

## Conference paper

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# Chelators confined into 80pvac-borax highly viscous dispersions for the removal of gypsum degradation layers

DOI 10.1515/pac-2016-0815

**Abstract:** In this paper a new method for the removal of gypsum degradation layers from carbonatic matrices in cultural heritage conservation, using aqueous Highly Viscous Polymeric Dispersions (HVPDs) based on partially hydrolyzed poly(vinyl acetate) and borax, embedded with chelators, is presented. Due to their interesting viscoelasticity, these systems guarantee a good adhesion to the treated surface and easiness of removal in one step, minimizing the residues. Thus, they can potentially overcome the “residue question” limit associated to traditional methodologies that use thickened solutions of chelators. Here the rheological properties of HVPDs containing different amounts of selected chelating agents are explored and their efficacy in the extraction of gypsum is verified through cleaning tests onto artificially sulfated travertine tiles. The homogeneous removal of gypsum across the surface was checked non-invasively via Fourier Transform Infrared Spectroscopy (FTIR) 2D Imaging. An analytical protocol for the pre-treatment and the analysis of HVPD samples by means of Ion Chromatography (IC) and Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) was set up and the approximate amount of calcium sulfate removed was determined.

**Keywords:** chelates; desulphatisation; gypsum layers; poly vinyl alcohol-borax; viscoelasticity.

## Introduction

Since ancient times, limestones have been used as base material for artworks, statues and mural paintings, constituting the larger part of our cultural heritage for many centuries.

A common degradation that affects artifacts made of natural or artificial carbonatic materials is the sulphatisation, the transformation of calcium carbonate in calcium sulfate dihydrate (gypsum) due mainly to the interaction with the atmospheric sulfur dioxide in the presence of humidity and oxidation catalysts [1]. The elementary cell of gypsum occupies almost a double volume compared to that of calcium carbonate. In the case of carbonatic supports, when this reaction takes place and new crystals of gypsum form inside the porous structure, the consequent volume expansion determine mechanical stresses that cause cracking,

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**Article note:** A collection of invited papers based on presentations at the 16th International Conference on Polymers and Organic Chemistry (POC-16), Hersonissos (near Heraklion), Crete, Greece, 13–16 June 2016.

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fissuring and pulverization of the carbonatic matrix [2]. In particular, for frescoes, when the phenomenon is particularly severe, we observe lifting and detachment of the paint layer, with loss of decoration and pigments [3].

One of the most effective traditional treatments for the gypsum removal from carbonatic supports is the Ferroni-Dini method [4], developed in 1966 by Enzo Ferroni, chemistry professor at the University of Florence, and Dino Dini, headmaster in the restoration of frescoes. It's a two-phases treatment consisting in the solubilization of gypsum with a water solution of  $(\text{NH}_4)_2\text{CO}_3$  (ammonium carbonate) followed by the application of barium hydroxide that ensures the consolidation of the degraded matrix and at the same time makes the sulfate unreactive and insoluble [5–7].

An alternative, widely used technique for the removal of soluble salts and, in particular, of calcium sulfate from frescoes, mural paintings and plasters consists in the use of ion-exchanger resins [8, 9]. Generally they are synthetic resins that swell when in contact with water and are completely insoluble in it [10]. Due to this feature, when ion-exchangers are in contact with an artwork contaminated by salts, their action is limited to the surface up to a depth of about 70–100  $\mu\text{m}$ , without penetrating into the porosity of the object, thus avoiding the interaction with the original materials to preserve [11].

Other substances used by restorers to treat the efflorescences are chelators. The most diffused are disodium EDTA, Rochelle salt (especially for the cleaning of gilded bronzes because of its mild action that preserve the original gilded foil [12]), citrate salts and benzotriazole [13–17]. Usually they are applied in aqueous solution (1–5 % of additive) [18]. The solution pH has a fundamental role for the dissociation equilibria of the chelator and its selectivity towards different ions.

A potential risk in the use of these substances, is that calcium ions coming from the carbonate matrix could be solubilized as well. To limit the penetration of the cleaning agent into the inner layers and to avoid the solubilization of the original material constituting the plaster and the paint layer, chelators aqueous solutions are usually adsorbed into poultices of carboxymethylcellulose or gelled with a thickener as Klucel G [19, 20] or Carbopol [6].

The main drawback of these applicative methods is the “residue question” [21], as the thickened systems release residues onto the treated surface. The necessity of a clearance step with a neat liquid (generally water) and/or extra mechanical action can be critical in presence of fragile or hydrophilic surfaces/materials.

At the Chemistry Department of the University of Florence and CSGI Consortium, innovative peelable poly(vinyl) acetate (PVAc)-borax based Highly Viscous Polymeric Dispersions (HVPDs) for cleaning artistic surfaces were developed and studied [22].

The viscoelastic and cleaning/removing properties of the HVPDs can be modulated by varying the entanglements density of the network [23, 24] and/or the polarity of the continuous phase by incorporating different organic solvents [25–27]. Their high elastic modulus and viscosity allow the minimization of the residues left onto the treated surface and of the penetration of the cleaning agent into the porous matrix of the artwork. The first applicative tests on canvas and wood paintings [22, 28] resulted in a controllable, gradual, selective cleaning action.

Recently, considering the great versatility of these HVPDs, the capability of embedding chelators was explored. This achievement could extend the application field of these systems to mural paintings and metal surfaces, both frequently affected by the presence of foreign patinas like salt efflorescences and corrosions/oxidation deposits, respectively. In fact, it must be noted that this class of HVPDs has a broad range of potential applications that include the cleaning of both classic and modern artifacts (easel/mural paintings, graffiti, metallic and plastic objects), therefore their current implementation will highly benefit from studies concerning their characterization and effectiveness.

In this work three chelating species were selected: disodium EDTA,  $(\text{NH}_4)_2\text{CO}_3$  and sodium/potassium tartrate. The maximum loadable amount of each, before observing phase separation, was determined. The viscoelastic properties of HVPDs containing different amounts of chelator were investigated to study how the additive influence their elastic response.

To evaluate the efficacy in the removal of calcium sulfate, these HVPDs embedded with chelators were tested onto artificially sulfated travertine tiles. The qualitative, non-invasive evaluation of the cleaning

treatment was carried out through FTIR 2D Imaging, in order to estimate the homogeneousness of the removal of gypsum across the treated surface. HVPD samples collected after the cleaning tests were analyzed through Ion Chromatography and Inductively Coupled Plasma techniques. The quantification of the gypsum extracted was possible thanks to the set-up of an analytical protocol for the pre-treatment and the analysis of samples that was suitable for IC/ICP.

## Materials and methods

Eighty percent hydrolyzed poly(vinyl acetate) was supplied by Kuraray Co., Ltd. as random copolymer ( $M_w = 47\,300$ ) and was used as received. Sodium tetraborate decahydrate (99, 5–100 %, Sigma-Aldrich),  $(\text{NH}_4)_2\text{CO}_3$  (Sigma-Aldrich), disodium EDTA dihydrate (99–100 %, ACS reagent, Sigma-Aldrich), potassium sodium tartrate tetrahydrate (99 %, ACS reagent, Sigma-Aldrich), ammonium hydroxide (Sigma,  $\text{NH}_3$  content 28–30 %), hydrochloric acid 37 % (CARLO ERBA, min. assay 36.5 %) and sulphuric acid 96 % ( $96 \pm 1$  %, CARLO ERBA) were used as received. Water was purified by a Millipore Elix3 apparatus ( $R \geq 15 \text{ M}\Omega \text{ cm}$ ).

## Preparation of the polymeric dispersions

The PVAc was dissolved in a water solution of the chelating agent; then a solution of borax was added and the system was stirred with a VORTEX apparatus until it became rigid in few minutes. The polymer/borax weight ratio was kept to 4 : 1. The pH of all the systems was adjusted in order to warrantee the maximum complexation ability. All the measurements and cleaning tests were carried out 1 week after the samples preparation to ensure their equilibration.

## Travertine samples sulfation

The sulfation of the travertine tiles was inducted by soaking one of their surface ( $4.8 \times 4.8 \text{ cm}$ ) into a 5 M  $\text{H}_2\text{SO}_4$  solution for 1 h. Then they were let dry until a constant weight was reached.

## Gravimetric determination of the calcium sulfate dihydrate formed onto the travertine samples

The average amount (g) of gypsum formed ( $W_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$ ) onto the travertine tiles was determined gravimetrically, according to the stoichiometric equilibrium of the sulfation reaction (1), using the formula (2):



$$W_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} = \frac{\Delta W \cdot MW_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}}{MW_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}} - MW_{\text{CaCO}_3}} \quad (2)$$

where  $\Delta W$  (g) is the difference between the final weight  $W_f$  (g) and the initial weight  $W_i$  (g) of the travertine tile after the sulfation,  $MW_{\text{CaSO}_4 \cdot 2\text{H}_2\text{O}}$  and  $MW_{\text{CaCO}_3}$  are the molecular weights of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  and  $\text{CaCO}_3$ , respectively. The total average amount of  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$  formed onto the travertine surface was 6.7 mg/cm<sup>2</sup>.

## Application of HVPDs embedded with chelators onto the sulfated travertine tiles

A weighed amount (1 g) of an HVPD containing the chelator was applied onto a confined area (2.28 cm<sup>2</sup>) of a sulfated travertine tile using a plastic ring, for different contact times: 5, 10, 20, 30, 60 min (Fig. 1). Each test



**Fig. 1:** Exemplifying images showing the four “60 min-long” applications of the HVPD containing EDTA onto the sulfated travertine tile (left) and the ease removal step (right) achieved by confining the HVPD into a plastic ring.

was repeated at least four times. HVPD samples were weighed before and after each application to determine the weight loss. For samples containing  $(\text{NH}_4)_2\text{CO}_3$  or Rochelle salt, additional applications lasting 1080 and 1380 min were performed.

## Rheological measurements

Oscillatory shear measurements were performed with a Paar Physica UDS200 rheometer working at  $25 \pm 0.1$  °C (Peltier temperature control system) using cone-plate geometry (25 mm diameter and  $1^\circ$  cone angle). The gap between the plates was 0.5 mm. After being loaded, samples were equilibrated for 30 min at 25 °C prior to start the experiments. Frequency sweep measurements were done in the linear viscoelastic region (2–3% strain) based on an amplitude sweep test. The storage modulus  $G'$  (Pa) and the loss modulus  $G''$  (Pa) were measured over the frequency range 0.001–100 Hz. The intrinsic elastic modulus  $G_0$  (Pa), represented by the asymptotic value of the elastic shear modulus  $G'$  was calculated as the average value of the last five  $G'$  points in the *plateau* region of the flow curves.

## Ion Chromatography (IC)

IC analyses were performed with a Dionex ICS-90 Ion Chromatography System, using a Dionex AG4A guard-column (4 mm diameter, 5 cm length) and a Dionex AS4A column (4 mm diameter, 20 cm length). The eluent was a buffer solution with  $\text{Na}_2\text{CO}_3$  (1.8 mM) and  $\text{NaHCO}_3$  (1.8 mM) in MilliQ water (1.65 mL/min flow). A 10 mM  $\text{H}_2\text{SO}_4$  solution was used as the regeneration fluid for the conductivity suppressor (3.36 mL/min flow). The injection loop was 25  $\mu\text{L}$ .

## Inductively coupled plasma optical emission spectrometry (ICP-OES)

ICP analyses were performed using a Varian 720-ES ICP-OES spectrometer with an optical detector. The external, auxiliary, and nebulizer flows were 16.5, 1.50, and 0.75 L/min, respectively. A 50 ppm solution of Germanium was used as the internal standard to quantify the analyte of interest.

## 2D imaging-Fourier transform infrared (FTIR)

The 2D imaging-Fourier transform infrared (FTIR) analysis of the travertine tiles was carried out on a Cary 620–670 FTIR microscope, equipped with an FPA (Focal Plane Array)  $128 \times 128$  detector (Agilent Technolo-

gies). The spectra were recorded directly on the surface of the samples (or of the Au background) in Reflectance mode, with a spectral resolution of  $4\text{ cm}^{-1}$ , acquiring 128 scans for each spectrum. The spatial resolution of each Imaging map is  $5.5\text{ }\mu\text{m}$  (i.e. each pixel has dimensions of  $5.5 \times 5.5\text{ }\mu\text{m}^2$ ). Five measurements were carried out on each type of travertine sample (untreated, sulfated, sulfated and cleaned with a HVPD containing 0.5 wt% of  $(\text{NH}_4)_2\text{CO}_3$ ; four consecutive applications with a contact time of 60' each were carried out), and the representative spectra for each sample are shown in this contribution. In order to improve the readability of the spectra, the background noise was reduced using the “smooth” tool (set at 10) of the Igor Pro software, taking care not to alter any diagnostic information deemed useful to this qualitative investigation. In each 2D map, the intensity of the gypsum absorption at  $3570\text{ cm}^{-1}$  (OH stretching of water) was imaged as the area of the absorption peak between  $3692$  and  $3542\text{ cm}^{-1}$ . The chromatic scale of the maps shows increasing absorbance of the band as follows: green < yellow < red.

## Results and discussion

Being the use of monophasic systems an essential condition to control the cleaning action of the HVPDs, the maximum amount of EDTA, Rochelle salt and  $(\text{NH}_4)_2\text{CO}_3$  loadable in the 80PVAc-borax systems before observing phase separation was determined. The obtained values were 0.5 wt%, 1 wt% and 0.5 wt%, respectively.

In a previous paper it was observed that to warrant an adequate performance in terms of ease of application and complete removal through a peeling action [27], the HVPDs should preserve adequate elastic properties even upon addition of additives active against the foreign patinas of the artifacts. In particular their intrinsic elastic modulus  $G_0$  values should be always higher than 400 Pa. To verify if these features were preserved after the addition of chelators, the mechanical properties of the HVPDs set up were explored. Figure 2 shows that upon the addition of  $(\text{NH}_4)_2\text{CO}_3$  (A) or Rochelle salt (B), the mechanical behavior of the HVPDs is invariant for chelator concentrations, respectively up to 0.5 and 0.9 wt%. Figure 3 displays that a further increase of Rochelle salt concentration up to 1 wt% determines the formation of a gel (the shear elastic modulus  $G'$  is higher than the shear viscous modulus  $G''$  over the entire range of frequencies explored) [29].

The frequency sweeps of the HVPDs containing different amounts of  $(\text{NH}_4)_2\text{CO}_3$  or Rochelle salt normalized to the crossover point between the  $G'$  and the  $G''$  curves (Fig. 4) indicate that even if changes occur in the timescale of the relaxation process when the concentration of the chelator is increased, the mechanism associated with the relaxation remains almost the same.

Figure 5 shows the trends of the  $G_0$  values as a function of  $(\text{NH}_4)_2\text{CO}_3$  (A) and Rochelle salt (B) content; for concentrations around 0.3 wt% and 0.9 wt%, respectively, the salts addition has a structuring effect on the systems as indicated by the increase of their elasticity. In presence of a higher amount of additive, the lowering of  $G_0$  indicates a reduction of the entanglements density of the PVA network.

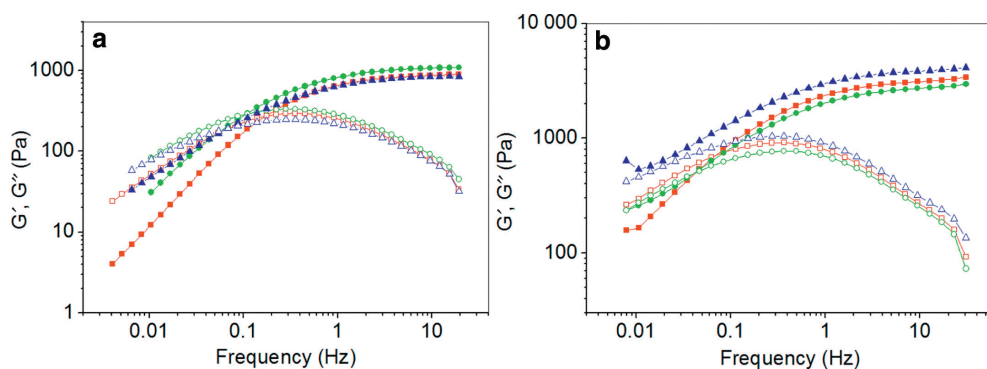
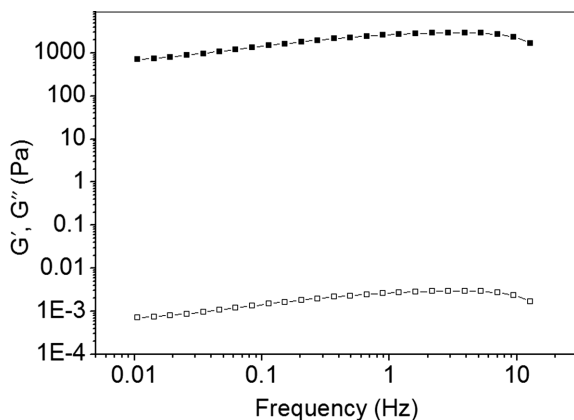
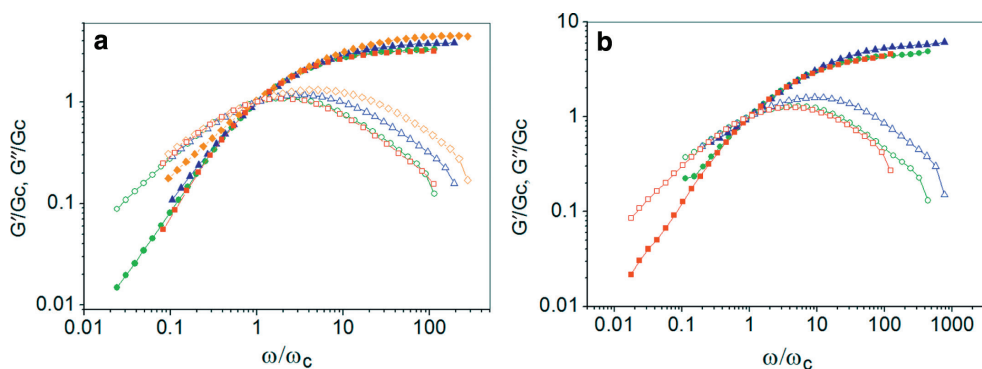


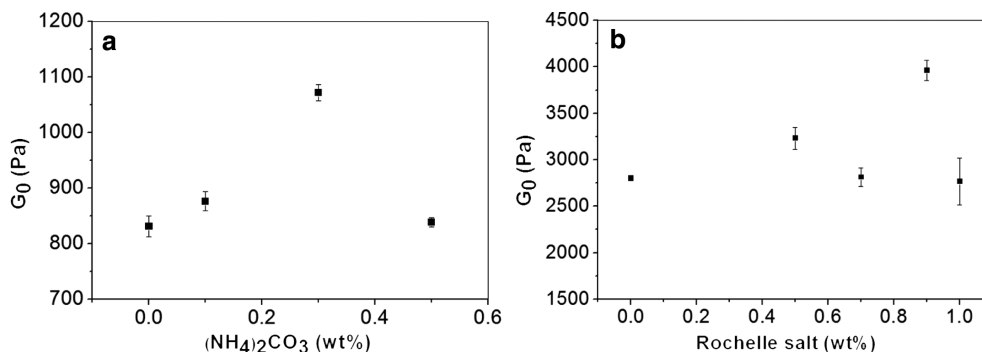
Fig. 2: Flow curves of the  $G'$  (●■▲) and  $G''$  moduli (○□△) for the HVPDs containing: (a) 0.1 wt% (■□), 0.3 wt% (●○), 0.5 wt% (▲△) of  $(\text{NH}_4)_2\text{CO}_3$ ; (b) 0.5 wt% (■□), 0.7 wt% (●○), 0.9 wt% (▲△) of Rochelle salt.



**Fig. 3:** Trend of  $G'$  (■) and  $G''$  moduli (□) for the HVPD sample with 1 wt% Rochelle salt, showing the rheological behavior typical of a gel ( $G' \gg G''$ ).



**Fig. 4:** Normalized mechanical histograms for the 80PVAc-borax with: (a) 0 wt% (■□), 0.1 wt% (●○), 0.3 wt% (▲△) and 0.5 wt% (◆◇) of  $(\text{NH}_4)_2\text{CO}_3$ ; (b) 0 wt% (■□), 0.5 wt% (●○) and 0.7 wt% (▲△) of Rochelle salt. Symbols ■●▲◆ indicate the  $G'/G_c$  ratios; symbols □○△◇ indicate the  $G''/G_c$  ratios.  $G_c$  (Pa) and  $\omega_c$  (Hz) are the coordinates of the crossover point.



**Fig. 5:** Intrinsic elastic modulus  $G_0$  of 80PVAc-borax HVPDs as a function of  $(\text{NH}_4)_2\text{CO}_3$  (a) and Rochelle salt (b) concentrations (wt%).

Finally, the addition of EDTA determines a significant increase in the intrinsic elasticity ( $G_0$ ) due to a structuring role of the salt. This behavior was ascribed to a combination of salt and pH effect, assuming that the EDTA tetra-anionic species  $Y^{4-}$  [30] ( $\sim 50\%$  at  $\text{pH} \sim 11$  as that of our EDTA-containing systems), mediates some cross-links between the hydroxyl groups of 80PVAc chains (Matarrese et al., paper submitted).

Even if traditional gel systems used for the conservation of artistic surfaces contain higher concentrations of chelators (1–5 wt%), the ones achievable with the 80PVAc-borax HVPDs, although significantly lower, were

expected to be still adequate for cleaning purposes. An auxiliary benefit of the lower chelator concentrations is that the cleaning action is more gradual and controllable, favoring the preservation of the original layers of the artifacts.

The HVPDs selected for the application tests on sulfated travertine tiles, contained 0.25 wt% EDTA (pH=11), 0.5 wt%  $(\text{NH}_4)_2\text{CO}_3$  and 1 wt% Rochelle salt, respectively (Table 1). The aim was to evaluate their efficacy in the gypsum patina removal as a function of both the additive type and the application time. To better confine the cleaning action, the systems were applied into plastic rings that ensured also a quick and easy removal step (Experimental Section, Fig. 1).

To verify the retentive capability of the HVPDs towards the liquid fraction confined into them once in contact with the porous matrixes, the HVPDs weight was monitored before and after each test. To eliminate the contribution due to the water evaporation, a “blank” adsorption was recorded by weighing a HVPD kept close to the samples on which the cleaning tests were carried out without being in contact with the porous matrix. The weight loss of the blank was subtracted to the one registered for the HVPDs applied onto the tiles [31]. The ratio between the water content before and after the test gives the Absorption Index (A.I.%):

$$\text{A.I.}\% = \frac{W_{Abs} - W_{Ref}}{W_i - W_{Ref}} \times 100 \quad (3)$$

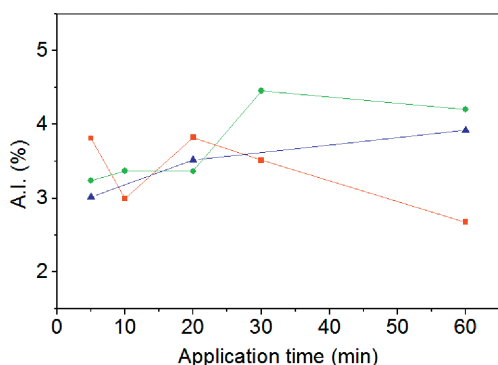
where  $W_{Abs}$  is the weight of the absorbed water,  $W_{Ref}$  is the weight of the evaporated water,  $W_i$  is the initial weight of the water in the HVPDs in contact with the travertine surface. Figure 6 shows the A.I.% as a function of the application times of the HVPDs containing the different chelators.

The weight loss undergone by the system due to the migration of the liquid fraction (water solution) into the porous structure of the stone resulted very low: around 4 % after 60 min of application for samples containing  $(\text{NH}_4)_2\text{CO}_3$  and Rochelle salt and around 3 % for those with EDTA. These data confirmed the very good retentive properties of the HVPDs, even when embedded with chelators.

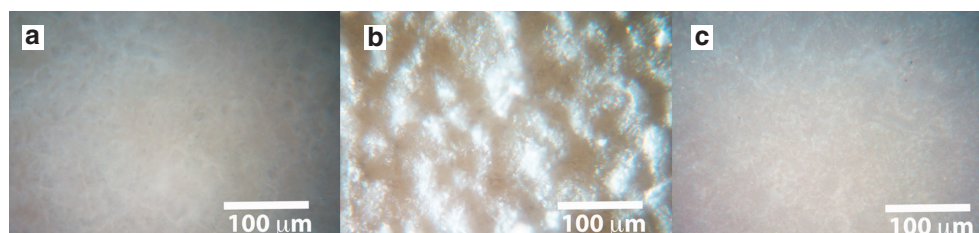
Optical micrographs (Fig. 7) of the sulfated travertine surfaces before (B) and after (C) the application of the HVPDs loaded with  $(\text{NH}_4)_2\text{CO}_3$  0.5 wt% (contact time 60') indicate that the system is effective in the superficial removal of the gypsum patina.

**Table 1:** Composition of the HVPDs used for the cleaning tests on sulfated travertine tiles.

HVPD	PVAc (wt%)	Borax (wt%)	Additive (wt%)	H <sub>2</sub> O (wt%)
System A	3 %	0.75 %	Disodium EDTA	0.25 %
			NH <sub>3</sub>	0.45 %
System B	3 %	0.75 %	$(\text{NH}_4)_2\text{CO}_3$	95.75 %
System C	4 %	1 %	Rochelle salt	94 %



**Fig. 6:** Absorption Index (%) as a function of the application time for the system containing 0.25 wt% EDTA (■), 0.5 wt%  $(\text{NH}_4)_2\text{CO}_3$  (●) and 1 wt% Rochelle salt (▲).



**Fig. 7:** Optical micrographs ( $20\times$  magnification) of the travertine surface before the sulfation treatment (a), the sulfated surface before (b) and after (c) the cleaning test with the HVPD containing 0.5 wt%  $(\text{NH}_4)_2\text{CO}_3$ .

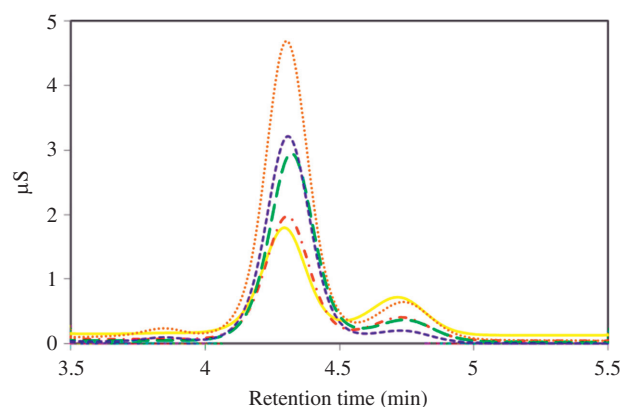
To quantitatively evaluate the amount of sulfates removed, IC analyses were performed and a measuring protocol for the preparation and the analyses of the samples was developed as follow.

Standard solutions for calibrations were freshly prepared in precleaned polyethylene vials by diluting a stock standard solution ( $1000 \text{ mg L}^{-1}$ ) purchased from Merck (Darmstadt, Germany). To take into account the matrix effect, a “blank” HVPD sample without the analyte of interest (the sulfate ion) was dissolved with HCl (37% mol), diluted 1:100 in MilliQ ultrapure water and added in each standard solution. The sample had previously been applied for 5 min onto a no-sulfated travertine tile, so that the standard solutions contained all the components present in the unknown samples except for the analyte of interest. Before being analyzed, the HVPD samples containing the extracted calcium sulfate dihydrate ( $\sim 1 \text{ g}$ ) were solubilized with  $50 \mu\text{L}$  of HCl 37% and diluted 1:100 using MilliQ ultrapure water. The sulfate concentration was determined from the calibration curve based on the signal intensity ( $\mu\text{S}$ ) of the analyte. Considering that the retention time of the sulfate ion and, thus, the instrument sensitivity can slightly change due to measurement conditions or to the matrix complexity, the calibration curve was constructed for each measuring session.

Figure 8 shows the IC chromatograms of the HVPD samples embedded with EDTA after the different cleaning tests. Sulfate shows a retention time of 4.30 min while the ionic species responsible for the peak at 4.70 min could not be identified but did not represent a drawback for the reliable measurement of sulfate peak.

Sulfate peak increased with the contact time between the sulfated surface and the HVPD, whatever was the chelator supported by the system (Table 2).

As regard samples containing Rochelle salt, IC technique was not suitable for the sulfates detection. The peak at 4.35 min due to the tartrate ions significantly overlapped with the sulfate peak at around 4.15 min (Fig. 9); thus, the quantification of the sulfates extracted was affected by a big error. Then, for these samples, the sulfates concentration was determined just by ICP. In particular, as expected, IC data regarding Rochelle

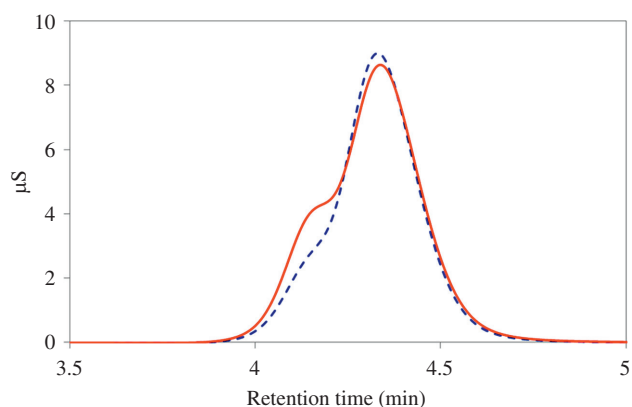


**Fig. 8:** IC chromatograms for the EDTA-containing samples after being applied onto the travertine tile for 5' (yellow solid), 10' (red dash-dot), 20' (green dashed), 30' (purple short dashed) and 60' (orange dotted). The peak coming from the sulfate ions is at  $\sim 4.30 \text{ min}$ .



**Table 2:** IC results displaying the amount of sulfates extracted (ppm) at different contact times for the HVPD containing 0.25 wt% EDTA, 0.5 wt% (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and 1 wt% Rochelle salt.

Contact time	EDTA		(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>	
	ppm	St. dev.	ppm	St. dev.
5'	2.76	0.21	4.30	0.26
10'	3.51	0.15	5.13	0.35
20'	5.19	0.16	8.52	1.14
30'	6.03	0.30	9.55	1.30
60'	8.92	0.30	25.11	3.62



**Fig. 9:** IC chromatograms for the Rochelle salt-containing samples after being applied onto the travertine tile for 5' (blue dashed) and 60' (red solid). The peak coming from the sulfate ions is at ~4.15 min while the peak at 4.35 min comes from the tartrate ions.

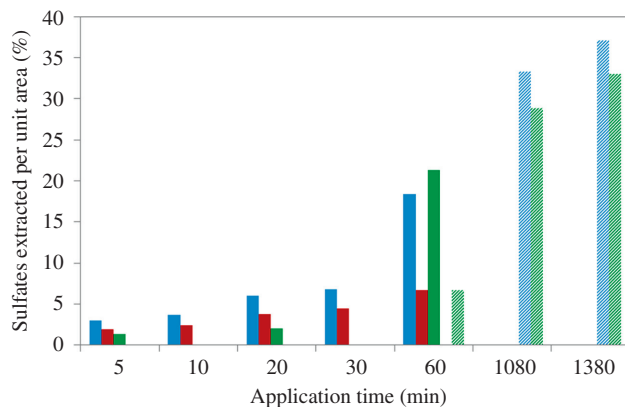
salt-containing HVPDs were overestimated. I.e. according to ICP analyses, only 6.58% of sulfates were extracted after a 60 min-long treatment against the 21.29% calculated on the basis of IC analyses.

On the basis of the results obtained by means of IC and ICP, the percent of sulfates removed by the additives was determined and compared (Table 3) and (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> resulted the most effective for the thinning of the gypsum patina.

A more accurate quantification of the sulfates extracted by the HVPDs containing 1 wt% Rochelle salt was achieved via ICP analyses by measuring the sulfur contained in samples collected after being applied for 60', 1080' and 1380'. To make a comparison, cleaning tests of the same duration were carried out also using the HVPD with 0.5 wt% (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (that had resulted the most performing according to the previous tests)

**Table 3:** Sulfates extracted per unit area (%) at different contact times for the HVPDs containing 0.25 wt% EDTA, 0.5 wt% (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and 1 wt% Rochelle salt.

Contact time	% of sulfates removed per unit area (2.28 cm <sup>2</sup> )	
	EDTA	(NH <sub>4</sub> ) <sub>2</sub> CO <sub>3</sub>
5'	1.91	3.04
10'	2.45	3.68
20'	3.81	6.04
30'	4.45	6.81
60'	6.67	18.43



**Fig. 10:** Sulfates extracted per unit area (%) at different contact times based on IC (filled histograms) and ICP (striped histograms) results for the HVPD containing 0.5 wt% (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> (light blue), 0.25 wt% EDTA (dark red) and 1 wt% Rochelle salt (green).

and the samples were analyzed through ICP technique as well. Also for ICP analyses a measuring protocol was developed. Before being analyzed, the HVPD samples (~1 g) were solubilized with 50  $\mu\text{L}$  of HCl (37 %) and diluted 1 : 100 using MilliQ ultrapure water. A standard solution with 1000 ppm of SO<sub>4</sub><sup>2-</sup> was used to obtain standard solutions with different SO<sub>4</sub><sup>2-</sup> concentrations in which 100  $\mu\text{L}$  of a solution containing Ge as internal standard was then added. For each sample, a triplicate measurement was carried on. The sulfur concentrations (ppb) were determined as the average in ppb recorded at two different detection wavelengths (180.669 nm and 181.972 nm). The concentration of sulfate anions SO<sub>4</sub><sup>2-</sup> present in the diluted HVPD samples was determined from the sulfur concentration given by the instrument, based on stoichiometric calculations (assuming that the detected sulfur came exclusively from the sulfates extracted by HVPD). Considering the 1 : 100 dilution, the effective concentration  $C_e$  (ppm) of sulfur removed resulted from equation (4):

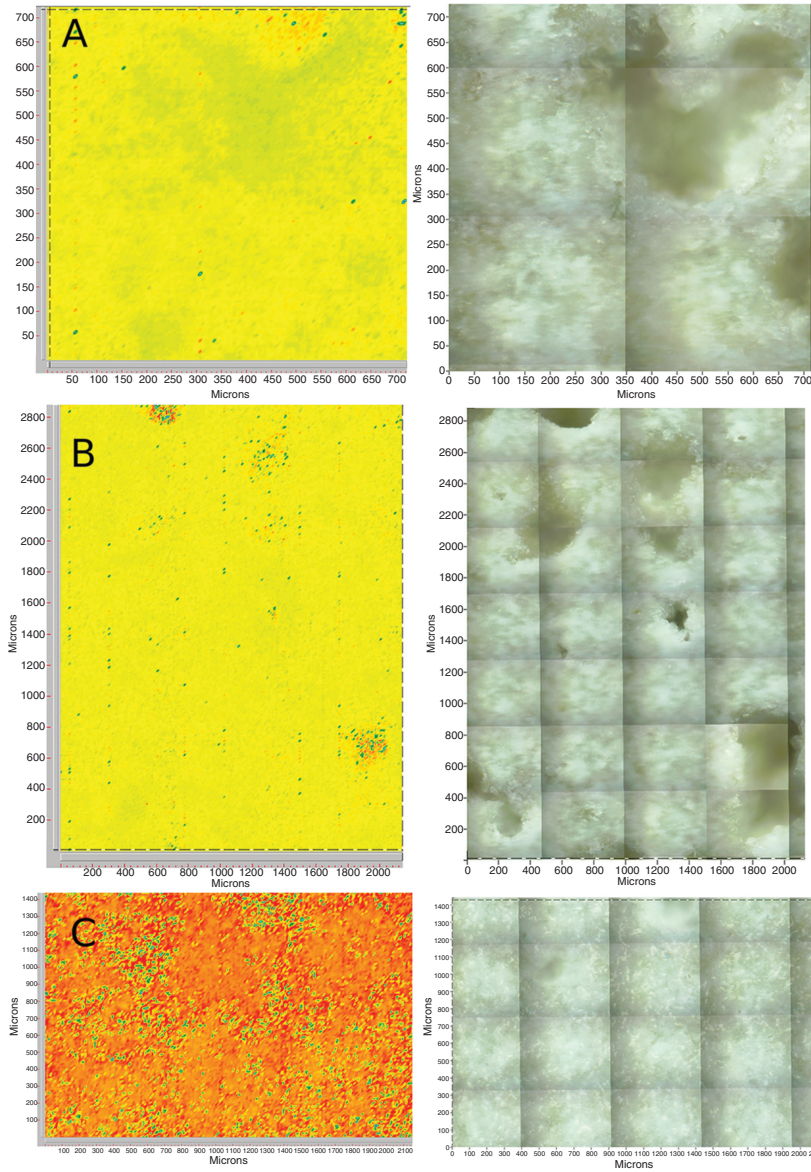
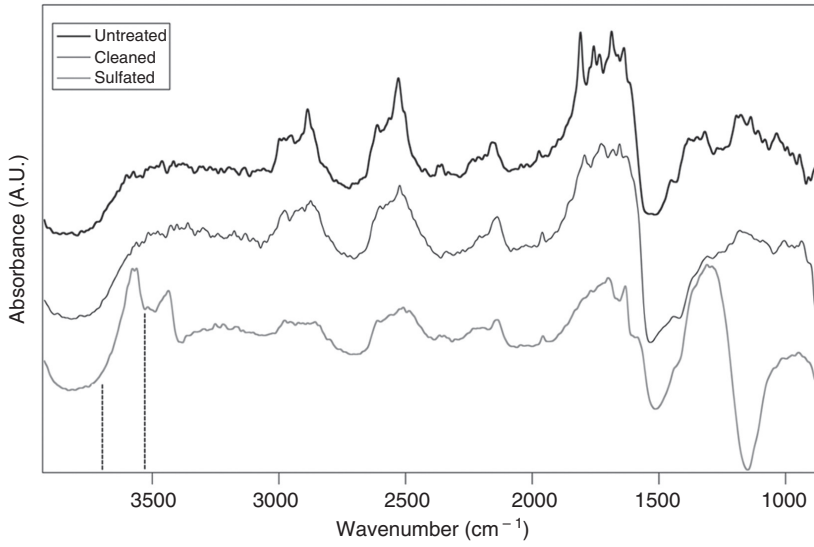
$$C_e = \frac{C_d \cdot P_i}{P_e} \cdot 100 \quad (4)$$

where  $P_i$  is the initial amount of HVPD sample used for the cleaning test (mg),  $C_d$  is the amount of sulfate anion (ppm) measured in the diluted HVPD sample,  $P_e$  is the effective amount (mg) of the HVPD sample collected after the cleaning test and actually used for the ICP analysis.

Comparing both IC and ICP analyses, the most performing additive for the extraction of gypsum still resulted (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub>, removing 37 % of sulfates after an application of 1380' (Fig. 10). Regardless of the additive, the extraction power increased with the contact time. Systems containing (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> and Rochelle salt gave significantly better performances when applied for 60' or more.

In order to evaluate the homogeneousness of the gypsum removal across the surface, 2D FTIR Imaging was carried out on travertine samples before sulfation, after sulfation, and after sulfation and application of the HVPDs loaded with (NH<sub>4</sub>)<sub>2</sub>CO<sub>3</sub> 0.5 wt% (four consecutive applications were carried out with a contact time of 60 mins each). Figure 11 shows the obtained results. The intense absorption bands in the spectrum of the sulfated travertine tile, respectively at 3572, 3437 ( $\nu_3$  and  $\nu_1$  H<sub>2</sub>O of gypsum) [32], and 1152 cm<sup>-1</sup> ( $\nu_3$  SO<sub>4</sub>, which looks inverted in the reflectance spectrum), are no longer clearly observable in the spectra of both the

**Fig. 11:** FTIR spectra of travertine tiles. The top panel shows the comparison between the Reflectance spectra of tiles that were: (i) untreated; (ii) sulfated and then cleaned with the HVPDs; (iii) sulfated. Each spectrum relates to a single pixel (5.5 × 5.5  $\mu\text{m}^2$ ) of the corresponding 2D Imaging maps shown in the bottom panels (A–C). The intensity of the gypsum absorption at 3570 cm<sup>-1</sup> (OH stretching of water) was imaged in the chromatic maps as the area of the peak between 3692 and 3542 cm<sup>-1</sup>. The chromatic scale of the maps qualitatively shows the increasing intensity of the band as follows: green < yellow < red. Beside each chromatic map, the corresponding image under visible light is shown. Map A (700 × 700  $\mu\text{m}^2$ ): untreated travertine; Map B (2800 × 2000  $\mu\text{m}^2$ ): travertine sulfated and then cleaned with the HVPDs; Map C (1400 × 2100  $\mu\text{m}^2$ ): travertine sulfated.



untreated and the cleaned tiles. It must be noted that, according to the literature, the FPA detector allows enhanced sensitivity as compared to attenuated total reflection (ATR) measurements, as for instance in cases where the lowest detectable concentration of drugs passed from 0.35 % (ATR) down to 0.075 % (FPA) [33]. The intensity of the gypsum band at  $3572\text{ cm}^{-1}$  (imaged as the area of the peak between  $3692$  and  $3542\text{ cm}^{-1}$ ) decreases dramatically upon cleaning, becoming comparable to that of untreated travertine. Namely, the gypsum peak absorbance is evenly decreased all across the surface, indicating the homogeneous removal of gypsum after the application of the HVPDs.

## Conclusions

In the present work, the effectiveness of 80PVAc-borax HVPDs embedded with three different chelators (EDTA,  $(\text{NH}_4)_2\text{CO}_3$  and Rochelle salt) in the removal of gypsum from a carbonatic matrix was explored.

As confirmed by the rheological measurements, upon the addition of the chelating agents the mechanical properties of the HVPDs resulted still adequate for their removal from the treated surface in one step by a simple peeling action, minimizing the potential residues. As concern the systems containing  $(\text{NH}_4)_2\text{CO}_3$  or Rochelle salt, the viscoelastic behavior was invariant for chelator concentrations respectively up to 0.5 and 0.9 wt%. However, a further increase of Rochelle salt concentration to 1, wt% determined the formation of a true gel. At concentrations around 0.3 wt% and 0.9 wt%, for  $(\text{NH}_4)_2\text{CO}_3$  and Rochelle salt, respectively, the addition of these salts had a structuring effect on the HVPDs as indicated by the increase of their intrinsic elasticity ( $G_0$ ). For higher amounts of additive, a lowering of  $G_0$  was recorded, indicating a reduction of the entanglements density of the PVA network.

The cleaning efficacy and the easiness of removal of the systems embedded with 0.25 wt% disodium EDTA, 0.5 wt%  $(\text{NH}_4)_2\text{CO}_3$ , 1 wt% Rochelle salt were tested through several applications on artificially sulfated travertine tiles: they were removed easily in one step (with the aim of plastic rings) without leaving any visible residue. Optical micrographs of the sulfated surfaces before and after the cleaning tests revealed their effectiveness in the thinning of the gypsum patina. The quantification of the sulfates extracted was achieved through IC and ICP techniques by setting up suitable measuring protocols for the pre-treatment and the analysis of samples. Regardless of the additive, the extracting power increased with the contact time between the surface and the cleaning systems, confirming their gradual, gentle action. The  $(\text{NH}_4)_2\text{CO}_3$  resulted the most effective, removing 37 % of sulfates after an application of 1380'.

**Acknowledgments:** Financial support from the University of Florence, from Consorzio Interuniversitario per lo Sviluppo dei Sistemi a Grande Interfase (CSGI), Florence, and SICAMOR Project PAR-FAS (Tuscany Region, Action Line 1.1.a.3) is gratefully acknowledged. This project has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement No 646063.

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