NORGANIC TREATMENTS FOR THE CONSOLIDATION AND PROTECTION OF STONE ARTEFACTS AND MURAL PAINTINGS

Mauro Matteini
Istituto per la Conservazione e la Valorizzazione dei Beni Culturali (ICVBC)
Consiglio Nazionale delle Ricerche, Firenze

1. Principal decay mechanisms affecting different kind of stones

The expression stone materials is referred here both to natural stones as well as to artificial stones such as mortars used for plasters, etc.

Stone materials are characterized by the following main properties: a prevalent or exclusive *mineral-inorganic nature*; *hydrophilic properties*. Both these aspects are very important when planning treatments for their conservation and have never to be forgotten.

When possible mechanisms of damage are considered as respect to stone materials, two main categories have to be mentioned: *acid attack* (caused by rains and humidity condense in polluted urban atmospheres); *soluble salts* cyclic *crystallization*. The first mechanism (acids) induces corrosion to carbonatic materials such as calcium and/or magnesium carbonates based stones while silicatic stones are only poorly affected.

The second mechanism (salts) is mainly active towards porous stones, independently of their nature. Less important is the effect towards compact low porosity stones. Decay

Table 1. Decay risk of different typologies of stone materials used in art objects.

		Chemical nature	
		calcium carbonate based stones	silicates based stones
Porosity	high	oo++	++
	low or null	oo	+

Table 2. Provenance of decay agents.

	From outside	*From inside*
Acids	atmospheric gas pollutants	/
Salts	deposit of atmospheric particulate	– capillary rise – water infiltration from neighboring architectonic structures

processes are also strongly dependent on the kind of porosity. Usually small pores increase degradation caused by soluble salts.

The scheme in tab.1 summarizes and simplifies what has been considered above.

The next scheme (tab. 2) puts in evidence the provenance of the decay agents (acids and salts), a further important point that has to be taken into consideration.

2. Consolidation and protection

It is well known that consolidation and protection are among the most important operations that are usually carried out in conservation work on stone objects.

Consolidation (structural consolidation is not considered here) is an operation addressed to stone materials affected by loss of cohesion, with the aim of re-building it. This is normally obtained through the permeation of special agents in liquid form (mainly solutions) in the bulk of the stone materials, close to the surface. In most of cases, loss of cohesion is limited to regions located near the surface at a major or minor depth. After the impregnation step, consolidation of the system occurs due to different mechanisms, among which *solvent evaporation* and *special chemical reactions* are the more frequently used. A texture is formed which, at some extent, is able to re-build lost cohesion. The final effect has never to prevail the original mechanical properties (cohesion) of the sound stone material.

Protection is an operation through which the surface of a stone artefact is preserved by the action of decay agents. We shall not forget that decay agents can reach the surface both from outside (acid attack and salts deposits) and inside (soluble salts), in case of porous materials (see tab. 2).

3. The organic polymeric products

Traditionally, the problem of consolidation and protection of stone materials has been mainly faced with the use of organic hydrophobic products, both natural products, in the past, and artificial synthetic products, more recently.

The reasons of that are various:

– organic materials (in solution form) are easy to be applied;
– positive effects are immediately visible;
– organic materials are usually free from immediate secondary negative effects;
– they are said to be reversible;
– the formation of a coating satisfies the general concept that protection has to be assured with respect to external decay agents.

Together with *pros*, as in any restoration treatment, *cons* have to be considered. Problems arise in particular situations and especially over time:

– while short-term effects are generally good, long-term behaviour is often not satisfying (because of alteration of aspect, loss of performance, etc.*)*;
– reversibility is often misunderstood or impossible. Reversibility is practically impossi-

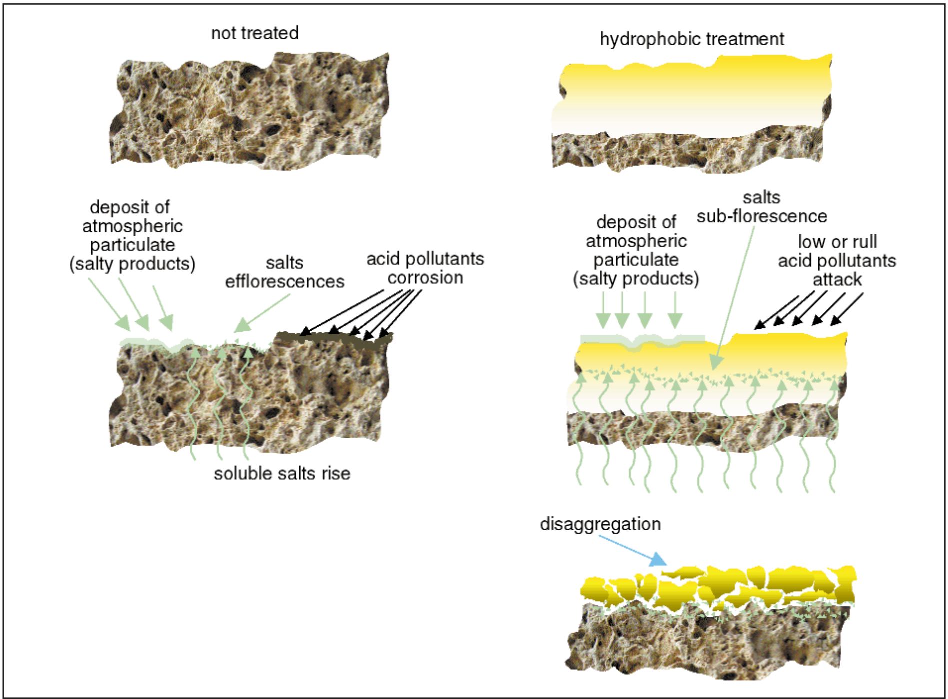


Figure 1. Behavior of not treated porous stones is compared with that of stones treated with surface hydrophobic organic agents used for protecting or consolidating them.

ble in the case of consolidation because the operation itself (rather than the product) is irreversible. In the case of protection it is often impossible because the product itself (poly-syloxanes, for instance) is irreversible;

– the most serious problems arise when objects made of porous materials exposed outdoors are considered. In that case the effect of soluble salts sub-florescences is evident.

In fig. 1 the drawing puts in evidence the mechanism through which porous stones affected by soluble salts may loose their integrity due to disaggregating processes caused by internal crystallization of soluble salts (*subflorescences*) favoured by surface hydrophobic treatments.

4. The mineral inorganic approach: the barium hydroxide method

At the end of the ’60 Enzo Ferroni, professor of chemistry at the University of Florence, together with Dino Dini, private restorer, found out a new treatment for de-sulfating frescoes. Since that time, that treatment is known as “*Method of Barium Hydroxide*” or “*Method of Ammonium/Barium*”.

As it will be seen later the *Barium method* revealed not to be only useful for desulfating frescoes but also for efficiently consolidating them.

It was not the first time that mineral-inorganic treatments had been proposed for the conservation of stone artefacts. In the second half of the XIXth century many patents appeared with the proposal of various inorganic products for the consolidation of stone. Among them *sodium and potassium silicates*, *fluosilicates* and *barium hydroxide* itself may be mentioned.

Nevertheless, given that at the end of the century they were no longer mentioned we have to think that most of them evidently had failed.

Coming back to the *barium hydroxide method*, as it has been anticipated, Ferroni and Dini, initially, proposed that kind of treatment, not for consolidating but for de-sulphating frescoes affected by gypsum cyclic crystallization and consequent disgregation.

Only after the first applications they realized of the other important function, the consolidating effect assured by the carbonation of barium hydroxide:

1) $$Ba(OH)_2 + CO_2 \rightarrow BaCO_3 + H_2O$$

Anyhow, sulfation and loss of cohesion are closely related.

Sulfation mainly refers to destructive effects caused in stone materials (plasters above all, but porous stones as well) by gypsum cyclic crystallization. Gypsum is a special salt, according to its water solubility.

Table 3. Molar water solubility of salts commonly found in stone materials compared to that of gypsum (logarithmic values).

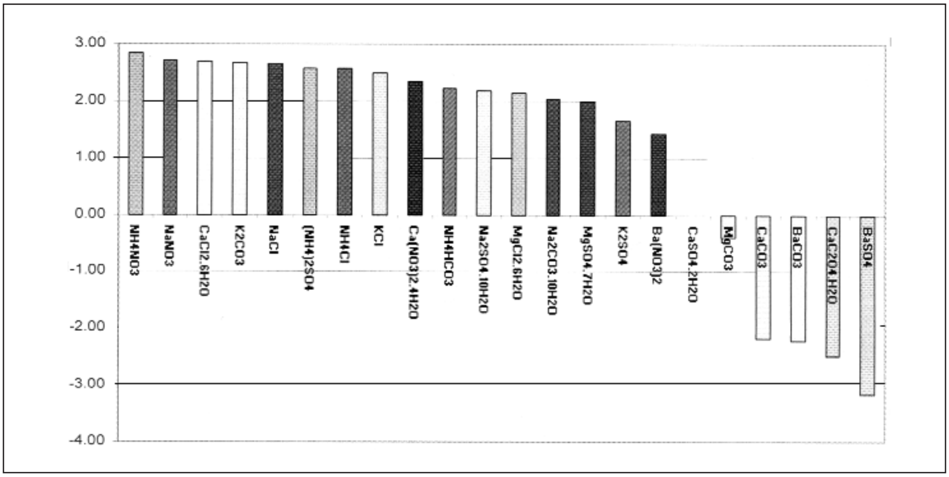


Table 3 illustrates the logarithm of molar solubility in water of various salts that can be frequently found in stone materials, compared to that of gypsum. Gypsum is taken as a reference soluble salt due to both its particular solubility as well as to its high diffusion in all kinds of stone materials.

Water solubility of gypsum is around 2% in water and does not practically change with temperature. It can be considered a slight solubility (that means a high tendency to produce saturated solution and consequent crystallization) but enough great to cause damage.

Water solubility of the majority of the other salts is much higher than that of gypsum. They can be considered highly soluble substances. Not frequently, their concentration within a porous stone can overcome the value of saturation. A minor group of salts has a much lower solubility compared to that of gypsum. Actually, they can be considered insoluble salts, and for that not harmful.

Now, what normally happens with gypsum?

In normal climatic condition such as those usually found in churches, palaces and other protected environments, crystal formation may be very slow. Crystal growth may then prevail to nucleation, causing serious damages also when low amounts of gypsum are inside the pores. Locally, the volume of gypsum crystals can exceed pore size, causing subflorescences and disgregation (fig. 2).

The barium method, through the two following poultice treatments (with ammonium

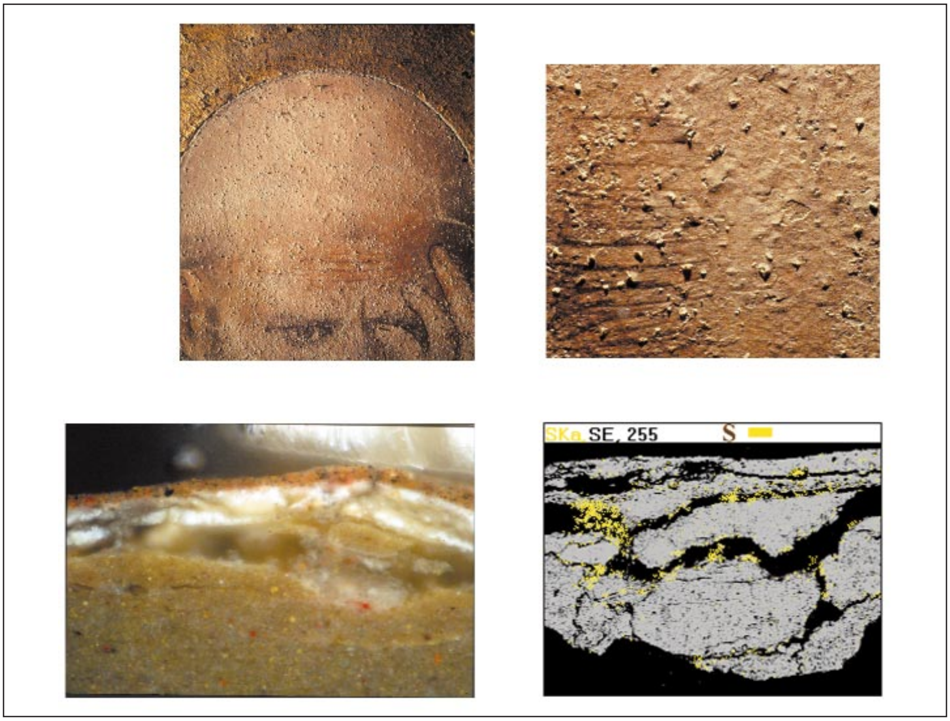


Figure 2. Blistering caused by crystal growth of gypsum under the paint layer in a mural painting (top left and right). A single pustule observed in cross section under optical microscope (bottom left) and with SEM/EDS (bottom right).

carbonate, the first; with barium hydroxide, the second), is able to stop sulfation caused by gypsum:

2) $$(NH_4)_2CO_3 + CaSO_4 \rightarrow (NH_4)_2SO_4 + CaCO_3$$

3) $$Ba(OH)_2 + (NH_4)_2SO_4 \rightarrow BaSO_4 + 2\ NH_3 + 2\ H_2O$$

Successively, through reaction 1), cohesion lost due to sulfation is rebuilt.

The great success of this method for the conservation of mural paintings, in years and decades after the first interventions, is justified by the double action guaranteed by the treatment.

Now, as far as the consolidation mechanism is concerned, the following two further reactions (lime neo-formation and carbonation), in addition to reaction 1), could also contribute:

4) $$Ba(OH)_2 + CaCO_3 \rightarrow BaCO_3 + Ca(OH)_2$$

5) $$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$$

Laboratory testing is still in progress. Given the above reactions confirm to be important, different operative condition should be adopted (i.e. much longer application times).

A third mechanism is also worth of attention: direct reaction between ammonium carbonate and barium hydroxide.

6) $$Ba(OH)_2 + (NH_4)_2CO_3 \rightarrow BaCO_3 + 2\ NH_3 + 2H_2O$$

Rapid ion reaction between barium and carbonate ions would not produce a consolidating effect but only an useless precipitate within the pores. Given this is experimentally confirmed a further variation in the application condition should be adopted. A preliminary treatment with distilled water poultice would be useful to cause migration of ammonium carbonate toward the interior of the plaster, far from the surface, before barium hydroxide is applied.

Laboratory testing to ascertain the role of each of the above mentioned reactions is in progress. It is not an easy task because of the necessity to create special conditions able to isolate each single reaction.

Now the question is: why the *barium method*, a kind of treatment that demonstrated to be so appropriate and successful in the conservation of mural paintings, was only episodically used for the consolidation of stone artefacts?

Due to different reasons is not easy to give an answer. Actually, only episodic applications have been reported in the literature of *barium* on marble objects. No systematic experimental testing and/or scientific investigation have been carried out, with the exception of an unique research work now in progress within the research European Project EUARTECH; but about this, results are not yet available. According to my personal opinion no objective obstacle should subsists to obtain with the *barium method* applied on stone objects the same excellent results experimented on decorated mural surfaces. This is probably true not only with regards to marble and limestones but also to sandstones and much likely to clay based materials, such as adobe and similar. Only laboratory and in situ testing is necessary and this is planned tobe done in the next months.

5. A further mineral inorganic approach: the ammonium oxalate (AmOx) method AmOx as protecting passivating agent

About 15 years ago the first experiments were carried out in the Laboratories of the

Opificio delle Pietre Dure in Florence in order to test the possibility of an innovative approach to the problem of protecting marble and limestone monuments and artifacts exposed outside.

In place of hydrophobing their surfaces by applying hydro-repellent barriers, it could be convenient to make their surfaces acid-resistant through a passivating treatment.

The new approach could result particularly advantageous and important in case of porous calcareous materials exposed outdoors, particularly in polluted urban centers.

This category of artifacts are highly exposed to acid rain and humidity condensation and also affected by salts migration followed by cyclic crystallization in their porous structure with formation of very devastating sub-florescences, that are favoured by hydrophobic protective treatments.

An appropriate passivating acid resistant agent could be calcium oxalate as demonstrated by the long lasting naturally formed calcium oxalate patinas on the majority of monuments.

Naturally formed patinas are usually coloured due to impurities that remain entrapped in the oxalate matrix during the formation (fig. 3). Pure calcium oxalate (both the monohydrate Whevellite $CaC_2O_4.H_2O$, and the di-hydrate Weddellite $CaC_2O_4.2H_2O$) is colorless or whitish.

A suitable treatment to passivate calcium carbonate through a moderate and controlled formation of calcium oxalate was found in the following reaction with ammonium oxalate (AmOx).

7) $$CaCO_3 + (NH_4)_2C_2O_4 \rightarrow Ca\ C_2O_4 + 2\ NH_3 + H_2O + CO_2$$

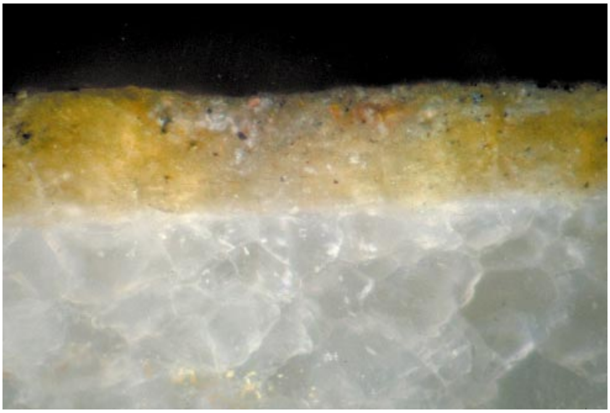


Figure 3. Cross section of a typical yellowish natural calcium oxalate patina on a marble monument.

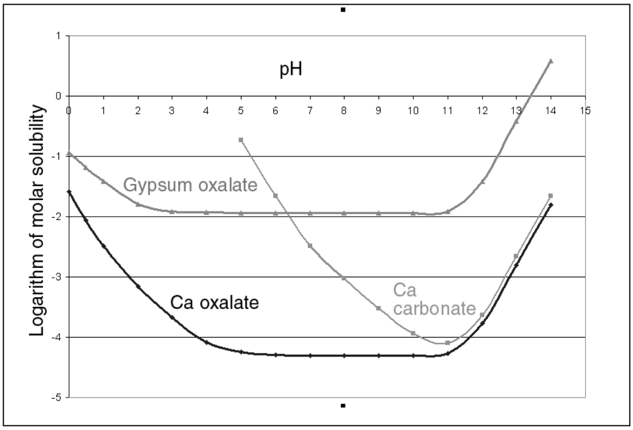


Figure 4. Logarithm of molar water solubility of calcium oxalate compared to calcium carbonate and gypsum.

Water solubility of calcium oxalate, is shown in the graph in fig. 4, compared to those of calcium carbonate and gypsum. CaC_2O_4 has a very low solubility, which is maintained, differently from $CaCO_3$, also in a strong acidic environment. It is the ideal passivating agent for limestones objects in urban acidic atmosphere.

A significant test for demonstrating passivation was obtained by treating 5 small Travertine cubes with the AmOx method. Couples of one treated and one not treated Travertine samples were then immersed in 5 acidic solution at pH 5, 4, 3, 2, 1. In the buffered acidic solutions Ponceau Red was also added. Ponceau Red is a highly sensitive red staining agent for free Ca ions. The not treated samples strongly red stained at pH 4, 3, 2, 1 while the treated samples did not stain up to pH 1.

The passivation process can be interpreted as the formation of a calcium oxalate shell on calcium oxalate pores surfaces till a certain depth from the surface. Precise analytical mapping of the above distribution have not yet been obtained. EDS/SEM cannot distinguish among CaC_2O_4 due $CaCO_3$. FTIR Microscope mapping is not enough sensitive. MicroRaman Spectroscopy investigation seems to be promising. Work is in progress.

Extensive laboratory investigation and testing have been carried out at the Scientific Laboratories of the Opificio in Florence and, in the following years, at the Istituto di Scienze e Tecnologie Molecolari (ISTM/CNR) in Perugia and at the ICVBC/CNR in Florence and Milan.

About 10 years ago the first applications started on monuments and artifacts in Florence and many other parts of Italy. Among the many objects treated with this method we want to mention the big marble statue ‘Eterno Padre’ by Baccio Bandinelli and the graffiti façade of Palazzo Barbolani Montauto, both in Florence. A further more recent example of AmOx passivating treatment is that of the Portale in Candoglia Stone of Santa Maria delle Grazie in Milan.

AmOx to improve color saturation

A second positive effect induced by AmOx treatment is a moderate but very interesting increase of the chromatic contrast (color saturation). This effect is probably due to lowering of surface micro-roughness and consequent reduction of light scattering after treatment.

In deep laboratory investigation has been recently carried out at the ICVBC in Florence to investigate this point on more than 20 different types of limestones. Color measurements, water absorption, crystalline structure of the surface under optical microscope, SEM, etc. were carried out. Results were presented at the Conference in memory of Cesare Brandi in Lisbon, May 3-5, 2006.

In the most of cases slight color change or no color change is observed. In some limited cases more evident change is caused. Apparently, it depends on the presence of free Iron(III) ions in stones or mortars. When some discoloration is caused by the treatment, it occurs immediately. It can be observed during preliminary tests on small areas and the AmOx treatment is not applied. No long term discoloring effects have been observed.

As said above, usually, color saturation is often observed after the treatment and this can be considered a positive effect. Actually, decay processes usually induce increase of surface roughness in stone and decorated plaster surfaces with a consequent light scattering effect (whitish appearance more easily visible in dark areas). AmOx treatment is often able to reduce this negative optical appearance by rebuilding more homogeneous surface texture.

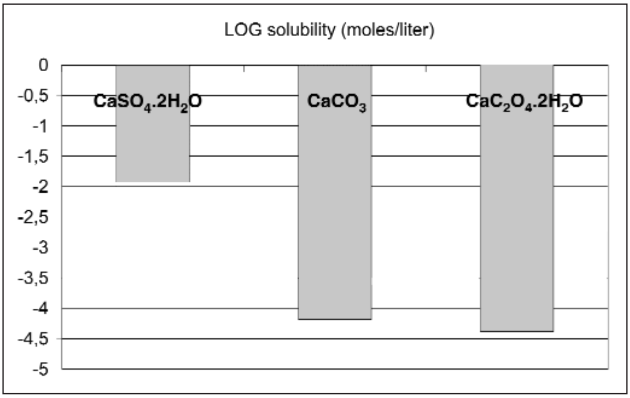
AmOx as an efficient neutral desulfating agent

A third interesting action assured by AmOx treatment is desulfating action towards gypsum. Gypsum is partially or totally converted into calcium oxalate, according to reaction 8):

8) $$CaSO_4 + (NH_4)_2C_2O_4 \rightarrow Ca\ C_2O_4 + (NH_4)_2SO_4$$

AmOx reacts with gypsum in a similar way it reacts with calcium carbonate. Slightly soluble gypsum is transformed into very insoluble calcium oxalate, favored by a great solubility difference between the two species (fig. 5). Residual ammonium sulfate can be

Figure 5. Logarithm of water solubility of calcium oxalate compared to that of gypsum and calcium carbonate.



easily removed by washing the treated surface with de-ionized water (stones) or by desorbing it with cellulose powder or sepiolite poultices (plasters).

Efficient de-sulfation is obtained with a final result comparable to that of *barium method*, with the advantage of no alkaline environment. Actually, AmOx water solution is practically neutral. Drawbacks can arise from a minor translucency of calcium oxalate compared to that of calcium carbonate. When gypsum is located over the surface, some whitish effect after the treatment may be observed. In that case, *surface desulfation* is first needed, with anion exchange resins.

The AmOx based desulfating method has been applied to the facades of the Pieve of Santa Maria and the Church of San Domenico, both in Arezzo, with good results as demonstrated by the analyses carried out by the ICVBC/CNR.

AmOx as a consolidating agent for marble and other limestones

A further very promising action induced by AmOx treatment is a good consolidating effect.

The consolidating action of AmOx was first observed on highly disaggregated marble (the so called ‘sugar-like’ marble). Preliminary experiments have been carried out both in the laboratory and as pilot tests, in situ, on small areas. At the moment most of the research in this direction has to be developed. Promising results have been recently obtained on a big fragment of a heavy decayed marble, a “*tortiglione*” column removed from Florence Cathedral to be replaced with a new one. The column showed blackish gypsum incrustation on most of its surfaces and a very serious de-cohesion of the marble underneath. The piece has been first cleaned with ammonium carbonate poultice in order to remove gypsum incrustations and then treated with AmOx (5% water solution dispersed in cellulose poultice, for 24 hours). Consolidating effect was measured by means of the "*drilling method* ". Evident increase of cohesion was demonstrated up to a a depth of about 5 cm.

6. Conclusion and future research

Inorganic treatments received much more attention in the last decade compared to the past. Barium Hydroxide and Ammonium Oxalate are at the moment the most promising agent for the consolidation and protection of stones and decorated plasters. They are usually less simple then the organic polymeric products but they some important advantages such as durability compatibility and more appropriateness in case of porous matrixes affected by salts crystallization.

The review illustrated above put in evidence the multiple action accomplished by these kind of treatments.

Nevertheless, a lot of further research is necessary in order to:

- ✓ better understand their mechanisms of action;
- ✓ study their behavior on matrixes different from the ones on which they were initially or traditionally tested and applied;
- ✓ investigate new procedures of application more appropriate to some of their multiple functions (much longer treatment times; treatment by immersion, etc.).

Further research is in progress to improve the quality of results that can be obtained with the use of these materials in the conservation of Cultural Heritage.

Bibliography

MATTEINI M. 1979, *Il "metodo del Bari" nel restauro degli affreschi*, in Critica d'arte n. 166-168, Firenze, Vallecchi Ed., July-December 1979, 182-184.

MATTEINI M., MOLES A. 1984, *Twenty years of application of "Barium" on Mural Paintings: Fundamentals and Discussion of the Methodology*, in Atti del "ICOM 7th Triennial Meeting-Copenhagen 1984", 84/15, 15-19.

CONVEGNO *Le pellicole ad ossalati: origine e significato nella conservazione delle opere d'arte*. Milano, 25-26 October 1989, Centro CNR Gino Bozza Ed.

II INTERNATIONAL SYMPOSIUM 1996, *The oxalate films in the conservation of works of art*. Milano, Edited by REALINI M. and TONIOLO L. (Centro CNR Gino Bozza), Editeam, Bologna, March 25-27.

CEZAR T.M. 1998, *Calcium oxalate a surface treatment for limestone*, in "Journal of Conservation and Museum Studies", 4, 15-31.

MATTEINI M. 1999, *Gli ossalati artificiali nella conservazione dei dipinti murali e dei manufatti lapidei di natura calcarea*, in "OPD" n. 11, Firenze, Centro D Ed., 30-38.

MATTEINI M. 1999, *The mineral approach to the conservation of mural paintings: Barium hydroxide and artificial oxalates*, in Wall Painting Conference: Conserving the Painted Past: developing approaches to wall painting conservation. English Heritage, London, 2-4 December 1999, 110-115.

MAIRANI A., MATTEINI M., RIZZI M. 2000, Firenze, *L'Eterno Padre di Baccio Bandinelli: fondamenti e tecniche del trattamento di protezione ad ossalato di calcio artificiale di una scultura marmorea*, in "OPD Restauro" 12, Centro Di Ed., 146-150.

MATTEINI M. 2000, *Restaurations récentes des fresques du Quattrocento en Toscane (Piero della Francesca, Masaccio, Benozzo Gozzoli* (abstract), Restauration et recherche scientifique, Louvre, Auditorium, 18 October 2000.

MESSORI M., ZANNINI P., MAIRANI A., MATTEINI M. 2000, *New proposals for the conservation - consolidation of stones and plasters: analytical characterization and trial applications of Ba aluminates*, in Proceedings of the 9th International Congress on Deterioration and Conservation of Stone (vol. 2), Venice, Elsevier Science, 19-24 June 2000, 561-568.

MATTEINI M. 2001, *Künstliches Oxalat bei der Konservierung von Wandmalereien und Kunstwerken aus Kalkstein*, in Konservierung von Wandmalerei - Arbeitschefte des Bayerischen Landesamtes für Denkmalpflege, Bayerisches Bundesdenkmalamt, München 2001, 63-66.

MAETZKE A.M., MATTEINI M., GIOVANNONI S., LAZZERI S. 2001, with the contributions of G. BONSANTI and C. ACIDINI, *Progetto Piero della Francesca. Il restauro della "Leggenda della Vera Croce", Dossier La Leggenda della Vera Croce. Progetto Piero della Francesca. La prima relazione tecnico-scientifica dopo il restauro simbolo del 2000*. Kermes 41, Nardini Editore, January-March 2001, 19-42.

MATTEINI M. 2002, *Mineralische Festigungsmittel zur Konservierung von Objecten aus porosem Material aus dem Bereich der Kunst und Archaologie*, in Mauersalze und Architecturobeflachen, Tagungsbeitrage, 1 bis 3, February 2002, 173.

HANSEN A., DOEHNE E., FIDLER J., LARSON J., MARTIN B., MATTEINI M., RODRIGUEZ-NAVARRO C., SEBASTIAN-PARDO E., PRICE C., da TAGLE A., TEUTONICO J.M., WEISS N. 2003, *A review of selected inorganic consolidants and protective treatments for porous calcareos materials,* in "Reviews in Conservation" International Institute for Conservation of Historic and Artistic Works, n. 4, 13-24.

MATTEINI M. 2003, *Materials and treatments for the conservation of outdoors cultural heritage: a complex task for science and technology*, in Atti del IV Convegno Nazionale sulla Scienza e Tecnologia dei Materiali, 28 June-2 July 2003, Ischia Porto, Napoli, Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali.

CAMAITI M., FRATINI F., MATTEINI M., RESCIC S., TIANO P, *Trattamenti protettivi della Lanterna michelangiolesca delle Cappelle Medicee a Firenze con il metodo dell'ossalato di calcio* (in press).

MATTEINI M., FRATINI F., RESCIC S. 2007, *Carbonatic lithotypes passivated with the "ammonium oxalate treatment": colorimetric and morphological study of treated surfaces*, in *Science and Technology for Cultural Heritage*, 16, 93-105.

Summary

Consolidation and protection are two of the principal kinds of treatments through which the decay of old statues, stone facades, plasters and mural paintings caused by both natural atmospheric agents and, above all in the last five decades, by atmospheric pollution, is faced.
The most traditional approach has been and is mainly based on the use of organic polymeric materials. They offer the advantage of easy application procedures and the possibility to obtain, at short times, very satisfying results. Different is their behaviour at long times. Some drawbacks come out over time both under the esthetical point of view as well as to the durability, compatibility and efficacy. Particularly critical is the situation when porous materials and soluble salts - gypsum above all - are simultaneously present. In such a situation inorganic treatments demonstrate to be much more appropriate. They assure durable and compatible results.
In the present paper two of the most efficient and appropriate inorganic methods are reviewed in detail: the barium hydroxide method, both as desulfating and consolidating agent, and the ammonium oxalate method as passivating agent, consolidant and as a treatment capable of improving the natural colour contrast of the stone, when it is lost due to decay processes.

Riassunto

Consolidamento e protezione sono i due principali interventi con i quali si cerca di contrastare il naturale degrado dei manufatti lapidei sia naturali (statue, paramenti) che artificiali (intonaci, pitture murali, etc.), fortemente peggiorato negli ultimi cinque decenni a causa dell'inquinamento atmosferico. L'approccio più tradizionale e diffuso ha fatto e fa uso di trattamenti basati su polimeri organici di sintesi. Essi presentano i vantaggi della facilità d'impiego e della possibilità di ottenere, a breve termine, risultati assai soddisfacenti. Diverso è invece il comportamento a tempi lunghi. Molti inconvenienti si manifestano con gli anni, sia sotto l'aspetto estetico che sotto quello della compatibilità e dell'efficacia. Particolarmente negati vi sono i risultati con i materiali lapidei porosi e in presenza di sali solubili, soprattutto gesso. In queste situazioni i trattamenti inorganici risultano vincenti. Essi assicurano risultati durevoli e compatibili. Nello scritto vengono rivisti in dettaglio il metodo dell'idrossido di bario, nei due ruoli di de-solfatante e consolidante, e quello dell'ossalato di ammonio, come agente passivante, de-solfatante, consolidante e capace di migliorare la saturazione cromatica dei manufatti trattati.

Résumé

Consolidation et protection sont les deux principales interventions avec lesquelles on cherche de contraster la naturelle détérioration des ouvrages pierreux tant naturels (statues, parements) qu'artificiels (enduits, peintures murales, etc.), fortement aggravés dans ces dernières cinq décennies à cause de la pollution atmosphérique. L'approche plus traditionnelle et diffusée a employé et emploie des traitements basés sur des polymères organiques de synthèse. Ils présentent les avantages de la facilité d'emploi et de la possibilité d'obtenir, dans un bref délai, des résultats assez satisfaisants. Dans des temps longs, au contraire, le comportement est différent. Beaucoup d'inconvénients se manifestent avec les années, tant sous l'aspect esthétique que sous l'aspect de la compatibilité et de l'efficacité. Particulièrement négatifs sont les résultats avec les matériaux pierreux poreux et en présence de sels solubles, surtout plâtre. Dans ces situations, les traitements inorganiques s'avèrent être gagnants. Ils assurent des résultats durables et compatibles. Dans ce texte sont revues, en détail, la méthode de l'hydroxyde de baryum, dans les deux rôles de dé-sulfatant et consolidant, et celle de l'oxalate d'ammonium, comme agent passivant, dé-sulfatant, consolidant et capable d'améliorer la saturation chromatique des ouvrages traités.

Zusammenfassung

Verstärkung und Schutz sind die wichtigsten Stichworte der Restaurationsarbeiten, die darauf zielen, dem natürlichen Verfall der Artefakten aus Stein entgegenzuwirken, sowohl der natürlichen (Statuen, Paramente) als auch der künstlichen (Verputze, Wandgemälde), deren Verfall in den letz-

ten fünfzig Jahren wegen der Luftverschmutzung immer schlimmer geworden ist.
Die traditionellste und verbreitetste Methode basiert auf Behandlungen mit synthetisierten organischen Polymeren, die einfach zu verwenden sind und die kurzfristig ziemlich gute Ergebnisse erzielen. Langfristig ist die Situation ganz anders, mit den Jahren kommt es nämlich zu Schwierigkeiten, was die Ästhetik, die Verträglichkeit und die Wirksamkeit angeht. Besonders negativ sind die Ergebnisse mit porösen Steinmaterialien und mit löslichen Salzen, vor allem Gips. In diesen Fällen sind anorganische Behandlungen die beste Lösung, sie bringen nämlich zu langfristigen und verträglichen Ergebnissen. In der Schrift werden zwei Methoden bis ins Detail betrachtet: die Methode mit Bariumhydroxid, das entschwefelnd und verfestigend wirkt, und die Methode mit Ammoniumoxalat, das passivierende, entschwefelnde und verfestigende Eigenschaften hat und das in der Lage ist, die Farbsättigung der behandelten Artefakten zu verbessern.

Resumen

Consolidación y protección son las dos principales intervenciones con que se trata de combatir la degradación natural de las piezas de piedra, tanto naturales (estatuas, paramentos) como artificiales (enlucidos, pinturas murales, etc.), que en los últimos cinco decenios han empeorado a causa de la contaminación atmosférica. El enfoque más tradicional y extendido siempre ha hecho uso de tratamientos basados en polímeros orgánicos de síntesis. Ofrecen las ventajas de la facilidad de uso y de la posibilidad de obtener, en corto plazo, resultados bastante satisfactorios. También es distinto el comportamiento en plazos más largos. Muchos inconvenientes se manifiestan con los años, tanto bajo el aspecto estético como bajo los aspectos de la compatibilidad y de la eficacia. Son particularmente negativos los resultados con los materiales lapídeos porosos y en presencia de sales solubles, sobre todo yeso. En estas situaciones, los tratamientos inorgánicos dan los mejores resultados. Aseguran resultados duraderos y compatibles. En el escrito se revisan detalladamente el método del hidróxido de bario, en sus dos funciones de desulfatante y consolidante, y el método del oxalato de amonio, como agente pasivante, desulfatante y capaz de mejorar la saturación cromática de las piezas tratadas.

Резюме

Укрепление и защита – вот те два главных метода, направленных на остановку процесса разложения каменных произведений искусства, как натуральных (статуи, облицовка), так и искусственных (штукатурка, настенные росписи и т.д.), степень сохранности которых сильно ухудшилась за последние 50 лет из-за атмосферного загрязнения. Самый традиционный и распространенный подход заключается в использовании при реставрационных работах синтезированных органических полимеров. Эти полимеры выгодны, так как легки в применении и дают возможность получить достаточно удовлетворительные результаты за короткий период времени. Иная ситуация складывается при применении полимеров более длительно. Негативные аспекты появляются по прошествию лет и затрагивают такие проблемы, как эстетический вид, совместимость материалов и эффективность реставрационных работ. Особенно негативными были результаты при реставрации пористых каменных поверхностей, а также тех, в которых находятся растворимые соли, в частности, мел. В этих случаях успешным является применение неорганических реставрационных материалов. В статье детально рассмотрены два метода: гидроксида бария, укрепляющего и выводящего из материалов серу, и гексалата аммония, вещества-пассиватора, выводящего серу, укрепляющего и способного сделать более ярким вид реставрируемых изделий.