First results on diethyl oxalate as a new product for the conservation of carbonatic substrates

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1. Introduction

Recently several studies have been carried out concerning the evaluation of the penetration depth and diffusion of conservation products, mainly consolidants, inside the stone substrates, an important topic in conservation science, using advanced analytical techniques combined with traditional analyses [Horie V., 2005; Casadio F., Toniolo L., 2004].

In particular, a special attention has been paid to the ammonium oxalate $(NH_4)2C_2O_4$, a treatment increasingly and widely used for some years to protect carbonatic surfaces. The ammonium oxalate water solution induces the transformation of calcium carbonate to calcium oxalate, a substance characterized by a very low solubility both in water and acidic solutions thus providing a better resistance to decay phenomena of carbonatic stones. At present the ammonium oxalate treatment could to be preferred, as a protecting agent, to organic products because of good durability and high compatibility of calcium oxalate with the carbonatic surface [Conti C., Colombo C., Matteini M., Realini M., Zerbi G., 2010].

In the perspective of extending the use of the ammonium oxalate treatment to consolidating goals, we are facing with the drawback of its relatively scarce penetration depth inside the plasters or stones. In fact, µRaman mapping on polished cross sections allowed to reveal that the penetration depth achieved by ammonium oxalate in plaster specimens is at most approximately 700 µm.4 The ionic interaction between the salt and the carbonatic matrix could hinders the penetration of the oxalate ions into the inner portion of the substrate5 therefore the consolidant action of this treatment would be limited only to the first few hundred microns, an insufficient depth. This finding brought the authors to test a new mechanism of calcium oxalate crystallization into the carbonatic substrates, trying to develop a treatment based on diethyl oxalate $(C_2H_5)2C_2O_4$, an organic liquid, thus separating the penetration phase from the consolidating phase. In neutral conditions the hydrolysis mechanism of this molecule should avoiding the ionic interaction during its penetration. Probably, in spite of the its less hydrophilic nature, diethyl oxalate should achieve a better penetration depth compared with that of ammonium oxalate for its slower hydrolyses and lower interaction with hydrophilic substrate such as in the case of the widely employed TEOS[6]. The consolidation action of diethyl
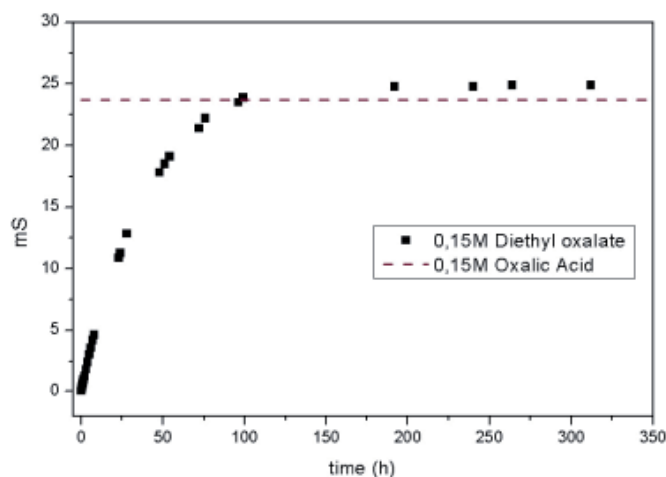
Fig.1 - conductivity of a 0.15M diethyl oxalate water solution in function of time. Time zero means the time of mixing. The conductivity of a 0.15M oxalic acid solution is reported as reference (dashed line)

oxalate should have the same chemical affinity with the substrate because the final product is the same as that obtained with ammonium oxalate: i.e. calcium oxalate. In this study preliminary findings obtained with X-Ray diffraction, conductometric analysis, Raman and Infrared spectroscopies are shown; in particular the kinetics and the mechanism of the hydrolysis of diethyl oxalate have been monitored as well as the interaction between a diethyl oxalate aqueous solution and calcite crystals has been reported and discussed.

2. Experimental
2.1. Raman spectroscopy
Raman experiments were carried out with a Bruker Senterra dispersive μ-Raman spectrometer coupled to an Olympus BX51 microscope with 20x, 50x and 100x objectives in light and dark field. Exciting line used is 785 nm (100 mW), with a Peltier cooled CCD detector (1024 X 256 pixels) and 1200 grooves/mm grating.
Measurements have been carried out on powders spread on an aluminium sample holder, using 20X objective, 3-5 cm^{-1} of spectral resolution, exposure time 40s, 3 accumulations, a maximum of 100 mW laser power at the sample in the 100-3600 cm^{-1} range.

2.2. Infrared spectroscopy
Infrared measurements have been carried out with a Bruker Vertex 70 bench equipped with single reflection ATR microsampler MVP-PRO (Harrick Scientific prodict Inc.). The detector was a liquid nitrogen cooled MCT. Measurements have been recorded in the spectral range from 400 to 4000 cm^{-1}.

2.3. Conductivity measurements
Conductivity measurements were performed using a YSI model 32 conductimeter equipped with a YSI model 3403 conductivity cell. The conductivity of a 0.15M diethyl oxalate water solution was monitored by acquiring conductivity data with regular and increasing time intervals.

2.4. Optical microscopy
The newly-formed phases formed after the reaction of calcite powder with diethyl oxalate were observed in reflected light using a Leitz Ortholux microscope with Ultropack illuminator equipped with a digital image capturing system.

2.5. X-Ray diffraction
A Panalytical X'Pert PRO X-Ray powder diffractometer (XRPD) was used to study the newly-formed phases formed after the reaction of calcite powder with diethyl oxalate. The instrument is equipped with a X'Celetator detector PW3015/20 and diffraction patterns have been collected from 5° to 60° 2J, scan speed 0.21°/sec, with a CuKa-radiation source, working conditions 40kV and 40mA. Powdered samples have been spread on an amorphous silicon holder and then analysed.

2.6. Analytical procedure
The hydrolysis reaction of diethyl oxalate was monitored analysing the behaviour over time of a solution of diethyl oxalate (Sigma Aldrich, purity ≥99%) 3% v/v in water. FTIR spectra were acquired every 6 hours for 4 days. Conductivity data were recorded at the time of the mixture of water with diethyl oxalate and with regular and increasing time intervals up to thirteen days. The hydrolysis of this molecule should theoretically provide the formation of ethanol (C_2H_5OH) and oxalic acid ($H_2C_2O_4$); for this reason conductivity of a 0.15 M oxalic acid water solution was measured as a reference.

As a further step, the reaction between diethyl oxalate and a marble powder has been studied in order to check the newly crystalline phases formed. Therefore, a stoichiometric amount of marble powder has been added to a solution of diethyl oxalate (3% v/v in water). Raman spectra have been acquired after 7 days on the dried reacted powders.

3. Results and discussion
During the hydrolysis of diethyl oxalate the conductivity measurements show an increasing and linear trend for approximately the first 50 hours; at about 100 hours a plateau is reached (Fig.1). The achievement of the plateau indicates that the hydrolysis reaction is over. With the aim to verify that all the oxalic acid has been developed from the hydrolysis, the conductivity of an oxalic acid solution with the same molarity of that of diethyl oxalate was measured. The conductivity values of the oxalic acid solution are very similar to those of diethyl oxalate after 100 hours (Fig.1). This could indicate that after 100 hours all the diethyl oxalate is hydrolyzed into oxalic acid and ethanol.

The behaviour of diethyl oxalate in water has been also followed by means of FT-IR spectroscopy for 96 hours in order to obtain more information about its hydrolysis mechanism. In figure 2, spectra of pure mono and diethyl oxalate are reported, while in figure 3 the spectra of the solutions in water of the diethyl oxalate at different hydrolysis times are reported and compared with the spectrum of monoethyl oxalate and ethylic alchol in the spectral range from 1400 to
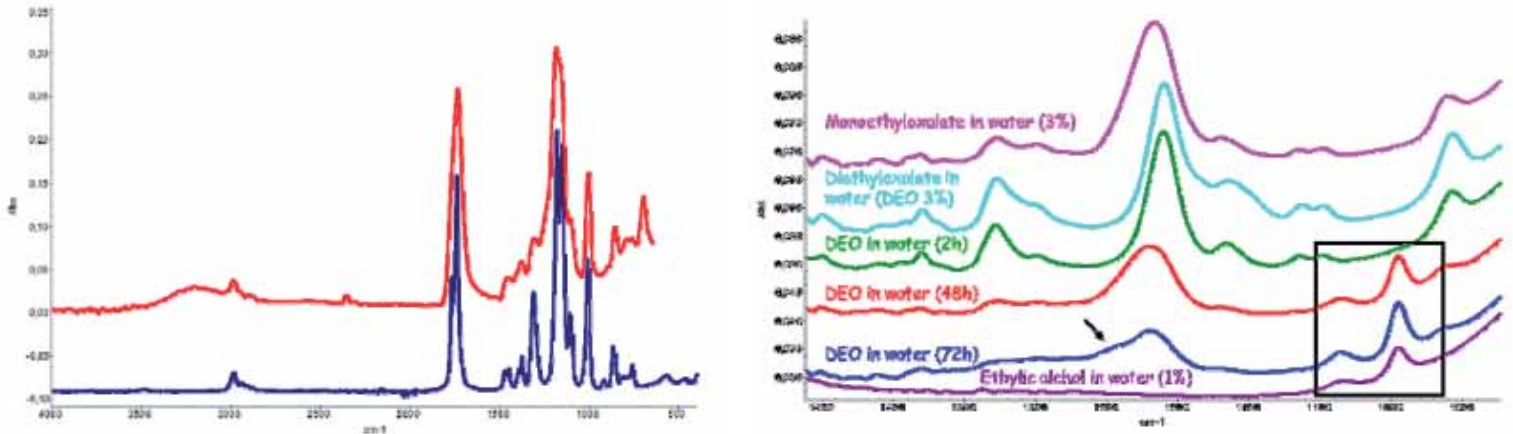
Fig.2 - FTIR spectra of pure mono (red line) and diethyl oxalate (blue line); Fig.3 - FTIR spectra of monoethyl oxalate (violet line), diethyl oxalate (light blue line) and ethylic alchol (purple line) in water solution. The other spectra are related to diethyl oxalate after 2 (green line), 48 (red line) and 72 (blue line) hours. Black box highlights alcoholic bands while the arrow shows the formation of the new band at 1243 cm^{-1}

900 cm^{-1}. FT-IR measurements in water are strongly affected, as predictable, by the water bands; nevertheless it has been possible to follow the behaviour of some weak bands related to the involved compounds. The beginning of hydrolysis in water of mono and diethyl oxalate seems to be immediate (typical bands of the pure compounds disappear) but the reaction does not seems to lead directly to the complete formation of alcohol and oxalic acid: after few minutes the spectra of the two solutions (mono and diethyl oxalate) show very similar pattern with only a slight difference of the band at 1210 cm^{-1} that in the case of monoethyl oxalate appears at higher wavenumbers (1218 cm^{-1}); nevertheless the presence of unreacted diethyl oxalate cannot be excluded for instrumental and methodological limits in the water measurements. After 48h, signals of alcoholic absorptions grow (approximately at 1045 and 1085 cm^{-1}), since the hydrolysis proceeds, while signal at 1210 cm^{-1} of diethyl oxalate slightly decrease, broaden and shifted through higher wavenumbers. After 72h the solution of diethyl oxalate seems to reach a final equilibrium where all the bands, except for alcoholic ones and the band at 1210 cm^{-1}, are just perceivable and there is the appearing of a clear shoulder signal around 1243

Fig.4 - Raman spectrum ascribed to caoxite acquired on the calcite powder reacted with diethyl oxalate solution; Fig.5 - XRD spectra of the calcite powder reacted with diethyl oxalate solution: caoxite (c) with Miller indices calculated from ICSD (1997), weddellite (D) and whewellite (M)
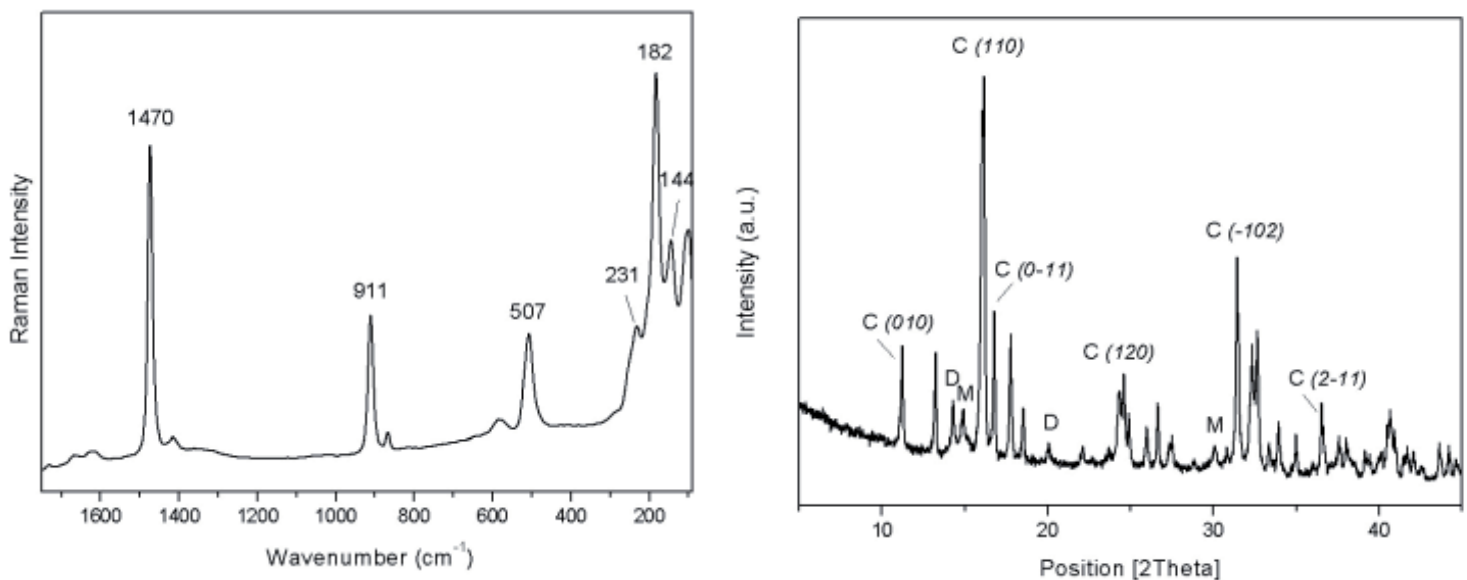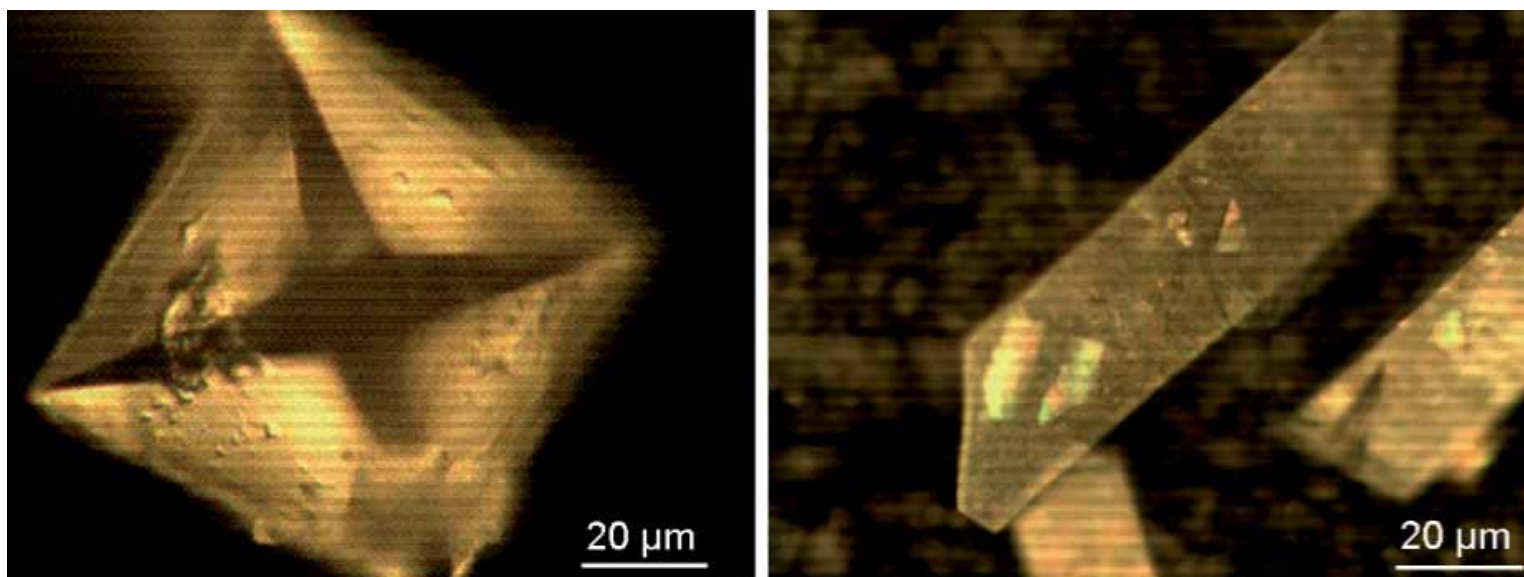
Fig.6 - Optical microscope images of weddellite (left) and whewellite (right) crystals formed after the reaction of calcite powder with diethyl oxalate solution

cm^{-1}. This signal cannot be easily assigned; it can be probably related to the formation of complex water ions in which, at the moment, the contribution of mono (di) ethyloxalate, alchool and the oxalic acid is not clear.

The micro-Raman analysis of the reaction products between diethyl oxalate and marble powder shows the predominant presence of calcite. Therefore, the calcite did not completely reacted. With respect to calcium oxalates whewellite, weddellite and caoxite have been detected. Whewellite and weddellite are the most common forms of calcium oxalates, while caoxite is rarely observed in nature and it has never been detected as a reaction product of ammonium oxalate treatment [Conti C., Colombo C., Matteini M., Realini M., Zerbi G., 2010; Conti C., Colombo C., Dellasega D., Matteini M., Realini M., Zerbi G., 2011]. To the best of our knowledge no Raman spectra of caoxite were published so far. Raman spectrum shown in figure 4 has been ascribed to caoxite after the X-Ray diffraction analysis that revealed the characteristic pattern of this mineral (Fig.5). A sharp line at 1470 cm^{-1} can be obviously ascribed to the stretching vibrations of the O–C–O group of caoxite; in fact whewellite and weddellite show two lines at 1460 and 1475 cm^{-1}, respectively. Optical images of the formed crystals show the elongated and bipyramidal morphologies of whewellite and weddellite,7 respectively (Fig.6). Their size ranges from a few tens of microns to 100 µm.

4.Conclusions

The conductometric data support that, at ambient conditions, the hydrolysis of 0.15 M diethyl oxalate solution takes approximately 4 days. The slow rate of the hydrolysis reaction could favour the crystallization of calcium oxalates inside the material at higher depths compared to those achieved with ammonium oxalate.
Based on the first FTIR results the presence of a reaction intermediate has

been inferred. Further investigation is necessary to assess the hydrolysis mechanism of the diethyl oxalate; this may support the existence of a reaction intermediate, as for instance the monoethyl oxalic acid, which may play a relevant role when it reacts with the carbonatic substrate.

The analyses of the reaction products formed after the reaction between diethyl oxalate and calcite revealed the unexpected occurrence of caoxite, in addition to whewellite and weddellite. The mineralogical fraction of the material has received a sound support from XRD experiments. A new optical evidence of caoxite is given by its Raman spectrum.

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