# Ammonium phosphates to consolidate carbonatic stone materials: an inorganic-mineral treatment greatly promising

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## 1. Introduction

Most of the treatments today available for the consolidation and protection of stone artifacts and monuments still suffer of significant limitations for various reasons.

There is first an undoubted responsibility of the scientific community and of the conservator restorers that have traditionally dealt with the problem without a sufficiently critical and deep approach, opting in most cases for the easiest and/or more immediate solutions, rather than privileging the more durable and reliable over long time. But there is, also, an objective great difficulty to find solutions that really meet the delicate task. The complexity lies in different aspects of the problem: the compatibility of the treatments with the stone matrix of the objects; the optical-chromatic alterations frequently induced by the treatments both immediately and, especially, over time; the actual possibility, in the case of consolidation, to interest homogeneously and effectively a sufficient depth within the treated material; the ability to retreat the object, at a distance of time, without incurring in the problem of accumulating the consolidating or protecting agent. Instead, in the light of the numerous experiences conducted in the recent decades, seems no longer a problem the condition of reversibility: this, for intrinsic reasons of the treatment, in the case of consolidation, and by the very nature of the materials that have to respond to other requirements, in the case of protection.

Following what said above, any new, more aware and more in-depth attention to the problem of the consolidation and protection of stone artifacts is therefore welcome. The consolidating products, employed in the conservation field, can be divided in two classes: the first one includes the organic-polymeric products; generally it deals with products marketed in solution of suitable organic solvents, whose consolidating effect of the stone material occurs upon of the evaporation of the solvent [Vicini, 2001,143; Wheeler, 2005]. The second class includes inorganic-mineral products; in this case the consolidating effect is the consequence of different chemical processes (hydrolysis, chemical interaction with the stone substrate etc.) which produce the crystallization of new mineralogical phases [Hansen, 2003, 13].

It is the authors' belief that the research of new more appropriate products for the consolidation and protection of stone monuments should be developed, primarily, in the mineral-inorganic field. It is for sure a more difficult field than the organic-polymeric one, but it offers the advantage of being based on materials theoretically more compatible with the substrate and more durable than those of the other area which at a minor extent can guarantee the reliability at long times requested from restoration.

The mineral-inorganic nature of the products is itself a necessary condition but not a priori sufficient; in fact a very important requirement is that the consolidating action, for instance, occurs even in the depth of the stone. To ensure this goal it would be necessary to separate the penetration process of the consolidant within the pores of the stone material from the actual consolidating process.

During the last decades, a conservation treatment based on ammonium oxalate has been applied for protection of different carbonatic materials both in laboratory experiments on carbonatic substrate [Cesar, 1998, 15; Doherty, 2007, 4477; Ambrosi, 2000, 873; Rescic, 2007, 93] and in numerous important conservation works [Serrao, 2005, 187; Mairani, 2000, 146; Doherty, 2007, 2007; Realini, 2007, 477; Realini, 2004, 330; Matteini, 2007, 219]. The Institute for the Conservation and Valorization of Cultural Heritage has been involving for many years in the development of new treatments and in the evaluation of their efficacy with laboratory experiments and pilot yards tests. In recent years, particular attention has been paid on the use of ammonium oxalate and ammonium phosphate respectively as protection and consolidation treatments of limestones and plasters [Conti, 2011, 372; Hansen, 2003, 13].

As regards the treatments with ammonium oxalate, the studies carried out so far have been aimed at defining the crystallization mechanisms and the stability of weddellite and whewellite, the two neo-formed phases of calcium oxalate, and at determining the penetration depth of the treatment in the crystal structure of a carbonate substrate [Conti, 2010,14560, Conti, 2011, 372, Conti, 2010, 1254].

Regardless of the above mentioned study, other innovative approaches are being investigated and perfected such as, in particular, the very promising use of the ammonium phosphates for the consolidation of calcareous materials [Matteini, 2011, 717; Sassoni, 2013, e103; Botticelli, 2010]. The mechanism of action of ammonium phosphates was inspired by the now more than a decade tested and applied ammonium oxalate. The consolidating agent, in this case, is calcium phosphate, the same highly resistant material that constitutes bones and teeth. The ammonium phosphates need deeper investigation but even now allow very effective operations of consolidation in buildings made of limestone materials [Sassoni, 2013, e103, Pittaluga, 2012, 303; Matteini, 2011, 717].

As well as the ammonium oxalate, even more ammonium phosphate require in-depth studies mainly focused to understanding the most appropriate protocols to be used (concentration, contact times, type of sorbent, re-feeding, etc.), according to the various stone properties (porosity, color, decay conditions, etc.). This paper presents the data obtained in two pilot yards where ammonium oxalate has been used on painted plaster and ammonium phosphate on natural stone material.

## 2. Mineral-inorganic consolidating treatment

Studies conducted in recent years by ICVBC, on treatment with ammonium oxalate has highlighted different issues including the importance of identifying direct analytical methods to investigate the effects of treatment within the po-

rous matrix. The experiments allowed to develop a procedure to evaluate the penetration depth and the diffusion inside the material of the consolidating product by scanning electron microscopy and μ-Raman spectroscopy. In particular, μ-Raman mapping applied to polished cross sections of plasters treated with inorganic products turns out to be an innovative and powerful tool for assessing their diffusion inside the porous substrate. The behaviour of ammonium oxalate applied to painted plasters has been studied, with an immediate consequence for the conservation works, in particular regarding the methodology of the treatment and the influence of the nature of plaster. The kind of plaster plays a relevant role on the penetration depth achieved by ammonium oxalate treatment. In particular, under the same treatment conditions, the chemical composition of the aggregate particles is the main factor that influences the diffusion of the product inside the plasters: the depth achieved by the reactive oxalate solution is larger in plasters with silicatic aggregate rather than in plasters with carbonatic aggregate. Moreover, laboratory experiments and pilot yards tests highlight that the treatment settings (time of contact of the poultice and addition of the solution) influence the penetration depth of ammonium inside the carbonatic substrate. [Conti, 2010, 1254; Conti, 2011, 372]. Currently, the same procedure has been applied by the authors to study an innovative treatment based on ammonium phosphate, a very promising product for the consolidation of carbonate surfaces because of its high water solubility, a negligible change in colour of the stone surface and the extremely low solubility of the reaction product, calcium phosphate [Matteini, 2011, 717]. Sassoni et al. [Sassoni, 2013, e103] investigated the effect induced by HAP on sandstones with different carbonate contents and different porosities; the results highlighted that the product has proved be able to restore mechanical properties  whiteout altering the pore size distribution of treated stone. Pittaluga et al. [Pittaluga, 2012, 303] studied the effect induced by the ammonium phosphate treatment applied on a lime mortar: the data acquired suggested a strengthening effectiveness and water absorption reduction although causing a slight chromatic alteration in one of the two treated zones.

## 3. Analytical methods

Polished cross sections of samples from pilot yards have been investigated by:
- optical microscopic in reflected light by a Leitz Ortholux microscope with an Ultropack illuminator;
- spectroscopic analyses by a Senterra dispersive μ-Raman spectrometer (Bruker) equipped with 400 and 1200 grooves/mm gratings and coupled to an Olympus BX51 microscope with 20x, 50x and 100x objectives in light and dark field, motorized X-Y microscope stage. The exciting line used is 785nm (100 mW), with a Peltier-cooled CCD detector (1024_256 pixels). In order to monitor the presence of oxalates inside the stone, linear maps have been obtained starting from the surface and moving inside the domains of the polished cross-sections. Measurements have been carried out with continuous scan in the 100–3500 cm$^{-1}$ range, 3–5 cm$^{-1}$ of spectral resolution, exposure time 5 s, 3 accumulations and a maximum of 5mW laser power at the sample.

Spectra used for Raman mapping have been MIN-MAX normalized and baseline corrected with the Bruker Senterra software (Opus). From the sample surface and throughout its thickness, 20 linear maps have been acquired with a variable number of spectra.

- JEOL 5910LV electron microscopy equipped with an X-ray spectrometer IXRF Systems/EDS 2000. The observations were carried out using backscattered electrons (BES) in low vacuum mode (LV) with an accelerating voltage of 20 kV. The EDX qualitative spectra of squared areas or spots were registered from 0 to 20 kV and at 1-3.10-7A.

## 4. Results

The effects induced by the treatment with ammonium oxalate and ammonium phosphate were assessed by laboratory tests in the cases of the pilot yards. The data collected showed that the inorganic treatments occur not only close to the surface but also inside the carbonatic material with an unhomogeneous distribution. The neo-formation products, such as whewellite and weddellite, or the characterizing element of the treatment, such as phosphorus, have been mapped.

### 4.1. Ammonium oxalate treatment and penetration depth

Micro-Raman mapping applied to polished cross sections of plasters treated with inorganic products turns out to be an innovative and powerful tool for assessing their diffusion inside the porous substrate. The behaviour of ammonium oxalate applied to painted plasters has been studied, with an immediate consequence for the conservation works, in particular regarding the methodology of the treatment and the influence of the nature of plaster [Conti 2010, 1254; Conti, 2011, 372].

Micro-Raman mapping has been used to investigate the penetration depth of ammonium oxalate treatment (4% for 10 hours by poultice) applied on an outdoor mural painting. In Figure 1 the stratigraphy is shown: the red layer consists of red ochre pigment spread in a magnesium lime binder with an average thickness of 100 μm. The plaster is made of a magnesium lime binder as well and a silicatic aggregate with a diameter ranging from 50 μm to 300 μm. Micro-Raman mapping allowed to define the distribution of the phases from the surface to the inner domains of the samples: whewellite and glunshinskite ($MgC_2O_4 \cdot 2 H_2O$) are the main oxalate phases detected, together with calcite and dolomite, ascribed to the binder, and gypsum as decay product (Figure 2). The occurrence of the magnesium oxalate is the result of the reaction of ammonium oxalate with the component of the binder rich in magnesium. As shown in Figure 1, the graphic reconstruction of the results obtained by μ-Raman mapping allow distinguishing the spread of newly formed mineral phases; the penetration depth of the treatment ranges approximately from 80 μm to 200 μm.

### 4.2. Ammonium phosphate treatment and penetration depth

On the decorative apparatus of a building in Milan made by Gallina limestone, four pilot areas have been identified to test the best way of treatment by am-

monium phosphate related to the state of conservation of the surfaces. The erosion was the main decay, producing a loss of cohesion of the material with phenomena of sulphation up to approximately 400 microns in depth.

A cleaning with ammonium carbonate (saturated solution by poultice for 24 hours) was carried out on three areas, while the fourth area was only washed with de-ionized water. Two of the three cleaned areas, were treated with a super-saturated water solution of barium hydroxide (8%). At least, all the areas have been treated with di-ammonium phosphate (7%) applied by a poultice for 20 hours. The use of barium hydroxide was aimed at increasing the desulphation of the surfaces, which is already partially made by the action of ammonium phosphate.
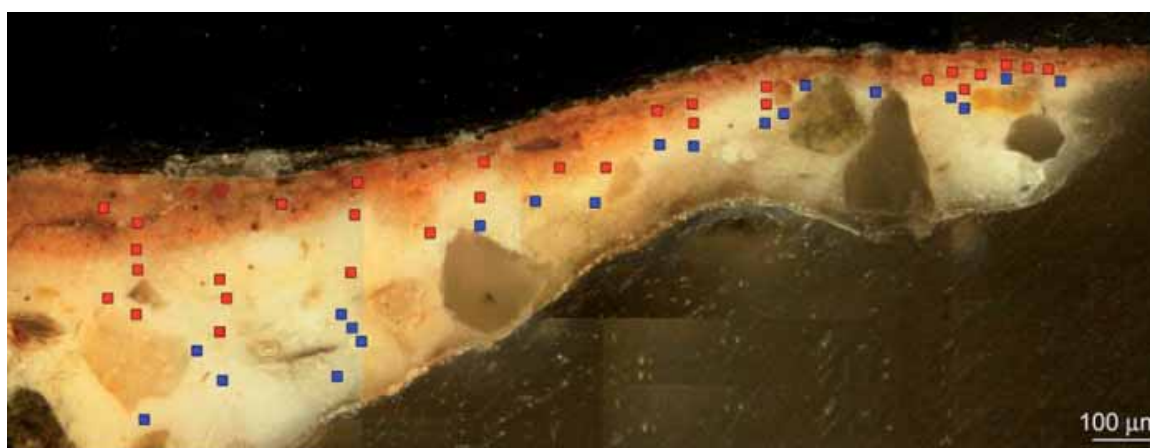


Fig.1 - Optical image of a cross section of a painted plaster treated with ammonium oxalate. Occurrence of calcium or magnesium oxalates (red squares) and of calcium or magnesium carbonates (blue squares) obtained with micro-Raman mapping
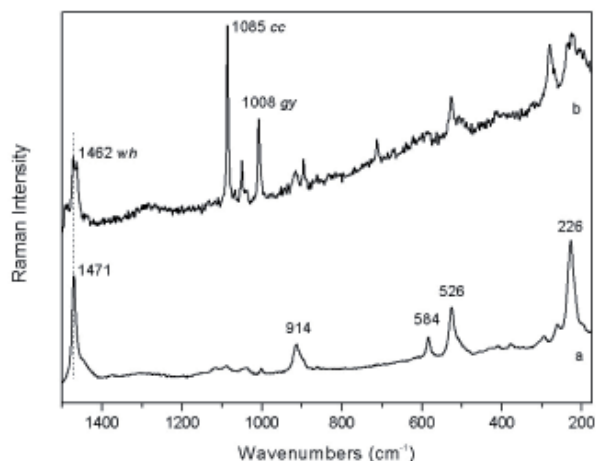


Fig.2 - Raman spectra recorded in a plaster treated with ammonium oxalate: glunshinskite (a), whewellite (wh), gypsum (gy) and calcite (cc) (b)

The achieved results highlight that the penetration of the phosphate and the residual presence of gypsum are influenced by the strong variability and heterogeneity of the stone material. Moreover, the distribution of phosphate inside the crystalline structure of the stone material, is directly influenced by the state of conservation. It is localized where the matrix has lost its the compactness, both in the discontinuity between the micro-crystals of calcite and where
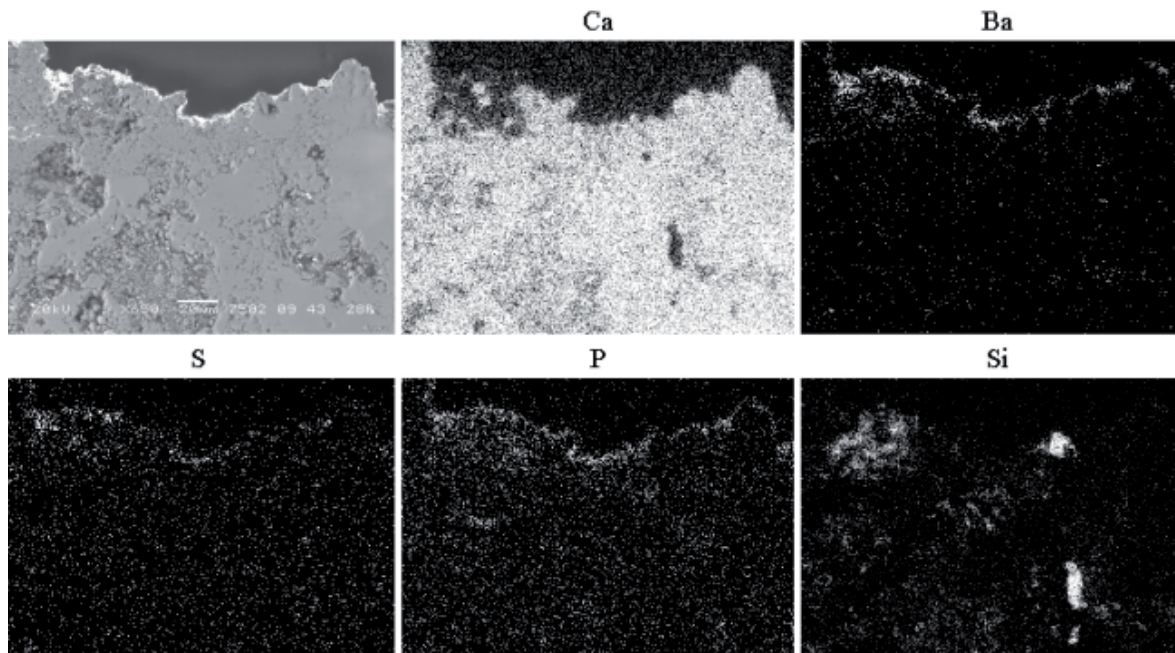
Fig.3 - Polished cross section observed by scanning electron microscope and distribution maps of the elements calcium, barium, sulphur, phosphorus and silicon. Close to the surface barium, sulphur and phosphorus are detected

gypsum was present as decay product. In the case of the areas previously cleaned and treated with barium hydroxide and di-ammonium phosphate, the analysis highlighted the presence of a thin layer (approximately 3 microns) along the surface composed of barium (Figure 3), sulphur and phosphorus (this suggests the presence of barium sulphate and barium phosphates), while inside the stone material phosphorus is diffused in decayed areas; it is normally detected in the microcrystalline matrix between clasts of calcite (Figure 4), which does not appear to be affected by chemical transformation induced by ammonium phosphate. The presence of phosphorus has been detected till to 6 mm inside the stone, while barium is almost absent. Gypsum as a decay product is scarcely occurred.
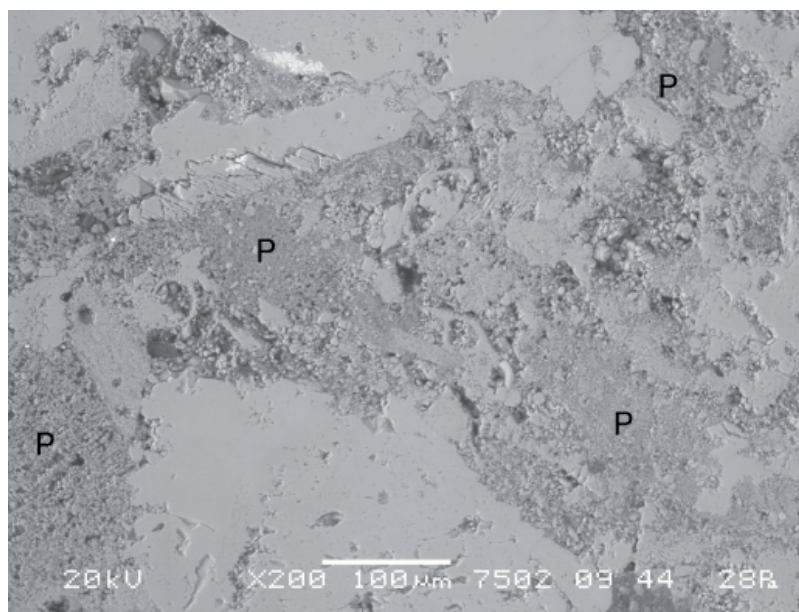


Fig.4 - Scanning electron microscope image. Presence of phosphorus (indicated with the letter P) in the portions with low compactness between the calcite crystals of the stone
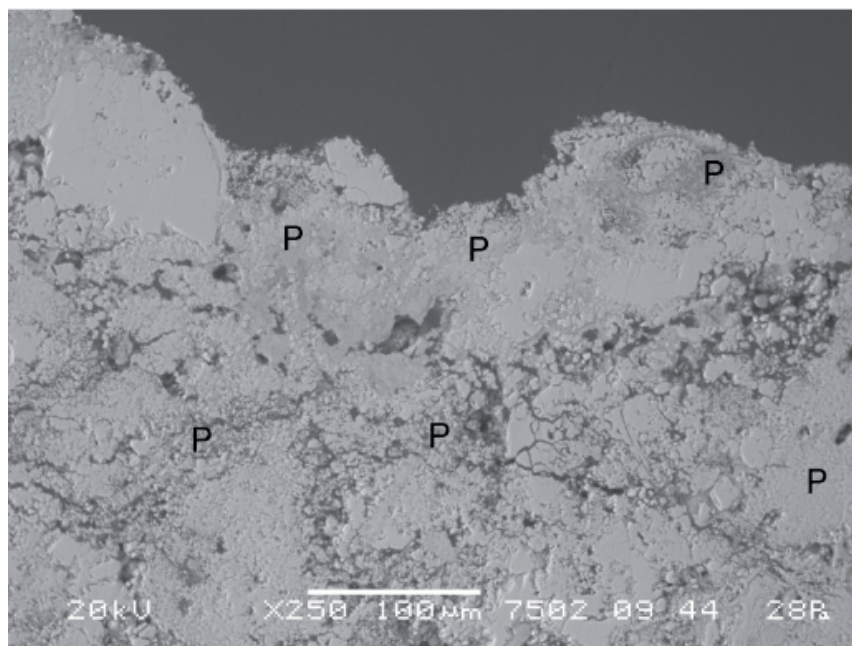
Fig.5 - Scanning electron microscope image. Presence of phosphorus (indicated with the letter P) in the poorly compact matrix of the stone

In the case of the area treated only with di-ammonium phosphate, where the material is more decayed due to the presence of sulphur, both on the surface and in depth, the phosphorus is mostly localized together with sulphur. Phosphorus is abundant and well-distributed up to a depth of approximately 60-70 microns (Figure 5); beyond that limit, the phosphorus is not homogeneously distributed in the crystalline structure, but it is localized only in restricted areas to a depth of 2-3 mm. This data could suggest that the formation of calcium phosphate occurs in the first few millimetres where calcium is provided by gypsum, highlighting the desulphating action of ammonium phosphate and, in addition, more in depth, where through the reaction with calcium carbonate the consolidating effect occurs.

## 5. Conclusion

In recent years many progress have been done to get ready the most suitable analytical methodology to study treated surfaces with the aim to obtain as much information as possible about the penetration of inorganic treatment; moreover, many investigations have been carried out on stone materials treated with ammonium oxalate and ammonium phosphate, allowing to understand the complex processes of formation, distribution and stability of the newly formed mineralogical phases.

This work concerns inorganic treatments on outdoor plaster and stone materials studied by µRaman mapping and SEM-EDS analyses. The penetration depth achieved by transformation products obtained with ammonium oxalate and ammonium phosphate have been investigated in a direct way, thus allowing to detect the distribution of the newly-formed minerals. In the case ammonium oxalate, the presence of mineral phases such as whewellite and glunshinskite altogether approximately 200 microns deep inside the material allows saying that obtained data have a great relevance for the restoration

works, because it is highlighted a good diffusion inside the porous substrate: from the red painting layer up to the plaster below.

In the case of ammonium phosphate, the presence of preferential paths in the treated stone, as micro-cracks and micro-decohesion, allow reaching greater deep of penetration, but the spread of phosphate is not homogeneous inside the material making it localized in specific areas. This fact could be also ascribed to the de-sulphating action of ammonium phosphate that occurs in the decayed areas, till to 6 mm in depth, where gypsum is present.

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