THE CONSERVATION OF THE STONE TODAY: CRITICAL APPROACH AND INTERNATIONAL TRENDS

Marisa Laurenzi-Tabasso
Visiting Professor, University "La Sapienza", Rome, Italy

Introduction

The success of conservation treatments depends on several factors: products and tools used, methodology for their application and skill of operators have the highest importance, along with the intrinsic characteristics of the stone, its condition of decay and the environment which the stone is exposed to.

While it is true that bad or unsuitable products and tools give bad results, it is also true that suitable products can have the best performance only when correctly applied by skilled personnel.

The selection of the right products to use is therefore of the utmost importance when planning a conservation treatment.

In 1996, the Freie Universität Berlin organised one of the so-called "Dahlem workshops", to discuss the hottest topics related to the conservation of "our architectural heritage" (Baer N.S., Snethlage R., Eds, 1997). According to the tradition of the Dahlem workshops, four groups of international experts were asked to debate on the most problematic aspects related to the conservation of historic stone structures: 1) "the state of our knowledge of the mechanisms of deterioration"; 2) the possibility of "diagnosing the condition of stone monuments"; 3) the possibility of "ensuring the responsible and effective use of treatments"; 4) the "economic, social, ethical and psychological" aspects related to our perception of "heritage and monuments".

One of the leading questions discussed by group N. 3 was: "How can we select the most appropriate products and methods for conservation treatments with regard to both their short-term and long-term performance"? The conclusions reached by the group were not very optimistic as they stated that "much more research is necessary... to arrive at better methods to predict effectiveness and durability".

Nevertheless, some reference guideline can be suggested to make the evaluation and selection of products and methods more reliable.

Two main paths are available: 1) to survey the condition of monuments treated in the past, for which reasonably good documentation on products and methods used is available; 2) to carry out *ad hoc* tests (either in the laboratory or *in situ* or in both contexts).

Condition surveys of monuments treated in the past

Studying the condition of monuments treated in the past is the closest we can get to a real assessment of the performance of products and methods, after a known time interval and under known environmental conditions.

The *sine qua non* condition is the availability of exhaustive, or at least sufficient, documentation of the works carried out, concerning not only the various treatments but also the conditions of the stone both before and after treatment.

Unfortunately, this approach presents serious difficulties, which go far beyond the mere bureaucratic or logistic problems, such as obtaining permission from the authority responsible for the monument, to carry out an inspection, or providing scaffoldings or lifting trucks that may be necessary to take a closer view of the various parts of the monument.

In fact, a monument in its environment is a complex system, frequently made up of several different materials, often with an only partially known "conservation history". The quantitative interpretation of its condition and its description, for instance through models, is a difficult task.

When a conservation/restoration project is carried out, this generally consists of different treatments, e.g. cleaning, gap filling, consolidation, surface treatments, etc. Each typology of treatment can be carried out using different products, applied in different ways by personnel, perhaps with dissimilar skills.

The long-term performance of the treatment is the resulting effect of the above many factors that may interact through only partially known, or even unknown, mechanisms. The system becomes much more complex to interpret and describe in simple

terms. Despite these difficulties, a number of experimental studies are now available on the results of past conservation treatments, which can provide useful information on the products used.

Two different approaches are possible for surveying, which do not exclude each other:

– Broad range surveys are very useful for setting u databases for first level knowledge (Sattler and Snethlage, 1988 in Germany; Vallet and Vergès Belmin, 1995 in France; Rossi Manaresi et al. , 1995 in Italy; FECS, Anon. 1997, in Italy; Martin et al. 2002 in the UK);

– Detailed experimental studies on specific monu ments for more accurate data.

The published results concerning monuments treated in the last 30 years, show few encouraging results along with others, erratic and more difficult to assess (Laurenzi Tabasso, 2004).

According to these results, inorganic "traditional" treatments (e.g. consolidation with Ba hydroxide, lime shelter coats) resulted to be ineffective or very poorly durable.

All the authors observed that good results were obtained when special care was taken in applying the products. This observation confirms and stresses that the skill of those who carry out the treatments, plays a vital role (fig. 1, 2)

***Ad hoc* tests**

The first systematic tests for the evaluation of products for the conservation of stone date back to the first quarter of the 20th century, but trials and assessment of products proposed for the "hardening" of natural stones were proposed and discussed in scientific papers even since the second half of the 19th century (M. Laurenzi Tabasso and S. Simon, 2006).

It was however during the 1970s, with the better understanding of the decay mechanisms and of the specific aims and requirements of the different conservation treatments, that the assessment of conservation products, before their adoption for any specific monument, slowly started to become a rather common praxis. Since then, an increasing number of scientific laboratories committed themselves to this activity, in order to respond to requests from conservators in the field.

Examining the relative publications, it is now evident that consensus has been reached as to the most significant parameters to be measured, in order to test the effects of a given treatment on suitable stone

Fig.1 . Venice, Scuola Grande di S. Marco, Lunette by Bartolomeo Bon (16th century): detail of showing the decay of the sculptures, with black crusts and heavy losses of the marble beneath. Photo shot in 1974, before the conservation treatmet

Fig. 2. The same detail as figure 1 in 2001, about 25 years after the conservation treatment

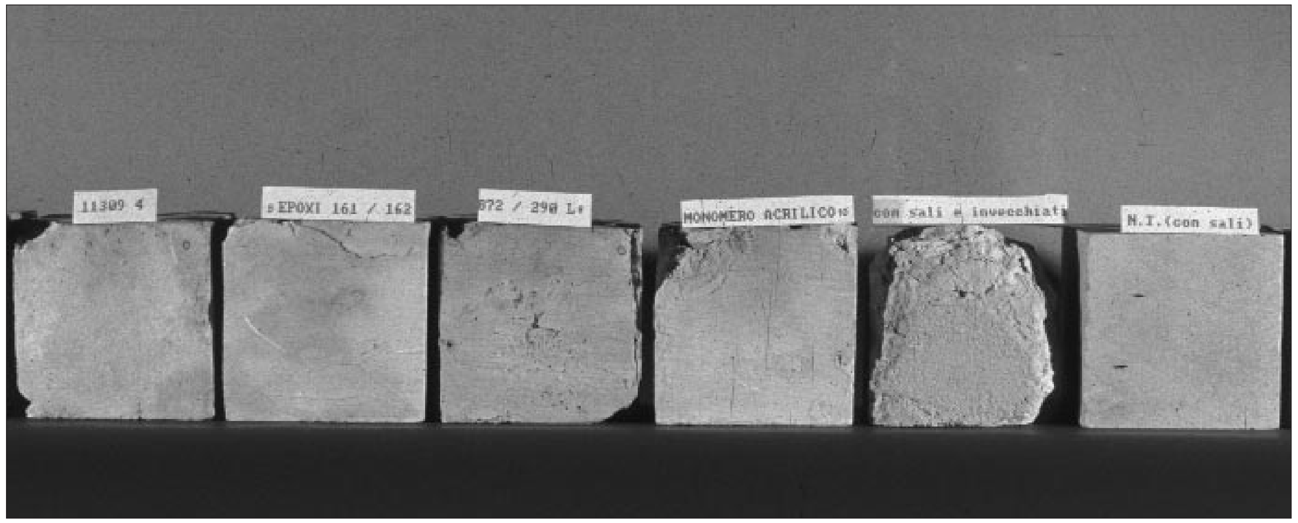

Fig. 3. Artificial weathering by salt crystallization cycles of samples of Lecce limestone. From the left to the right: four samples consolidated with different products, sample untreated, sample untreated and not aged

samples. Unfortunately, internationally agreed standard methods, specific for stone conservation, are still lacking, but it is encouraging to know that the CEN-TC 346 (WG3), a Working Group of the Technical Committee 346, specifically dedicated to the definition of standards in the field of cultural property, is working to this purpose.

At present, each laboratory either uses the methods of its own country or adopts other well-known methods. Therefore, the comparison of results obtained by different laboratories on the same type of product or treatment is not easy, but nevertheless not impossible. Much tougher problems are involved in preparing samples, applying the product or treatment to test, determining the weathering conditions for the assessment of durability and, finally, in establishing criteria for the interpretation of the experimental results. An extensive, critical discussion on these problems and a list of testing methods currently adopted nowadays has been recently published (M. Laurenzi Tabasso and S. Simon, 2006).

In author's opinion, one of the major problems when testing products concerns the weathering conditions to which the treated samples must be exposed, in order to test the durability of treatments.

Three alternatives are available:

1) Laboratory artificial, accelerated weathering: small stone samples are exposed to conditions that try to reproduce the effects of one or more decay factors. Many different parameters are measured before and after the weathering (fig. 3).

2) Natural weathering: suitable portions of a given monument are treated, in order to test the treatment in real conditions. Some parameters are measured by non-destructive techniques, before and after the weathering (fig. 4).

3) Natural weathering: small stone samples are exposed outdoors, on the monument itself or in other

Fig. 4. Natural weathering of water repellent products applied to the Gothic bell tower of the Agrigento Cathedral (Italy). Stone ashlars treated with different products, 5 years after the application. Colour and water absorption by the "contact sponge" method were measured to evaluate the performance and durability of the tested products

well-defined environmental conditions (fig. 5). Many different parameters are measured before and after the weathering. A good example of this last alternative is given by Vallet et al. (1996) on water-repellent products.

The figures show two weathering alternatives: Laboratory samples exposed *in situ*; Laboratory samples artificially aged. Each of the alternatives has advantages and limitations that cannot be discussed here, as they would require a much more detailed treatment. In general, it would be preferable to expose samples to natural weathering conditions whenever the long time required to obtain significant results is compatible with the needs and time limits of specific conservation activities.

"Sample areas" to monitor the treatments performance

A step forward in the assessment of the performance of treatments (which goes beyond the two alternatives "condition survey/ *ad hoc* tests") could certainly be achieved, if a number of "sample areas" were selected on completion of the works. These areas would serve as a reference, a kind of zero point, for a monitoring programme that should be carried out at regular time intervals, in order to detect any negative change. This will also indicate if and when maintenance operations are required.

The sample areas should meet the following requirements. They should be:

– representative of the whole or a part of the monu ment (e.g. the lower parts, affected by rising damp; parts exposed to the north, or to the prevailing wind, etc.);

– easily accessible, possibly without the need fo scaffolding or a mobile lifting vehicle;

– be out of the visitors' reach

– be large enough to enable measurements of severa parameters.

The parameters to measure depend on the specific deterioration factors that could continue to play a role even after the conservation treatment. It is however necessary that non-destructive methods are available to measure the selected parameters.

A basic list to propose would include: surface colour by reflectance spectrophotometry; water absorption under low pressure (using the "Karsten pipe" or the "contact sponge" or an equivalent method); amount of dust deposited per unit surface; amount of water-soluble salts (extracted by applying Japanese paper poultices wetted with deionized water); surface roughness (using a portable rugosimeter); and biological contamination. Other more specific investigations could be added, if necessary, to check specific aspects, such as those related to the presence of fractures or to the adhesion of re-joined parts by ultrasonic techniques.

Furthermore, the monitoring programme must obviously include accurate photographic documentation of the areas, taken in repeatable conditions.

It is, however, advisable that the monitoring protocol is simple enough and not too costly, so as to be feasible with respect to the budget constraints that often afflict conservation activities.

Once the first set of data has been recorded at the conclusion of the conservation project, the same measurements must be repeated periodically and the results compared with the "zero" values. In this way, evaluation of the treatment durability will be less uncertain. Last but not least, the results from monitoring provide essential information for planning maintenance works, as soon as they become necessary.

It is a simple, and not very difficult or expensive proposal, to implement, which however requires the establishment of certain administrative procedures and the participation of a small, multidisciplinary team to inspect the monument and carry out the measurements. The results of yearly monitoring campaigns on a group of Baroque monuments in Lecce (in the Salento region, South Italy), submitted to similar conservation treatments from the end of the 1980s and the beginning of the 1990s, have been recently published (A. Calia et al., 2006). In this case sample areas were not selected soon after the conclusion of the conservation treatments, but only in 2003, when the first campaign started. Among the results, it is interesting to mention those concerning the measurements of the residual hydrophobicity of the surfaces treated with different alkyl-alkoxy-silanes: through the use of the "contact sponge" method (P. Tiano and Pardini C., 2004) on three different monuments, it was measured that the treated surfaces were still more water repellent that the untreated stone and, moreover, the same values were confirmed during the second monitoring campaign, one year later.

Characterisation and quality control for the products to be used for conservation treatments

Along with tests and surveys for the evaluation of conservation products, another important aspect must be considered: their chemical and chemical-physical characteristics.

Products should be properly identified through the description of the chemical nature of the active principle, of its concentration, of the solvent and other "additives", if any. More detailed characterisation obtained through appropriate analytical methods (e.g. FTIR, Proton or silicon NMR, GS-MS, etc.) would be desirable, but they are costly and more difficult to obtain from manufacturers or from wholesale dealers and to be checked by independent laboratories.

The Italian NORMAL Committee, in the year 2000, following a similar approach, proposed a kind of "fingerprint card" of products for the different types of treatment (cleaning, consolidation and surface protection), where the most relevant chemical characteristics and physical-chemical parameters would be indicated by the product vendor. This would have a double advantage: 1) the preliminary selection of products to test, among the many products offered by the market, would be easier and better acquainted; 2) the guarantee that the product eventually purchased by the conservator/restorer keeps the same characteristics as the product submitted to the preliminary tests.

Waiting for official regulations in this sense, it is at least important to inform and warn users (conservator/restorers, architects and archaeologists) on the importance of rejecting products whose composition (at least for the basic components) is not clearly described and declared by the producer and retail dealer (if any).

Present trends

The theoretical approach to stone conservation, as well as its practical implementation through the use of products, tools and methods, evolved tremendously during the last century, especially in the last quarter.

To cite an example of this positive evolution: in 1938, H. Plenderleith had to stop the cleaning of the Elgin marbles in the British Museum as it was being carried out by a museum team of masons using copper scrapers in order to obtain "even white colour" surfaces (Oddy, 2002). Nowadays, nobody would even dare suggest such mechanical tools to scrape the surface of sculptures in a museum collection!

Of the types of treatment, cleaning is the one that has the highest visual impact and has always raised the most heated controversies in the world of conservators and historians (Koller, 2000). Cleaning technology followed the evolution of cleaning concepts and the understanding of decay processes. Consequently, the use of too drastic methods has gradually been eliminated, at least, for important monuments and for sculptures.

Fig. 5. Natural weathering of laboratory samples exposed near the Reims Cathedral (France)

Conservators can now chose from a large range of options for stone cleaning, as regards both equipment and products, due to the ever-increasing demand by users for more cautious and better-controlled systems and thanks to the efforts made by manufacturers to meet those demands.

Many products are available for the extraction of water soluble salts through the application of poultices, ranging from sepiolite, that has been used since the 1960s, to different grades of paper pulp, mixtures of cellulose fibres and amorphous silica.

For mechanical cleaning by sand-blasting, the market offers a range of equipment that works at low, well-controlled pressure and claims to impart a tangential movement to the abrasive powder, in order to mitigate the mechanical impact on the surface to be cleaned. Abrasives of different hardness, size and shape are available, from corundum and quartz sand to glass spheres and calcite (both obtained from crushed limestone and from a chemical process that produces rounded aggregates of micro-crystals that have an even milder impact), just to mention some of the products from which conservators can select those suitable for their specific needs.

The use of already prepared chemical mixtures seems to have declined compared with some years ago, as simple solutions (e.g. ammonium carbonate solution) personally prepared by the user are now preferred. To solve special cleaning problems, ion exchange resins have been in use since the late 1970s and are now also available in mixtures with additives and thickeners that make their application to the stone surface easier and more effective (Guidetti, 2000).

Finally, it is indisputable that, of all the cleaning methods adopted, laser technique represents the most sophisticated one. Proposed for the first time by J. Asmus (Lazzarini, 1973), for many years laser cleaning remained restricted to very specific cases of museum objects, partly due to the high cost of the equipment and the skills required for its safe use, and partly because of doubts being raised on the actual or potential damage to the treated surfaces. But after this slow beginning, with the technological evolution that led to equipment becoming more flexible and easier for the operator (fig. 6), laser application became more and more common, at least, in many European countries. Parallel to the technological evolution, studies and assessments to determine the safest conditions for effective and selective cleaning without damaging the "original" stone surface have been taking place, as numerous scientific papers and the workshops on Laser in the Conservation of Artworks attest (e.g. the LACONA series of international congressess).

Concerning consolidation treatments, products containing Si are the most frequently used. Ethyl silicate or tetra-ethoxy-silane (TEOS), monomer/oligomer, either on its own or mixed with other alkyl-alkoxy silanes, has been the most popular consolidant for at least twenty years, not only for silicate stone but also for limestone and marble. For these carbonatic stones a "conversion treatment" has been proposed, in order to improve the adhesion with the silica polymer and increase the mechanical strength remarkably, through the reaction with ammonium tartrate (Weiss, 2000): the Ca tartrate layer, formed on the calcite crystals, provides – OH groups which can give chemical bonds with silica produced by the hydrolysis of TEOS.

Following a similar approach, the use of alkyl ammonium compounds and of amino-alkyl-alkoxy-silanes to reduce the hygric swelling of clay minerals and as priming agents for alkoxy-silane was studied in Germany for several years and commercial products of this type are already available (Wendler et al., 1991).

It is also worth stressing that a series of products based on TEOS are now on the market, ranging from those mainly based on monomer and oligomers, to the so-called pre-condensed products, up to silica sols. Also available are products with mineral additives (very probably silica) that should work better than "pure" TEOS to fill micro fractures or as binders for gap-filling mortars

Finally, to overcome the rigidity of the silica polymer formed by TEOS, short, linear aliphatic chains are added to the alkoxy structure. The elastic properties are improved as demonstrated by Wendler (1997), who tested treated sandstone samples where "the modulus of elasticity remains relatively low despite the strengthening effect". Also in this case, commercial products are already available.

Another interesting trend is the addition of fluorine to alkyl-alkoxy-silanes to increase the chemical stability, thanks to the high energy of the C-F bond. Products of this type are claimed to be very stable, water-repellent and oil-repellent. Some of them have therefore been proposed also for anti-graffiti use.

The synthesis of more tailored products, where the peculiar characteristics of a given type of polymer (or pre-polymer) are modified and, hopefully, improved by the introduction of functional groups typical of other classes of chemicals, seems to be one of the most popular trends nowadays.

The challenge is to find products that overcome the weaknesses of each of the initial components while still enhancing their strengths.

It is also worth stressing that water based systems, namely water emulsions and micro-emulsions, are becoming more and more common, especially for the protection of surfaces from the penetration of liquid water.

Finally, it is interesting to mention the trend concerning inorganic products proposed for consolidation and/or surface protection. In many countries it is very frequent to protect not only stone ashlars in walls, but also sculptures with a non-transparent lime coat (Nimmrichter J., 2001). Even if the durability is not very good, the protection can, however, be ensured by frequent maintenance and repeated applications of the coat. In other countries, on the contrary, lime coating is much less frequent or even controversial. An example of the latter is provided by the "Palazzo dei Diamanti", one of the most famous Renaissance palaces in Ferrara (Italy), designed by architect Biagio Rossetti. The two facades, made up of Verona limestone and other compact limestones, have a very notable "dog-tooth" decoration and are crowned by a cornice in cotto. Some remains of the original lime plaster were observed on this cornice during the restoration works carried out during the late 1980s. On the basis of archival documents, the relevant bibliography, stylistic studies and the results of laboratory analyses of plastered cotto samples, the local Superintendence decided to apply a new thin lime coat to restore the chromatic "continuity" of the cornice (Di Francesco, 1991). The decision raised a storm of tough protests, not only by a group of intellectuals and architects but also among the local non-specialist public, so that the problem had to be discussed by the relevant committee in the national parliament! This is just a further example of the fact that the adoption of technical solutions is never "solely" a technical problem!

Conclusions

The discussion on the present approaches and trends in stone conservation given in the previous chapters is, by no doubt, only partial and not exhaustive as many aspects were not included (such as the problems of gap filling, joining pieces and addition of new parts to old, already weathered stones), and other products and techniques were not mentioned.

Fig. 6. A modern Laser equipment with optical fibres for the transmission of radiation

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However, even within these limits, from the above discussion it is evident that in the last decades the conservation of stone did important steps forward. There is much more to study and understand in order to optimise products and techniques for treatments, but the panorama is fairly good.

The experience gained up to now tells us that the KEY WORDS for successful treatments are: accurate diagnosis, careful selection of products, skilful application by conservator/restorers, regular monitoring and maintenance.

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