

PROBLEMS ABOUT THE CORTICAL REINFORCEMENT BY AMMONIUM OXALATE OF CARBONATIC MATERIALS WITH DIFFERENT MICROSTRUCTURES

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ABSTRACT

Limestone is the most common used material for the realization of artefacts and monuments. Unfortunately this tipe of stone is particularly vulnerable to environmental hazards especially those produced by anthropic pollution. This paper presents the results of an investigation on cortical reinforcement of carbonate stones with different fabric and specific surface area by means of $(\text{NH}_4)_2\text{C}_2\text{O}_2$ (AmOx). The kinetics of the reaction between AmOx and CaCO_3 has been studied in a batch reactor, in order to evaluate the relative availability of Ca^{++} for the reaction. The same kinetics and the physical modification induced by AmOx treatment were also investigated for bulk limestone as fresh and naturally weathered marble. The results have pointed out the critical dependence of the reaction rate between AmOx and CaCO_3 from the specific surface area of carbonate matrices. Whewellite is the only oxalate formed through a mechanism substantially topochemical. On the surface of compact carbonate materials only low thickness of coating can be formed, while in the case of weathered limestone characterized by flaws, voids, weak granular cohesion and micropitting, the treatment results in a more marked reaction rate as emphasized by instrumental investigations.

INTRODUCTION

The cortical reinforcement of carbonate stones is one of the most investigated topics in which the international research concerning the monument conservation is actually engaged.

Many problems regarding the decay of these materials come from their intrinsic vulnerability to many aggressive agents of acid nature, like pollutants and acid rains.

In the case of materials subjected to mechanical stresses, the conservative interventions are often finalized to the structural consolidation; the carbonate stones mainly used in artefacts as statuary are principally marbles (or in any case rocks rather compact) whose conservation is critically related to the material-environment interface.

In the first case the reinforcement involves the bulk of the structure, while in the latter may be

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sufficient to ameliorate the characteristics of a thin cortical thickness. A compatible surface treatment requires: no chromatic or optical modification; a uniform absorption of the consolidation product as deeply as possible; no interruption between the deteriorated parts and sound ones that could cause the formation of superficial crusts easily detachable; minimization of the difference of linear thermal expansion coefficient between the parts reached by the treatment and those untreated in order to avoid stresses produced by thermal and thermo-hygrometric cycles.

These requirements have guided the restores to use inorganic chemical products or hybrid as TEOS. This product is far and widely employed also in the consolidation of carbonates slightly marly (impure limestone) or pure and unpatterned white marbles.

The effectiveness of these treatments, coming from hydrolysis, polycondensation and drying [1-2], with a final formation of xerogel, can be related to the critical size of grains and defects that must be stabilized and minimized. Some experiments carried out with TEOS on carbonate crystalline matrices with different specific surface area have shown that this later property is the critical factor in modulating the filming capability of the xerogel. The TEOS treatment on marble grains in the range 150÷200 μm did not show effective because of its defragmentation in flakes excessively brittle and uncooperative [3].

For the treatment on marbles, in particular those used in statuary of artistic significance, the passivating effect generated by $(\text{NH}_4)_2\text{C}_2\text{O}_4$ is well-known. This inorganic chemical compound in fact, reacts with calcium to produce calcium oxalate hydrates particularly resistant to environmental aggressive agents [4]. Such calcium oxalates create a quite dense superficial covering, whose thickness is in the range of 600÷800 μm . In the most cases this treatment has been considered as passivating. In the case of marble finely inlaid, where the surface requiring reinforcement can be submillimetric, the treatment can produce an aggregating effect that improves the physical and mechanical characteristics of the interfaces.

The very low solubility of calcium oxalate in a large pH range makes this treatment very attractive; the scientific community is nowadays busy to synthesize nanostructured oxalate in order to improve its effectiveness and penetrability into matrices of low porosity.

In this paper we present the results of a study on the reaction Ca-AmOx for some carbonate matrices ground at different fineness investigating on the kinetics and nature of the formed hydrates (batch reaction in stagnant flow).

Similar experiments have been carried out on prismatic-shaped blocks of fresh and naturally weathered marbles.

EXPERIMENTAL

a) Materials

The different samples of carbonate materials with identification codes and the main compositional characteristics are summarized as following:

CC: analytical grade and fine grain sized calcium carbonate;

MN: calcium carbonate obtained by grinding and micronization of a high-pure marble ($\text{CaO} > 56\%$; $\text{LOI} = 44\%$);

MI: calcium carbonate obtained by grinding and micronization of a marble ($\text{CaO} > 56\%$; $\text{LOI} = 44\%$) aged for over 100 years outdoor;

C: calcium carbonate obtained by grinding and micronization of a carbonatic mudstone with high porosity ($\text{CaO} > 49,6\%$; $\text{LOI} = 41,5\%$);

PF: calcium carbonate obtained by grinding and micronization of a compact boundstone ($\text{CaO} > 56\%$; $\text{LOI} = 44\%$), the so-called "Pietra Forte of Cagliari".

b) Methods

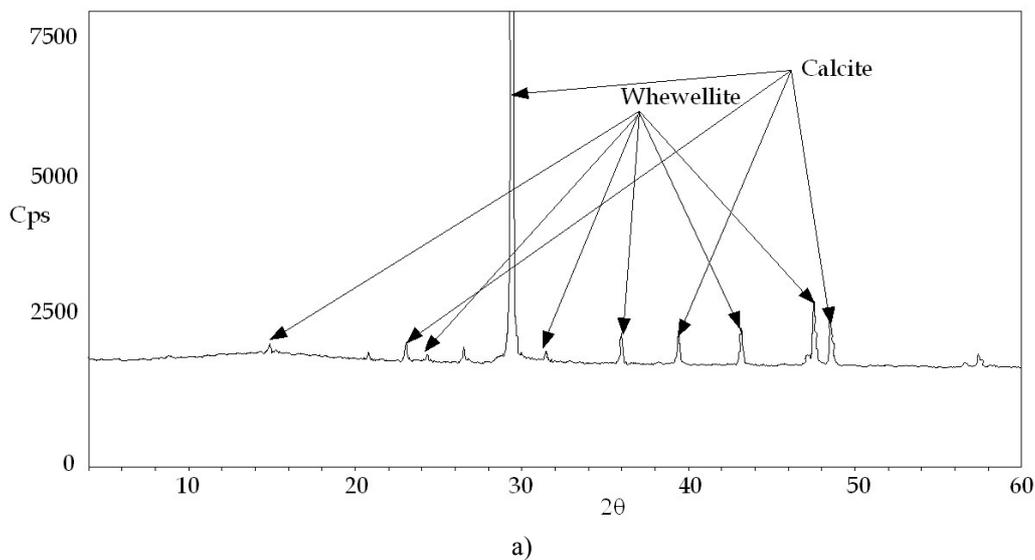
The carbonate materials were ground by ceramic ball mill and two size classes, $< 63 \mu\text{m}$ and $125\div 250 \mu\text{m}$, were selected for the experiments. The powders were put in contact until 144 hours with an aqueous solution containing 4% by weight of AmOx. The reaction was followed by means of weight variations and thermal analysis TG-DTA, using an apparatus Stanton STA-780 Series. The nature of the crystalline phases formed after the reaction was also detected by means of XRD technique, using a Rigaku Geigerflex powder diffractometer operating at 30 kV, 30 mA using $\text{CuK}\alpha$ radiation. The reaction products on the surface of the samples were observed by SEM analysis.

On 13 prismatic-shaped blocks $2\times 2\times 8$ cm of marble with flattened and smoothed faces P-wave velocities were measured using a Pundit equipped with two transducers (a transmitter and a receiver) having a frequency of 150 kHz in order to evaluate the difference induced by the treatment.

RESULTS & DISCUSSION

Whewellite proved to be the only reaction product between carbonate and AmOx.

In figure 1 X-Ray diffraction patterns of different size classes for weathered marble maintained 144 hours in contact with the solution are depicted. We can see the critical role exerted by specific surface area of the particles. In fact only in the powder under $63 \mu\text{m}$ whewellite peaks are clearly evident while in the coarser one they are very weak.



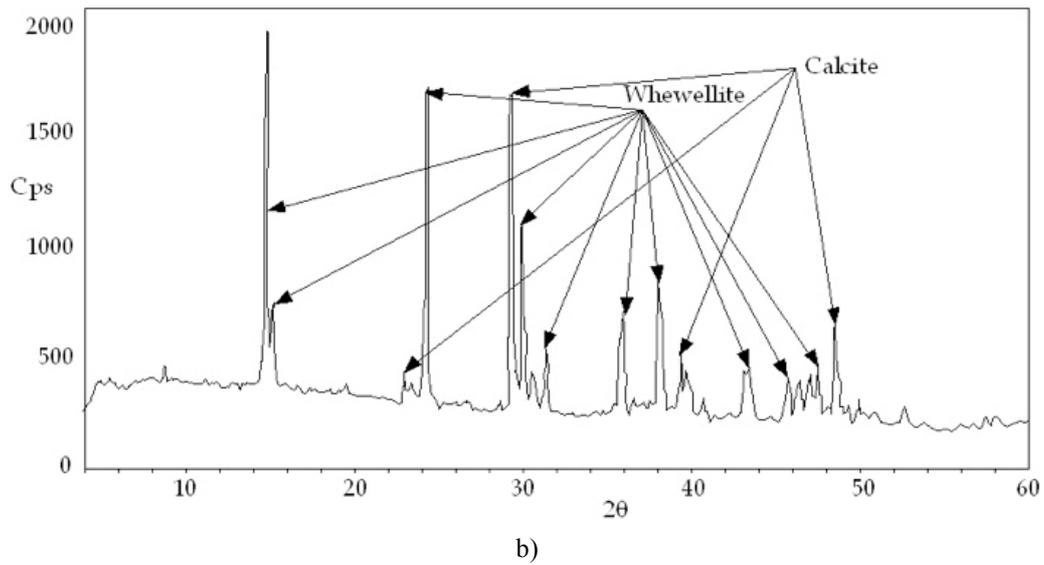
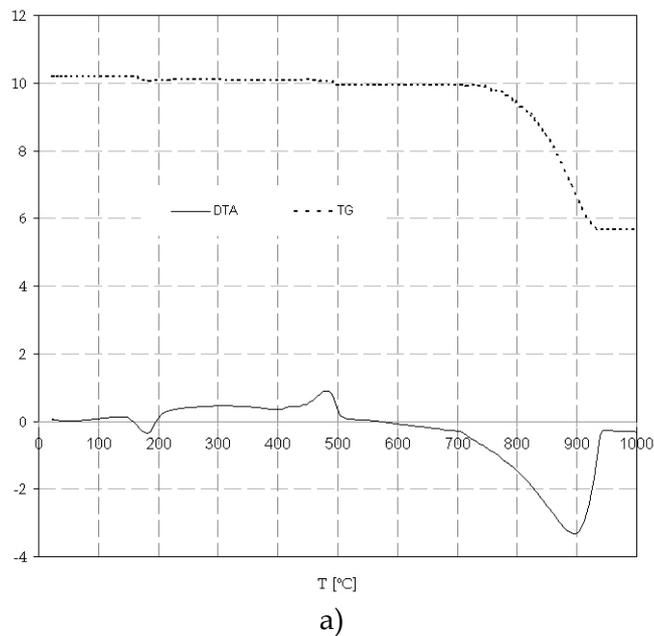
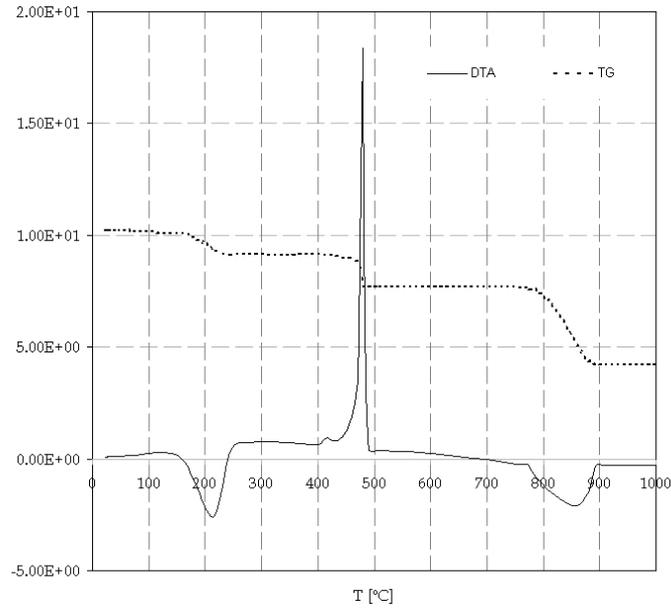


Figure 1: XRD pattern of weathered marble treated with AmOx for 144 hours:
 a) size class 125÷250 μm
 b) size class <math><63 \mu\text{m}</math>

Quantitative data of the reaction rate can be obtained only through thermal weight measurements investigating about the thermal transition in the relative temperature interval. Figure 2 shows two thermograms of weathered marble after 144 hours of contact with the AmOx solution.





b)

Figure 2: DTA pattern of weathered marble treated with AmOx for 144 hours:

a) size class 125÷250 μm

b) size class <63 μm

The results of the elaboration of TG measurements for two different contact time among the carbonate stones at different size class and AmOx are given in Table 1.

The reactivity of the different carbonate matrices has been evaluated considering the whewellite ($\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$) as the only product of the contact as confirmed by XRD analysis, Figure 1.

Table 1: Whewellite formation [mol %] as reaction product between calcium carbonate and AmOx

Specimens	Size class [μm]	Whewellite [mol%]	
		24 hours	144 hours
Pure CaCO_3	< 63	85	89
Unweathered Marble	< 63	52	75
	125/250	2	4
Weathered Marble	< 63	52	76
	125/250	1	4
Mudstone	< 63	55	65
	125/250	30	35
Boundstone "Pietra Forte"	< 63	50	67
	125/250	2	4

As can be observed pure carbonate (CC) exhibits the better reactivity with over 85% moles formed after 24 hours of contact with AmOx solution. The percentage of whewellite formed in the other

samples under 63 μm is lower. It can be seen that, already after 24 hours, the specific surface area plays a fundamental role in the reactivity of the material.

Apart from the carbonate mudstone, the 125÷250 μm size class is practically inert, with whewellite formation always under 5%, as result of a topochemical character of the $\text{CaCO}_3\text{-AmOx}$ reaction.

Figure 3 shows a SEM image for the weathered marble where grain size, large boundary grains and micropitting forms are well highlighted.

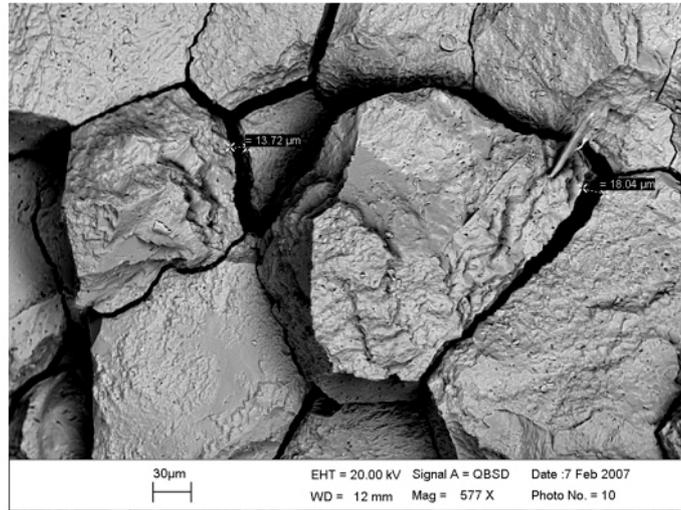


Figure 3: SEM image of weathered marble with large boundary grains and pitting corrosion

The carbonate mudstone is depicted in the SEM image reported in Figure 4; in this case the grain size is very small (about 2-4 μm). This particular fabric composed by clusters with high specific surface and porosity, explains the strong progressive reaction; in fact already after 24 hours and also in the 125÷250 μm size class the formation of whewellite reaches about 30%.

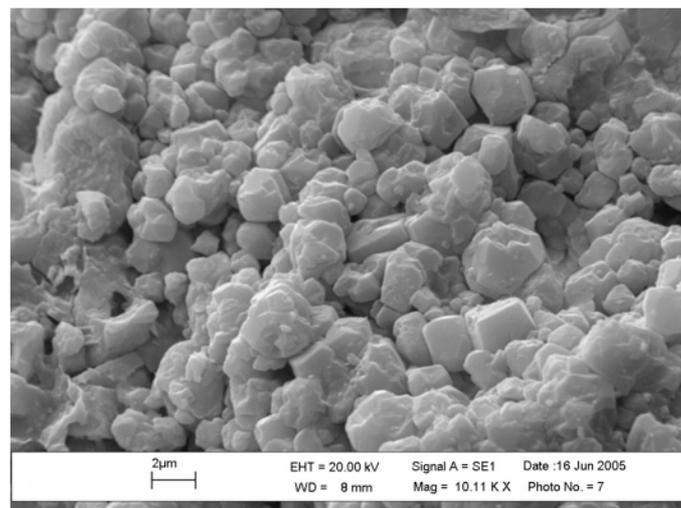


Figure 4: SEM image of carbonatic mudstone

The results obtained for the prismatic samples of bulk marble in contact with the AmOx solution

for different times show always small percentages of whewellite; however the mole fraction of whewellite for naturally weathered marble, per unity of exposed surface area, is double if compared to the unweathered one after a contact time with AmOx of about three months. In this case whewellite forms not only on the surface but also within the grain boundaries that appear rather enlarged following the long lasting environmental exposure of the material, Figure 5.

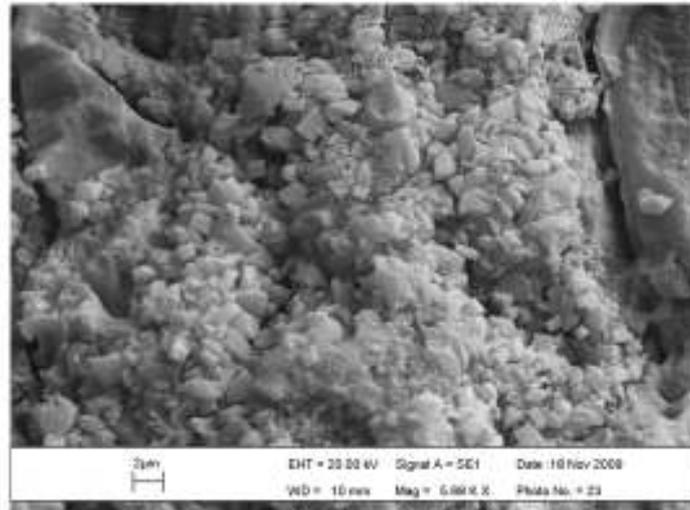


Figure 5: SEM image of weathered marble treated with AmOx for 144 hours

In Table 2 the results of P-wave velocities on prismatic-shaped blocks of untreated and treated marble for different contact time are reported. We can observe an increase in P- wave velocity changing from 36% to 50% of its initial value.

Table 2: Ultrasonic velocities for untreated and treated marble

Specimens	Vp [m/s] Not Treated (NT)	Vp [m/s] Treated (TR)	
		24 hours	144 hours
Unweathered Marble	5344 ± 238	5147±251	5000±10
Weathered Marble	2330 ± 238 188	3175± 275	3478± 120

CONCLUSIONS

On the base of these results the following conclusions can be summarized.

The only oxalate hydrate formed is whewellite.

The mechanism of the reaction between CaCO₃ and AmOx and the formation of calcium oxalate has an essentially topochemical character.

A critical role is exerted by specific surface area of material. In a compact material, as in marbles used in statuary, the superficial covering of the substratum is very thin; however the presence of defects as fissures or micro-fractures in weathered marbles increases the contact surface with reactant products so positively influencing the effectiveness of the treatment that can be considered not merely passivating but also moderately consolidating.

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