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A novel approach to consolidation of historical limestone: the calcium alkoxides

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Potential utilization of calcium alkoxides as stone consolidants was considered. Reaction of $Ca(OCH_3)_2$, $Ca(OCH_2CH_3)_2(CH_3CH_2OH)_4$ and $Ca[OCH(CH_3)_2]_2$ with the atmosphere in different experimental conditions was studied. The reaction produced $CaCO_3$ and two different pathways seem to be involved, the first taking place through CO_2 insertion into the Ca–O bond of $Ca(OR)_2$ species with formation of an alkylcarbonate derivative, subsequently transformed into $CaCO_3$ through ROH elimination; the second takes place through hydrolysis of $Ca(OR)_2$ to $Ca(OH)_2$, which is then carbonated to $CaCO_3$. The vaterite/calcite ratios found in the final $CaCO_3$ vary considerably with the experimental conditions adopted. Investigations demonstrated the potentiality of $Ca(OCH_3)_2$ to act as a stone consolidant. In fact, impregnation of a porous substrate, simulating the deteriorated stone, with a methanol solution of $Ca(OCH_3)_2$, produced a crystalline vaterite film, which gradually filled all the pores and cavities of substrate and seems to fulfil the necessary requirements for a consolidant. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: stone consolidation; calcium alkoxides; limestone; calcium carbonate deposition; building heritage

Introduction

Various deterioration agents act on historic buildings and the effects on the stone surfaces differ. Water, soluble salts and microorganisms are the most powerful natural deterioration agents,[1–8] and their effects are enhanced by anthropogenic pollutants.[9–12] In addition to aesthetic effects, i.e. superficial chromatic effects (blackening, yellowing, discoloration) and efflorescences, which may be mitigated by cleaning procedures,[13] deterioration processes involve stone decohesion, macroscopic micro-fissuring, cracking, scaling and flaking, which tends to disaggregate the stone materials into a series of micro- and macrofragments. Several strengthening treatments, namely consolidation, and materials have been tested to restore the original stone cohesion.[14,15] Materials and procedures adopted for consolidation are key parameters to ensure positive results: organic polymers and alkoxysilane-based products have been tested and widely applied, with methodologies that range from simple application by brush to impregnation under vacuum.[16–19]

Different synthetic organic polymers, i.e mainly polyacrylates, polyvinylacetates, epoxies and silicones, have been widely employed as consolidants and surface coatings for limestone to prevent further deterioration since the middle of the last century.[20–24] Although they are still in widespread use, their conservation efficiency has been drastically reconsidered because of the irreversibility of the treatments, as a consequence of severe alteration and degradation processes, such as photo-oxidative reactions leading to chain scission and/or reticulated structures in acrylic products and hydrolytic and condensation reactions causing cross-linked structures in silicon-based products. These processes are induced either by environmental conditions and by the substrate itself.[25,26] Besides physico-chemical changes, a correlated strong decrease in the applied polymer solubility has also been detected, which, in conservation practice, results in limited removability of deteriorated polymers from treated surfaces.

Alkoxysilanes and alkylalkoxysilanes have also been extensively applied on limestones, especially methyltrimethoxysilane (MTMOS) and tetraethoxysilane (TEOS).[27–29] Although the drawbacks are well known in consequence of limestone consolidation with these products, i.e. poor affinity with the substrate and cracking during shrinkage,[30–32] according to Ferreira Pinto and Delgado Rodrigues,[19] their current use results from the lack of better alternatives.

Alternatively, inorganic treatments, especially those involving calcium hydroxide, look more suitable for the carbonate stones, due to their higher physico-chemical compatibility with respect to polymers. Water suspension of slaked lime is a traditional stone treatment in UK,[33] even though poor penetration inside the stone pores and inconsistent deposition of small amounts of applied product have been demonstrated.[34] One critical point in the use of $Ca(OH)_2$ is its extremely low solubility in water (1.7 g/l at 20 °C), which necessitates repeated treatments of stone surfaces before achieving an increase of substrate strength. Micro- and nano-emulsions of calcium hydroxide in alcohol have also been prepared and successfully tested for consolidation of wall paintings, as they can penetrate the thin painting layers, ensuring their recohesion to the underlying plaster.[35–37] Furthermore, the biomediated reinforcement of deteriorated calcareous stones has recently been tested, which is achieved through natural and synthetic polypeptides which control the calcium carbonate crystal growth within the stone pores.[38]

Besides the intrinsic consolidant properties, treatments should be reasonably inexpensive, easy to apply, safe to handle and environmental sustainable, but the most critical requirement is effectiveness over a period of time and compatibility of the

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applied product with the original stone substrate. Although research has been conducted over more than a century, good long-term results are the exception rather than the rule.[25,26,39]

In this paper we investigate the potential use of calcium alkoxides as an alternative class of compounds to conventional consolidant materials. The development of metal alkoxides chemistry[40,41] dates back to the middle of last century, but it has received renewed attention due to their utilization in the synthesis of inorganic materials via sol–gel and chemical vapor deposition (CVD) techniques.[42–44]

Metal alkoxides are usually reactive compounds which undergo a large variety of reactions with different substrates. They are easily hydrolyzed, also by atmospheric moisture, leading to formation mainly of metal hydroxides according to the reaction

$$M(OR)_n + nH_2O \rightarrow M(OH)_n + nROH \qquad (1)$$

although in some cases oxide alkoxides could be produced.[40,41] On the other hand the carbonation reaction of hydrated lime (calcium hydroxide)

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

is one of the oldest known reactions, and extensively used in past centuries in building manufacture.[45,46]

The aim of our work is: (a) to verify calcium alkoxides conversion into $CaCO_3$ in the presence of moisture and carbon dioxide from the atmosphere; (b) to evaluate the possibility of use, as a consolidating agent, the calcium carbonate produced from calcium alkoxides, in a similar way to the carbonation of calcium hydroxide leading to the hardening of a lime mortar.

Experimental

General instrumentation

A Nicolet microscope connected to a Nicolet 560 FT-IR system, equipped with a mercury–cadmium–telluride detector, was used for spectra collection of calcium alkoxides and related conversion products. The investigated microareas were about $50 \times 50\ \mu m^2$ in size. IR spectra were recorded in reflectance mode in the $4000–650\ cm^{-1}$ range, with a resolution of $4\ cm^{-1}$. Recorded spectra have been expressed by absorbance units and baseline corrected.

NMR spectra were recorded on a Bruker AMX300 spectrometer, equipped with inverse and direct 5 mm broad-band multinuclear probes, operating at the frequency of 300.13 MHZ for ^1H and 75.43 MHz for ^{13}C. Saturated solutions were analyzed, obtained by dissolving the samples in 0.5 ml of the appropriate deuterated solvents ($CDCl_3$, CD_3OD or C_6D_6), which were also used as internal references. The usual operating conditions for ^1H NMR spectra were: $T = 25\,°C$; $P1 = 12\ \mu s$; $TL0 = 3d\beta$; $SW = 12.43$ ppm (direct probe).

Elemental analyses were performed with a Fisons EA 1108 (CHNS-O version) elemental analyzer. Observation of $CaCO_3$ films deposited on glassy substrates was performed with a Fei Quanta 200 FEG-ESEM instrument to evaluate their morphology and the distribution inside the pore network. The semiquantitative elemental compositions were obtained using an energy dispersive X-ray spectrometer, EDAX Genesys, using an accelerating voltage of 25 keV. The samples were coated with a graphite film before ESEM-EDS investigations.

X-ray diffraction measurements were carried out on sample powders on a Philips X'Pert PW3710 diffractometer, using Cu Kα radiation (40 kV, 30 mA), a high-resolution graphite monochromator, a rotating sample holder and a proportional detector. Measurements were carried out in the range $5° < 2\theta < 90°$ with a step of 0.02°. X-ray diffraction (XRD) patterns show diffraction peaks in agreement with JCPDS standards at 2θ of 29.4, 35.9 and 39.5°, corresponding to (104), (110) and (113) crystallographic planes of calcite, of 2θ of 24.9, 27.1, 32.8°, corresponding to (110), (112), (114) planes of vaterite, and of 2θ of 18.0, 28.6, 34.1°, corresponding to (001), (100), 101) planes of portlandite, i.e calcium hydroxide. The semiquantitative estimation of the different phases formed within the single sample were obtained by the reference intensity ratio method.[47]

Calcium alkoxides

Synthesis of calcium alkoxides, involving the direct reaction of metallic calcium granules with the corresponding alcohol, were carried out in nitrogen-filled gloves-boxes with exclusion of moisture and oxygen according to procedures already described in the literature.[41,48–51] Calcium granules (99%) and $Ca[OCH(CH_3)_2]_2$ (**3**) (99.9%) were purchased from Aldrich Chemical Company and used as supplied without any further purification. Elemental analysis results of the commercially available $Ca[OCH(CH_3)_2]_2$ (**3**) were: found C 43.76, H 10.07; calcd for $C_6H_{14}CaO_2$ C 45.57, H 8.86%. Solvents were purified by standard procedures.[52]

Synthesis of $Ca(OCH_3)_2$ (1)

Calcium granules (2.5 g), previously cleaned by vigorous stirring in dry diethyl ether, were added to CH_3OH (100 ml). The mixture was stirred overnight and the calcium granules were consumed to give a white precipitate. This precipitate was filtered, dried and analyzed. Found: C 22.91; H 5.74. Calcd for $C_2H_6CaO_2$: C 23.53; H 5.88%. ^1H NMR of (**1**) in CD_3OD, δ, ppm: 3.35 (s, CH_3O); in $CDCl_3$, δ, ppm: 3.49 (s, CH_3O).

Synthesis of $Ca(OCH_2CH_3)_2(CH_3CH_2OH)_4$ (2)

Calcium granules (3.2 g), previously cleaned by vigorous stirring in dry diethyl ether, were added to CH_3CH_2OH (100 ml). The mixture was refluxed for 6 h and the calcium granules consumed. A crystalline white precipitate was formed at room temperature, filtered, dried under vacuum and analyzed. Found: C 44.53; H 9.87. Calcd for $C_{12}H_{34}CaO_6$: C 45.86; H 10.83%. A prolonged drying process duration (>7 h) led to the formation of the unsolvated complex $Ca(OCH_2CH_3)_2$ (**2′**) instead of **2**, but without a strict reproducibility. Found: C 36.35; H 8.41. Calcd for $C_4H_{10}CaO_2$: C 36.92; H 7.69%.

^1H NMR of (**2**): in C_6D_6, δ, ppm, 4.13 (q, 2H, CH_2, EtO), 3.71 (sb, 10H, CH_2, EtO/EtOH), 1.67 (t, 3H, CH_3, EtO), 1.23 (17H, CH_3, EtO/EtOH); in $CDCl_3$, δ, ppm, 3.73(sb) + 3.71 (q) overlapping (2H, CH_2, EtO/EtOH); 1.24 (sb + t overlapping, 3H, EtO/EtOH).

^1H NMR of (**2′**): in C_6D_6, δ, ppm, 3.29 (q, 2H, CH_2, EtO), 0.93 (t, 3H, CH_3, EtO); in $CDCl_3$, δ, ppm: 3.73 (q, 2H, CH_2, EtO), 1.23 (t, 3H, CH_3, EtO).

Impregnation studies and $CaCO_3$ deposition

The porous substrate, chosen to be impregnated by the methanol solution of **1** in order to study the behavior of the calcium alkoxide in its transformation to calcium carbonate inside pores and cavities, was the glass frit generally used for chemical filtration (Bibby Scientific, diameter 30 mm, thickness 3.5 mm, porosity 4, experimentally calculated pores diameter 5–15 μm). A methanol solution of **1** was applied either by contact imbibition (method A) or percolation on the glass substrate (method B). A 1 mm layer of calcium alkoxide solution was added to totally saturate the frit horizontally placed on the bottom of a glass beaker for method A. The solution was percolated through a second frit not in contact with the beaker bottom for method B. Operations were continually repeated several times after solvent evaporation.

To compare the morphology of $CaCO_3$ coating with traditional consolidant, porous substrates were treated with solutions of TEOS (the commercially available consolidant product ESTEL1000 product, tetraethyl-*o*-silicate 75% in white spirit D40, was used as received by the supplier CTS s.r.l., Altavilla Vicentina, Italy) and of $Ca(OH)_2$ (*ca* 3 g of slaked lime in distilled water). The suspension was stirred for 12 h, left to stand for 24 h and the resulting $Ca(OH)_2$ saturated solution collected applied by method A. The treatments were performed in a natural atmosphere (relative humidity ranging from 40 to 60% and average temperature 25 °C) in order to simulate the average condition of a real treatment in a mild climate.

Results and Discussion

Three calcium alkoxides have been selected for our study: (1) $Ca(OCH_3)_2$; (2) $Ca(OCH_2CH_3)_2(CH_3CH_2OH)_4$; and (3) $Ca[OCH(CH_3)_2]_2$. Metal alkoxides can undergo alcohol interchange reaction, according to the equilibrium:

$$M(OR)_x + yR'OH \leftrightarrow M(OR)_{x-y}(OR')_y + yROH \qquad (3)$$

Since alcohols are candidate solvents for application of calcium alkoxides as stone consolidants on deteriorated substrates of works of art, we checked the occurrence of reaction (3) in order to verify such possible interaction with the solvent.

Before checking the possible alcohol interchange reaction, the alkoxides were characterized by NMR spectroscopy. While the ^1H spectrum of $Ca(OCH_2CH_3)_2$ (**2′**) shows the expected signals at 3.73 ppm (q, 2H, $OC\underline{H}_2CH_3$) and 1.23 ppm (t, 3H, $OCH_2C\underline{H}_3$), the situation is different for $Ca(OCH_3)_2$.

In particular, ^1H NMR spectra of **1** show the singlet of the methoxide group at 3.35 ppm in CD_3OD and 3.49 ppm in $CDCl_3$. Moreover, spectra recorded in $CDCl_3$ show the presence of another peak of variable intensity at 3.51 ppm coupled with a quartet at 0.91 ppm (integration ratio 3/2); checks at different times show decreases in these two signals until their complete disappearance after 3 months. Spectra of different preparations and also in different deuterated solvents (deuterated toluene, C_6D_6) show this ambiguous result, without strict reproducibility. This could be due to the formation of different molecular aggregates in solution[53] or to interaction with the solvent; it is still under investigation.

Compound **1** was left stirring in EtOH at room temperature; at different times 5 ml aliquots were taken, the solvent evaporated and the residue dissolved in $CDCl_3$ and checked by ^1H NMR. After 4 h, only the signals of the OCH_3 group of **1** at 3.49–3.51 ppm and the corresponding quartet at 0.91 ppm could be detected. After 24 h, signals of the unsolvated complex $Ca(OCH_2CH_3)_2$ (**2′**) (see Experimental section) appeared at 3.73 ppm (q, 2H, $OC\underline{H}_2CH_3$) and 1.23 ppm (t, 3H, $OCH_2C\underline{H}_3$), which increased until reaching, after a week, a stable ratio of **2′**:**1** = 2:1. Conversion of **1** into **2′** was not complete, this indicating a good stability towards reaction (3) of the compound (Fig. 1).

When the same experiment was performed for **2** left in CH_3OH at room temperature under stirring, a completely different result was obtained: after 24 h, only the signals of **1** were detected in the NMR spectrum, indicating that complete conversion of **2** in **1** took place (Fig. 2). Exactly the same behaviour was observed for **2′**.

Such experiments point out the easy setting up of the above equilibrium (3) for the calcium derivatives; consequently, the easy interchange of alkoxy groups between the calcium complexes and alcohol must be taken into consideration in the choice of the solvent to introduce calcium alkoxides into the deteriorated stone substrate. Further studies will be carried out to identify the most

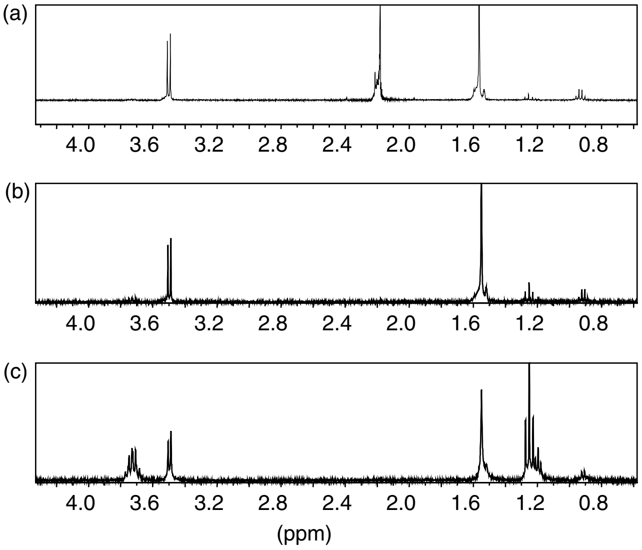

Figure 1. ^1H NMR spectra in $CDCl_3$ of $Ca(OCH_3)_2$ (**1**). The products originating from the reaction of **1** with ethanol at room temperature: (a) after 4 h, (b) after 24 h and (c) after a week. After 4 h (a) only the signals of **1** could be detected. After 24 h (b), signals of the unsolvated complex $Ca(OCH_2CH_3)_2$ (**2′**) appeared, which increased until reaching, after a week (c), a stable ratio **2′**:**1** = 2:1.

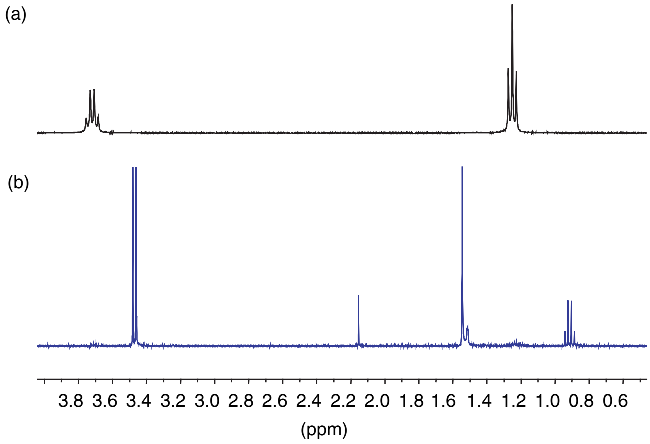

Figure 2. ^1H NMR spectra in $CDCl_3$ of $Ca(OCH_2CH_3)_2$ (**2′**) before (a) and after (b) 24 h reaction with methanol at room temperature: only the signals of**1** $Ca(OCH_3)_2$ are detected in the NMR spectrum, indicating the complete conversion of **2** to **1**.

appropriate solvents to fulfil the requirements of handling safety and environmental sustainability.

Calcium alkoxides reactions

Reactions of **1**, **2** and **3** with the atmosphere have been studied and the products analyzed. Powdered samples of **1**, **2** and **3** were left in contact with air for 90 days and then analyzed. The phase identification of final decomposition products was carried out by powder X-ray diffraction technique (Table 1, Fig. 3). The results of the semiquantitative estimation of the different phases, formed within each sample, are reported in Table 1 (a–c). All the alkoxides produce $CaCO_3$, although with different degree of order: the polymorphic carbonate vaterite is the main product from **2** and **3**, while the more ordered calcite is the predominant phase coming from **1**. Elemental analysis were also carried out. The results were: final product from **1**, C 10.83%, H 0.00%; final product from **2**, C 12.08, H 0.13%; final product from **3**, C 18.46, H 2.08; calcd for $CaCO_3$ C 12.00, H 0.00%. Measurements were validated by comparison with analysis of a pure commercially available $CaCO_3$ sample which gave C 12,26, H 0.00%. Substantially, formulation as $CaCO_3$ was confirmed for the final products from **1** and **2**, while the higher percentage values for C and H suggest that a small organic fraction remains trapped in the $CaCO_3$ formed in the reaction of **3** with the atmosphere.

Table 1. Semiquantitative XRD estimation of the different phases formed from reaction of **1**, **2** and **3** with the atmosphere

	Calcium alkoxide	Calcite (%)	Vaterite (%)	Portlandite(%)
a	**1** (powder)	77	23	–
b	**2** (powder)	5	95	–
c	**3** (powder)	6	94	–
d	**1** (methanol dispersion)	47	53	–
e	**3** (methanol dispersion)	15	85	–
f	**1** (H_2O dispersion)	74	5	21
g	**3** (H_2O dispersion)	100	–	–
h	**1** (methanol solution)	25	75	–
i	**1** (deposition on glass frit)	0	100	–

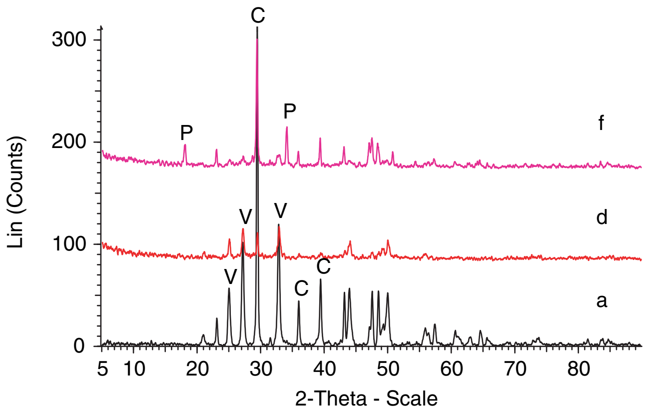

Figure 3. X-ray diffractograms of **1**: as powder sample left in contact with air (a); as powder sample from methanol dispersion after solvent evaporation (d); as powder sample from water dispersion after solvent evaporation (f). Peak assignments: P, portlandite ($Ca(OH)_2$); C, calcite ($CaCO_3$); V, vaterite ($CaCO_3$).

The decomposition studies were also carried out under other experimental conditions. We investigated the interaction with alcohol and performed similar studies for **1** and **3** in methanol. In fact, **2** seems to be unstable even under a dry nitrogen atmosphere, the white powder turning brown in several weeks; intramolecular decomposition processes would occur, ruling out its utilization for our purpose.

Methanol dispersions of **1** and **3**, respectively, were left in contact with air for 14 days, then the solid decomposition products dried, filtered and analyzed. The final product, in each case $CaCO_3$, was a mixture of calcite and vaterite for **1**, while a predominant formation of vaterite came from **3** (d and e in Table 1).

A clear filtered methanol solution of **1** was also considered. It was left for 1 month in contact with the atmosphere and the solid residue produced was analyzed. The product was $CaCO_3$ and the results are shown in Table 1(h). Elemental analysis was also carried out, and the carbon percentage was found to be 11.95%, while hydrogen was not detected (0.00%). This is in agreement with the $CaCO_3$ formulation.

A different behaviour was observed when **1** and **3** were treated with water. Interestingly, when powders of **1** and **3,** respectively, were dispersed in water and left in contact with air for 3 days, full conversion to calcite was observed for **3**, while a mixture of calcite (74%), vaterite (5%) and portlandite (21%) originated from **1** (f and g in Table 1).

The reactions occurring between **1** and the atmosphere were monitored by μ-FT-IR measurements (Fig. 4). A few drops of a CH_3OH solution of **1** were placed on a gold flat surface and reflectance IR spectra were collected after alcohol evaporation at different times until complete conversion to $CaCO_3$ occurred. The spectrum collected just after solvent evaporation showed absorptions at 1450 and 1047 cm^{-1}, due to C–O stretching and the CH_3 deformation mode of methoxide group respectively and absorptions at 2928, 2861, 2806 cm^{-1} due to CH_3 stretching.[54] Broad bands at 1634 and 1328 cm^{-1} were also detected, disappearing in a few hours, which could be respectively attributed to antisymmetric and symmetric stretching vibrations of CH_3OCO_2 groups, presumably formed by insertion of CO_2 into the Ca–O bonds of **1**, with formation of methylcarbonate

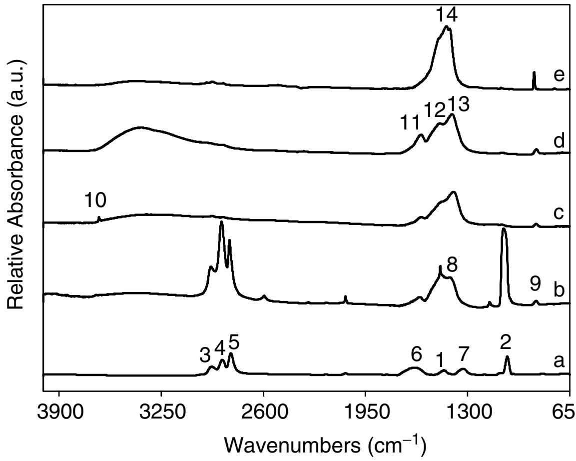

Figure 4. IR spectra of the products resulting from the reaction of **1** with atmosphere. Time of collection: (a) 0; (b) 15 min; (c) 4 h; (d) 8 days; (e) 45 days. IR absorbance assignments (cm^{-1}): 1450 (1); 1047 (2); 2928 (3); 2861 (4); 2806 (5); 1634 (6); 1328 (7); 1409 (8); 864 (9); 3645 (10); 1595 (11); 1473 (12); 1394 (13); and 1440–1420 (14).

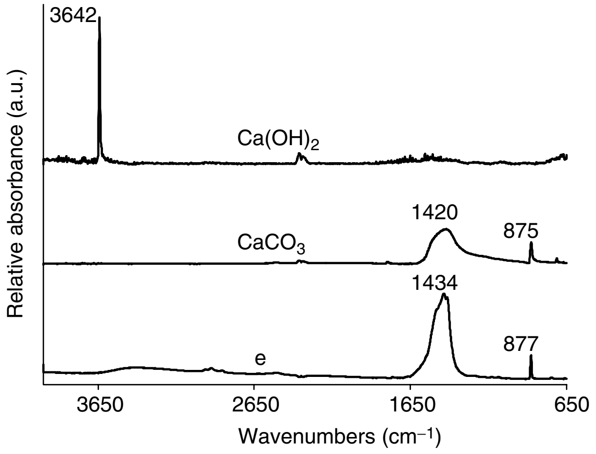

Figure 5. IR spectra of final product of **1** (e), $CaCO_3$ and $Ca(OH)_2$. The comparison of the spectra clearly indicates that the spontaneous chemical pathway of **1** under environmental conditions leads exclusively to calcium carbonate formation.

derivatives.[49,55] Disappearance of these two absorptions together with appearance of new signals at 1409 and 864 cm^{-1}, ascribable to $CaCO_3$,[56] suggests that methylcarbonate species undergo a methanol elimination reaction with formation of $CaCO_3$.

The IR spectra suggest that conversion of **1** (still present after complete conversion of methylcarbonate) to $CaCO_3$ also occurs with a second pathway. This would take place through hydrolysis of **1** by moisture with formation of $Ca(OH)_2$ [reaction (1)], confirmed by the appearance of the sharp absorption at 3645 cm^{-1} due to OH stretching, and subsequent CO_2 insertion into the Ca–O bond of $Ca(OH)_2$, which generates variously coordinated bicarbonate groups,[57] giving new bands centered at 1595, 1473 and 1394 cm^{-1}, as proved for Cu complexes.[58]

The bands between 1440 and 1420 cm^{-1}, due to $CaCO_3$ formation, are hidden by methylcarbonate and bicarbonate absorptions and can be clearly recognized when their complete conversion takes place after several days. Nevertheless the carbonate formation can be inferred from the clearly detectable absorptions at 862–877 cm^{-1}, ascribable to out-of-plane bending of the carbonate group.[56]

Depending on the thermohygrometric conditions and the thickness of alkoxide particles, the time required for the complete carbonation ranges from 2–4 to 35–45 days. The IR data from alcoholic solutions of **2** and **3** parallel the results obtained for **1**, suggesting similar chemical pathways leading, in both cases, to $CaCO_3$ as final product (Fig. 5).

IR spectra collected from **1** and **3** after water dispersion and solvent evaporation initially show a sharp absorbance at 3642–3646 cm^{-1} ascribed to OH stretching, of $Ca(OH)_2$, formed in consequence of hydrolysis of alkoxides with water. The IR spectra, collected later on, prove the evolution of $Ca(OH)_2$ into $CaCO_3$, which takes several weeks to reach completion.

IR and XRD measurements on the final products resulting from water solution of **1** and **3** indicate that hydrolysis is the predominant reaction of these alkoxides with water as solvent. The hydrolysis and subsequent carbonation show slower kinetics in comparison to that occurring for carbonation via CO_2 insertion in the Ca–O bond of Ca alkoxide.

Impregnation studies and $CaCO_3$ deposition

Once it has been verified that decomposition in air of **1**, **2** and **3** produces $CaCO_3$, we tried to estimate the potentiality as strengthening agent of **1**, which appeared to be the most promising among the calcium alkoxides selected for our study.

Generally the consolidant product should penetrate into the pore network of the decayed stone, creating a cohesive layer capable of binding the fragments together. We verified that **1** could accomplish this task. In fact, after impregnation of a porous substrate by a methanol solution of **1**, calcium carbonate

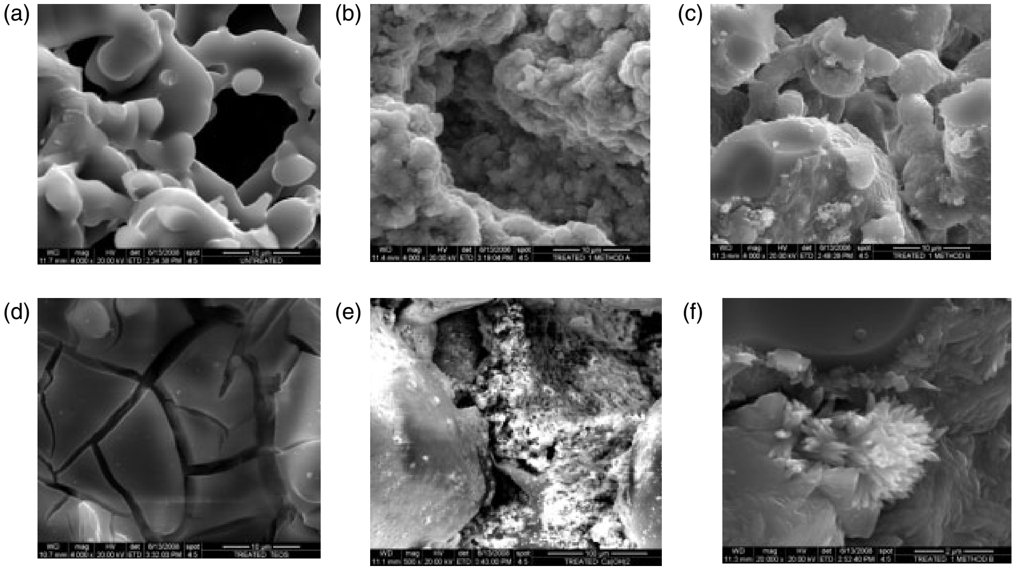

Figure 6. Secondary electron images of porous substrates untreated (a) and treated with **1** methanol solution by contact imbibition (b) or percolation (c). A detail of $CaCO_3$ crystals grown on the substrate is reported in (f). The $CaCO_3$ coating from alkoxides appears more homogeneous and more adherent to the substrate in comparison to the silica cracked coating from TEOS deposition (d) and the incoherent deposition of $CaCO_3$ from the treatment with water suspension of slaked lime (e). Magnification: (a–d) 4000×; (e) 500×; (f) 20.000×.

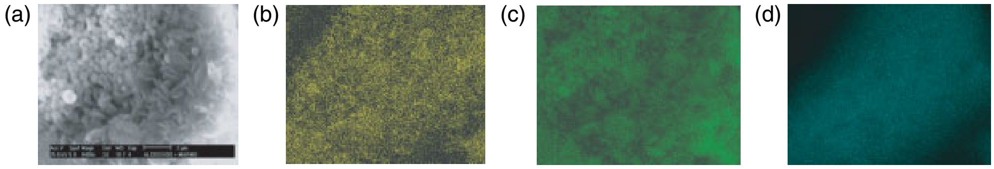

Figure 7. SE image of silica substrate treated with **1** (a) and the relative X-ray maps of Si (d), C (c), and Ca (b), markers of the silica substrate and $CaCO_3$, respectively.

deposited as an homogeneous and adherent film on the grains, gradually filling all the pores and cavities of the substrate. We used only methanol as solvent for the **1** impregnating solution in order to avoid the alcohol interchange reaction (3), which would complicate our study at this stage. The chosen porous substrate was a glass frit, generally used for chemical filtration for the following reasons: (i) EDS analysis excluded the presence of calcium in the frit, allowing accurate SEM/EDS investigations; and (ii) the assured and reproducible glass frit porosity, together with the neutral behavior of the frit glassy material allowed easy comparison of different series of experiments. These factors are difficult to find in naturally occurring stone substrates.

SEM morphological observations were performed either on the surface or on a transversal section of the frits treated with **1** according to methods A and B. The observation, carried out one month after treatment of the substrate, showed a homogeneous film of roundish and platelet-like crystallites grown on the grains [Fig. 6 (a–c, f)]. The coating thickness ranged from 0.8 to 1.5 μm and particle morphology strictly resembled vaterite.[59] The pore network was coated for the whole frit thickness, indicating that the alkoxide ensures a penetration depth of 3.5 mm at least.

X-ray maps of Ca, C and Si were carried out on the coating; Ca and C were selected as markers of $CaCO_3$, while Si was indicative of the glass substrate. The maps (Fig. 7) clearly prove the distribution of Ca and C on the coating and the absence of Si, thus indicating that the formed $CaCO_3$ homogeneously permeates the pores, without any cracks. Moreover, the film strongly sticks to the surface without any formation of ungrafted particles. The application methodology does not influence the coating morphology, although, a higher number for percolation in comparison to impregnation is necessary to obtain the same coating thickness.

In order to compare the coating formation of alkoxide with traditional stone consolidants, SEM observation were also performed on the same frit treated with TEOS and a water suspension of slaked lime. The $CaCO_3$ coating deriving from alkoxides appeared more homogeneous and more adherent to the substrate in comparison to the silica cracked coating from TEOS deposition [Fig. 6(d)] and the incoherent deposition of $CaCO_3$ from the treatment with water suspension of slaked lime [Fig. 6(e)].

The phase identification of the film was carried out by XRD measurements on a ground frit treated with a methanol solution of **1** according to method A; the resulting film was composed exclusively of vaterite (Table 1, i).

Conclusions

Our investigations have shown that the selected calcium alkoxides react with atmosphere producing calcium carbonate. Two different pathways seem to be involved: the first occurring through CO_2 insertion into Ca-O bond of Ca $(OR)_2$ species with formation of a methylcarbonate derivative, subsequently transformed into $CaCO_3$ through ROH elimination; the second through hydrolysis of $Ca(OR)_2$ to $Ca(OH)_2$ (reaction 1), followed by carbonation to $CaCO_3$ (reaction 2). Depending on the experimental conditions, the vaterite/calcite ratios found in the final calcium carbonate, vary considerably, underlying the importance of the solvent/dispersion-agent interactions and the role of the substrate, where the film grows, in this process.

Moreover, our studies demonstrated the potentiality of **1** as a consolidant product, expecially for carbonatic stones. In fact, impregnation of a porous substrate, simulating the deteriorated stone, with a methanol solution of **1**, produces a crystalline calcium carbonate film in the vaterite form, which deposits with good adhesion on the grain surface of substrate without cracks and the formation of ungrafted particles, different from traditional consolidants such as TEOS and slaked lime; this film homogeneously permeates all the pores and gradually fills all the cavities of the porous substrate, binding the grains together and fulfilling the necessary requirements a consolidant should have.

Many advantages are offered by the possible utilization of calcium alkoxides as consolidants, the first of which is, unlike synthetic organic polymers, the high compatibility with the stone substrate, especially in the case of carbonatic stones, where consolidant and stone have the same chemical composition. Moreover, no undesired reaction products are generated, which could remain in the stone altering the system.[25,26] In fact, alcohol is the only other product in the conversion of calcium alkoxides to calcium carbonate and easily leaves the stone by evaporation.

The obstacle, which at this stage hampers the possibility of success of the consolidation treatment here described, is the low solubility of **1** in methanol, which implies a low amount of $CaCO_3$ deposited in each application and, consequently, disadvantageous repetitions of the treatment. Low solubility is a general characteristic of metal alkoxides and is due to their tendency to oligomerize through alkoxide groups, bridging two or three metal centres through their oxygen atom.[41] Research is currently in progress to overcome this obstacle, aiming to increase the solubility of **1** to explore the possibility of using more soluble $Ca(OR)_2$ derivatives.

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