

CALCIUM ALKOXIDES: A NEW PROMISING ROUTE FOR CONSOLIDATION OF DETERIORATED LIMESTONE

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Restorers, firstly, and conservation scientists have always had to face the problem of stone deterioration, an issue that has become more and more urgent since atmospheric pollution due to human activity has worsened the effects of natural environmental agents.

Many products have been proposed and applied: they can be grouped in two main categories, the organic and the inorganic materials. Organic materials included synthetic polymers, extensively used in the past and still widely applied, with an efficiency in preventing further deterioration to be drastically reconsidered; they frequently undergo chemical modifications induced either by environmental conditions and by the substrate itself, which cause loss of efficacy and irreversibility of the treatment.¹⁻³ Inorganic materials are supposed to be more suitable because of their physico-chemical compatibility with the stone: they have been traditionally applied since the beginning of conservation and recently drastically reconsidered.

In our laboratory we have synthesized and tested calcium alkoxides for the strengthening of limestone with the aim of a durable and compatible treatment.⁴ Linear and branched calcium metallorganic compounds have been designed, synthesized and their potential as stone consolidants evaluated.

Alcoholic solutions or suspensions of $\text{Ca}(\text{OCH}_3)_2$ have been studied by NMR and IR techniques to evaluate their stability towards hydrolysis and alcoholysis and the conversion products have been characterized by XRD measurements. In order to study the behavior of the calcium alkoxide and its transformation to calcium carbonate inside pores and cavities, we choose to treat glass frit (generally used for chemical filtration; experimentally calculated pores diameter 5-15 μm) as porous substrate. This choice is to avoid misleading interpretation of morphological FEG-ESEM observation and EDS analyses on treated stone specimens as a limestone substrate and the effective consolidant have both the same mineralogical and chemical composition.

In order to verify the consolidation effects, the same solutions have been applied on artificially aged Carrara marble specimens (5x5x1 cm^3) by capillary imbibition (contact time: 2h) from the wider surface side. The application was repeated every 24 h for three times. For comparative purposes, ethyl silicate (TEOS), solution of $\text{Ba}(\text{OH})_2$, $(\text{NH}_4)_2\text{CO}_3$ and alcohol suspension of $\text{Ca}(\text{OH})_2$, prepared according to literature,⁵⁻⁷ have been applied by the same procedure. Consolidation efficiency on marble specimens treated with the different products has been evaluated by measurement of ultrasonic velocity (USV) before and after treatments.

The consolidation efficiency (C.E.) has been evaluated with particular emphasis to the following requirements: *i*) physico-chemical compatibility of the applied products with the substrate; *ii*) morphology and distribution of the inorganic products inside the pore network, i.e. evidences of consolidant adhesion to the substrate and/or cracks and fissures, powdering deposition, intergranular links, etc.; *iii*) low product inva-

siveness, as a detrimental consolidation effect is the pore saturation instead of a coating formation on the pore walls because it doesn't ensure thermohygrometric equilibrium of outdoor stone with the environment.

The C.E. has been expressed as:

$$\text{C.E.} = (\text{US}_f - \text{US}_i) / \text{P}_f$$

where: US_i and US_f are respectively the ultrasonic velocity (km/s) measured before and one month after the product application; P_f is the amount of the final product, expressed in mg inside marble substrate after treatment, calculated according to quantitative reactions.

Due to space limitation, exclusively the results obtained from $\text{Ca}(\text{OCH}_3)_2$ and comparison with TEOS and $\text{Ba}(\text{OH})_2$ will be discussed.

The transformation reactions occurring between $\text{Ca}(\text{OCH}_3)_2$ and environmental H_2O and CO_2 have been investigated by infrared measurements: few drops of their alcoholic solutions have been placed on a gold flat surface and reflectance IR spectra have been collected after alcohol evaporation at different times until complete conversion of the alkoxide, occurred after one to two months after the treatments. Micro-FT-IR investigations confirmed the formation of CaCO_3 as the final product in all cases although two different reaction pathways can take place (Figure 1). XRD measurements allow identifying the crystalline phase of the final products, which resulted to be calcite and vaterite.

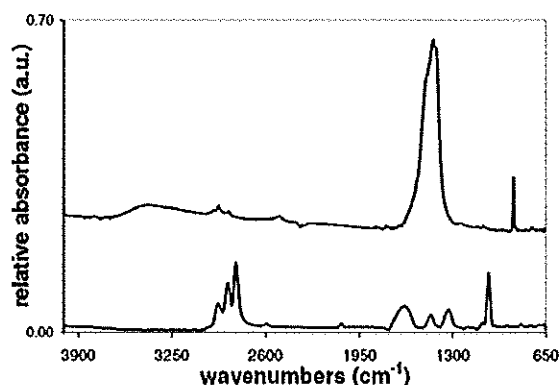


Figure 1: IR study of reaction of $\text{Ca}(\text{OCH}_3)_2$ with atmosphere. The spectra show the absorbance bands of $\text{Ca}(\text{OCH}_3)_2$ (lower one) just after deposition and the calcium carbonate absorption after complete conversion of the alkoxide (upper one). A detailed description of the different absorbance can be found in reference 4.

FEG-ESEM and SEM morphological observations, performed either on surface and on transversal section of glass frit and marble specimens, aimed at investigating the carbonate formation from $\text{Ca}(\text{OCH}_3)_2$, were carried out two months after treatments. They show a homogeneous film of roundish and platelette-like crystallites grown on the grains (Figure 2). The coating strongly sticks to the surface without any formation of the ungrafted particles and its thickness ranges from 50 nm to 1.5 μm . Similar observation performed on the same substrates treated with TEOS (Figure 2), show a thick deposition on the surface and an uneven impregnation of the pores. Furthermore, the shrinkage occurring during TEOS polymerization and silica formation is responsible for the extensive fissured network of the silica coating.

Table 1: Amount of different applied products related ultrasonic velocities, measured on marble specimens before and after treatments, and C.E. (Consolidation Efficiency).

| product | applied amount (mg) | v_i untreat. Marble (km/s) | v_f treated marble (km/s) | v % | C.E. (km/sg) |
|-----------------------------|---------------------|------------------------------|-----------------------------|-----|--------------|
| $\text{Ca}(\text{OCH}_3)_2$ | 4.0 ± 0.6 | 1.1 ± 0.2 | 1.3 ± 0.1 | 18 | 51 |
| TEOS | 188.5 ± 19.5 | 1.1 ± 0.3 | 3.8 ± 0.6 | 245 | 50 |
| $\text{Ba}(\text{OH})_2$ | 39.8 ± 1.0 | 0.9 ± 0.1 | 1.4 ± 0.1 | 56 | 11 |

The consolidation efficiency, evaluated on marble specimens through ultrasonic velocity measurements before and two months after treatment with the different products (Table 1), shows that the increase of ultrasonic velocity, measured after marble treatment, strongly depends on the amount of applied products: 4 mg of $\text{Ca}(\text{OCH}_3)_2$, 39.8 mg of barium hydroxyde and 188.5 mg of TEOS respectively induced a positive variation of ultrasonic velocity of 18-56 and 245% with respect to untreated marble. Notwithstanding the high amount of amorphous silica introduced inside pores and the corresponding increased ultrasonic velocity, the silica coating appears highly fissured; thereby its function is more similar to a filler rather than to a consolidant (Figure 2).

To estimate the consolidant efficiency C.E. of the applied products, the ratio between the variation of ultrasonic velocities (measured before and after treatment) and the amount of the final product deposited inside the pores was calculated. The obtained C.E. data for $\text{Ca}(\text{OCH}_3)_2$, TEOS and $\text{Ba}(\text{OH})_2$ clearly show a better performance for the alkoxide compared to the other inorganic products, with the following performance scale: $\text{Ca}(\text{OCH}_3)_2 > \text{TEOS} \gg \text{Ba}(\text{OH})_2$.

The properties of these novel materials are still under investigation especially to improve their stability and solubility; the preliminary encouraging outcomes make Ca-alkoxides good candidates to become new compatible and durable materials for the strenghtening of limestone and a newsworthy replacement of currently used materials.

1. References

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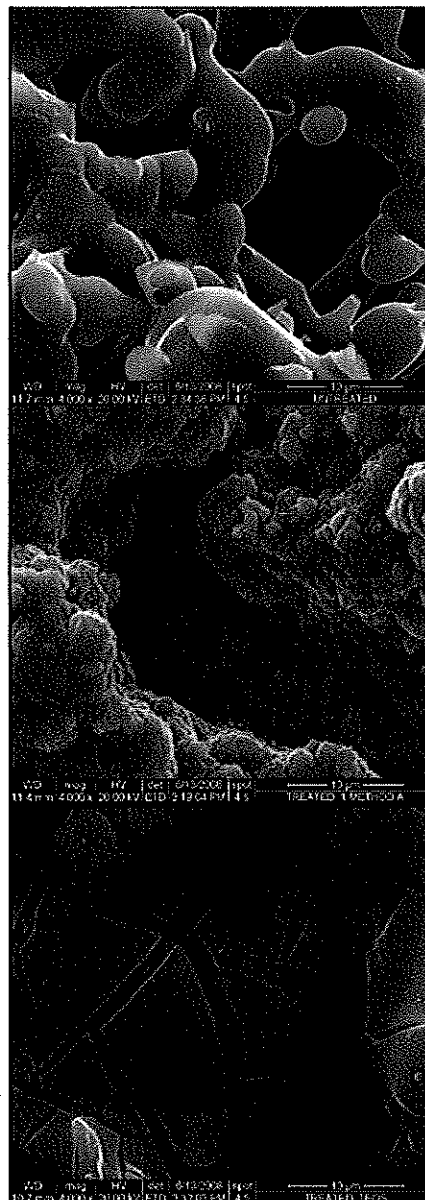


Figure 2: Secondary electron images collected on silica frit untreated (up), treated with $\text{Ca}(\text{OCH}_3)_2$ (middle) and TEOS, (4000-fold magnification) (bottom). The CaCO_3 coating from alkoxides appears more homogeneous and more adherent to the substrate in comparison to the silica cracked coating from TEOS deposition.