction rate of gypsum with the oxalate is generally observed to be more rapid than that of the oxalate with calcite. However, the reaction rate of the oxalate with gypsum is much slower than with ammonium carbonate.

Treatment effects

Surface appearance is not usually altered by the treatment, except when gypsum is present on the surface, in which case, a chalky appearance may be exhibited. The much lower solubility of calcium oxalate has been verified by placing acid on porous travertine previously treated with ammonium oxalate. Also, the water-absorption rate measured in oxalate-treated samples is typically reduced by between 60 and 85% [63] when compared to the untreated stone. The hydrophilic properties of the surface are fully preserved.

Other experiments with oxalate treatments include Cezar's application [83] in 1998 of the ammonium oxalate treatment to English limestones, with mixed

results. Cezar found that with certain kinds of limestone, iron is mobilized by the treatment, resulting in a slightly discolored surface. It should be noted that alkaline treatments, especially ammonium carbonate, might cause discoloration. However, ammonium oxalate is not alkaline (with a pH of around 7) and should present fewer problems with discoloration. The conservation issues related to the ammonium oxalate treatment are briefly summarized in Table 5. It should be noted that the depth of penetration has not yet been accurately measured.

Table 5 Advantages and disadvantages of the ammonium oxalate treatment

advantages

- much lower solubility than calcite or gypsum, yet permeable to water (liquid + vapor); remarkably resistant in acidic environments
- proven stability and compatibility of natural oxalate patinas in a range of environments and materials
- simple chemistry
- some advantages over other treatments (less water than lime and simpler application than barium)
- lower application pH (pH 7) than barium hydroxide
- less affected by nitrate salts than barium hydroxide

disadvantages

- has not seen wide application; track record still developing
- discoloration by iron mobilization may occur in some stones
- may form a thin crust that may be incompatible with some materials
- calcium oxalate crystals formed are extremely fine-grained
- limited penetration/consolidating effect may be more limited than other methods
- ammonium may alter pigments (verdigris, malachite, etc.)

Areas for future research

The important questions are:

Does the oxalate treatment work as a consolidant or rather primarily as a conversion coating, protecting against future acid attack? This could be verified by testing on incoherent (sugared) marble.

What effect does the treatment have on the appearance of plaster and limestone surfaces? The discoloration of Portland limestone during ammonium oxalate treatment appears to be related to variations in iron content. On other types of stone there is generally a good overall color compatibility observed when compared to other treatments. The small grain size of the calcium oxalate in comparison with the original calcite tends to result in a lighter appearance.

What is the grain size and micro-distribution of the oxalate produced and how does the pore structure change at the calcite/oxalate interface? What is the homogeneity of the oxalate treatment versus natural oxalate?

The formation of a less porous layer on the surface of stone or plaster may result in the accumulation of soluble

salts below the surface, which may eventually cause the detachment and loss of the treated layer. Is the calcium oxalate layer permeable enough to avoid this problem? Tests conducted thus far suggest that while porosity is reduced, water permeability and the hydrophilic nature are maintained.

What is the field performance of objects treated with ammonium oxalate thus far? In situations where carbonate sculpture is unavoidably exposed to an aggressive outdoor environment such as acidic air pollution, the ammonium oxalate treatment may provide some useful protection.

Tartrate conversion

General premise

Under conditions of low pH, tartaric acid (2,3-dihydroxysuccinic acid) anions react with calcium ions to form calcium tartrate tetrahydrate (CTT). CTT has relatively low solubility in water (see Table 3) and it can be grown as a surface layer on carbonate rocks. Weiss *et al.* [71] have recently suggested using a pH-minus adjusted solution of tartaric acid to form a hydroxylated conversion layer on carbonated mineral grains. As it is hydroxy-functional, such a layer may enhance surface bonding with tetraethoxysilane-based consolidants as well as with alkylalkoxysilanes, although there is, as yet, no experimental evidence for this. The layer may also act as a passivator, protecting against acid rain.

However, the growth of CTT on a carbonate surface in contact with solution may also be of use as a consolidant, presumably by intergrowth of CTT layers at points of contact between calcite grains. Advantages of this system are the low solubility of CTT and its stability (with a thermal decomposition of $>400^{\circ}\text{C}$). Disadvantages are the limited range of pH (low enough to optimize concentration of CTT and high enough for application to calcium carbonate) and the limited amount of testing to date.

Commercial availability and experimental evaluation

A tartaric acid treatment is now available in the United States. Product literature describes advantages in the treatment of marble, limestone and travertine with the formation of a well-adhered hydroxylated conversion layer that increases the resistance to acid attack and strengthens deteriorated carbonate stones. It is interesting to note that the material is only suggested for unpolished marble or limestone, indicating that matt effects on a polished surface are possible.

The material has undergone preliminary studies in the laboratory on single calcite crystals, graded marble aggregates and stone cores. Additional testing both in the laboratory and in the field is needed. The current program for testing an Hydroxylating Conversion Treatment (HCT) is described in the *Prosoco Technical Bulletin* [84]. Treated stones are being tested primarily for resistance to acid rain and strength increase. The testing program includes modified ASTM tests (American Society for Testing and Materials, now ASTM International) for strength and water absorption along with a variety of acid

treatments, micro-abrasion, a cross-axial chisel splitting test and freeze/thaw resistance. Substrates include carbonate stones from both the United States and the United Kingdom.

Areas for future research

It should be underscored that product testing is currently underway by the manufacturers holding the patent and questions regarding long-term stability, compatibility, efficacy, retreatability and other issues need to be addressed both through independent materials analysis and through the long-term documentation and monitoring of treatments.

Conclusions

Problems in evaluating the consolidation and protective treatments reviewed in each section fall into two categories: the general lack of knowledge of specifics in the reaction chemistry and application procedures; and the lack of sufficient experimentation and testing methods necessary to quantify the required strength of consolidation, compatibility and long-term effects. A necessary, though difficult, corollary to the latter is the transference of knowledge gained in laboratory testing to performance in the field.

This review suggests both general issues that should be addressed through future study and specific areas of research that can be prioritized. Areas for research can be categorized as:

- those related to penetration (and depth profile) of consolidant solutions
- those related to the extent of consolidation and passivation that has been achieved by a particular treatment
- the long-term consequences of these treatments on future conservation concerns, including retreatability, durability and required maintenance

With regard to health and safety, the factors affecting the treatments under review are primarily those that relate to aqueous systems. It may be possible to manipulate wetting and retard deposition (through inhibiting evaporation rates of solvents, agglomeration potential and the saturation point for crystallization) in order to increase penetration and decrease preferential surface deposition. Enhancement of the solubility of calcium hydroxide and calcium carbonate through additives has been suggested. Additionally, for passivating systems (oxalates and barium sulfate) isolation and manipulation of the factors affecting the deposition of an even, coherent and unbroken passivation layer are important areas for further study.

In addition to differences in the color of consolidant and substrate, the optical properties of stone and plaster are strongly related to factors affecting gloss and/or diffuse reflectance (e.g. surface roughness and porosity). Therefore, the effect of a treatment on appearance may be minimized, both by manipulating the concentration profile and by conforming closely to the original roughness of the affected or applied surface layer. This is one explanation for the small change in appearance

resulting from the ammonium oxalate conversion treatment.

In reality, it is not only the delivery of a consolidant in a specific concentration profile but also the increase in cohesion related to depth; the changes in durability (in its broadest sense understood as resistance to future environmental or stress-induced deterioration); and options for retreatment or maintenance that are of interest. Therefore, the deposition and manipulation of crystal growth of inorganic materials is of primary concern. The varying crystal sizes and morphologies of calcium hydroxide and calcium carbonate have been mentioned for both solution and biological deposition. Their dependence on solution properties (pH, temperature and concentration) and additives has been discussed. The effects of these phenomena on carbonation rate, porosity, strength and dissolution/precipitation deserve further examination, particularly in the case of barium carbonate where few investigations have been carried out in comparison to calcium carbonate. Additionally, the same factors affecting magnesium compounds (magnesium hydroxide and magnesium carbonate), dolomitic limestones and dolomitic-derived plasters (including both binder and aggregate) are not well understood.

Testing needs to be developed that focuses on both treated and untreated substrates with respect to strength gain, consolidation distribution and changes in physical properties such as porosity. For example, a newly considered consolidant treatment such as tartaric acid (CTT) requires a systematic analysis and long-term field testing to be seen as a viable alternative. Results of laboratory testing of treated cubes of stone or plaster do not necessarily predict the field performance of a consolidant, although such testing might serve as a screening tool. New advances are also being made in detecting consolidants, both qualitatively and quantitatively, and profiling their concentration from the exterior surface inwards.

The potential usefulness of the treatment methods employed to deal with weakened limestone and plaster attests to the need for further focused research. Only through continued research can the questions raised herein be addressed, in relation to both the evaluation of the performance of previous treatments and the development of new or modified materials and application procedures.

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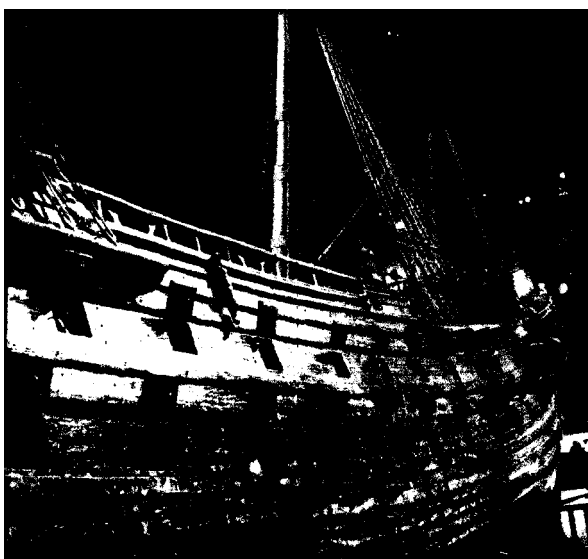
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