ASSESSMENT OF CONSERVATION TREATMENTS ON PADUAN NANTO STONE MONUMENTS: NEW FINDINGS

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Abstract
Since 1975, in Padua, the external surfaces of many buildings made of Nanto Stone have been restored using silicone polymers.

The development of efficient long-term on-site monitoring procedures to evaluate restoration of historic buildings and monuments is useful for conservation experts, as it is often necessary to assess if treatment was properly carried out or must be repeated on a previously treated but later weathered surface. Different cases are compared and a useful tool for planning maintenance operations is thus provided.

Information on possible bond formations between consolidation and stone materials was collected with FT-IR spectroscopic analysis. Literature data on chemical and/or chemico-physical interactions between porous stone and polymer product are scarce.

Samples were collected and examined, and polymer presence, distribution and morphology were detected to evaluate the condition of treated surfaces. A scanning electron microscope equipped with an energy dispersive micro-analyser (SEM-EDS) examined polymer distribution and penetration depth in treated samples.

Keywords: Nanto stone decay, soluble salts, conservation treatments

1. Introduction

Many types of polymers and protective coatings are commonly used to counter stonework degradation due to natural weathering. Attention should focus on the durability of these synthetic products and their side-effects on many materials.

Although there are many reports on the performance of water repellents and consolidants in laboratory-based situations (Favaro et al., 2006, 2007), conservation scientists should be aware that results obtained from stone samples treated in a laboratory are not necessarily the same as those obtained on actual buildings.

Recently, systematic analyses have been carried out on monuments (Favaro et al., 2001, Favaro et al. 2005). The literature on this subject reveals an array of previous research and published works that generally focus on laboratory-based and destructive site methods, and there are only a few standard recommendations for non-destructive site assessment of surface-treated structures. In addition, many of these are based on the use of only one test method, which can only provide a partial and sometimes ambiguous picture of treated surface conditions. Since procedures and methods for evaluating interventions do not yet exist, research aims at applying new techniques and methodologies to assess restoration effectiveness and, in particular, at carrying out
tests certifying that the material to which they are applied will not be subjected to irreversible damage. The final goal is to develop efficient long-term on-site monitoring procedures to evaluate restoration of architectural and monumental artworks. There has been considerable interest in developing methods that enable conservation authorities to establish when treatments have been properly applied and when already treated but subsequently weathered surfaces need to be treated again. Different cases may be compared and a useful tool for planning restoration schemes is thus provided.

Since 1975, in Padua, the external surfaces of many buildings, made with Nanto Stone of the Berici Hills have been restored using silicone polymers. One of them is the Loggia Cornaro, undoubtedly one of the most important monuments restored in this period. Twenty years after the first intervention and four after the latest one, we evaluated both the state of conservation and residual efficiency of treatments. The Loggia Cornaro (Fig. 1a), built in Nanto Stone in 1524 by the famous architect Giovanni Maria Falconetto, is one of the most important historic buildings of Padua.

2. History of treatments and forms of decay

The Loggia Cornaro was restored twice, in different stages, between 1979 and 2003. Although polysiloxane resin was used each time, the actual type changed according to market availability. Experimental laboratory and on-site tests were carried out to identify the most suitable product to be used for consolidation purposes. Work started on the lower outer part of the monument, which was treated with a type of methyl phenyl siloxane (trade name Rhodorsil 11309 by Rhone Poulenc) and provided good results. In 1989, on the basis of these results, a new conservation intervention was planned. This intervention focused on the severely deteriorated areas of the upper part of the monument, and included structural work and roof repair to prevent water leaking inside. In the latest restoration work, Rhodorsil RC-90 (by Rhone Poulenc, now Rhodia) was used, and work ended in 2003. In all phases, the method adopted involved:

- Pre-consolidation with Rhodorsil 11309 (or RC90) spray applied to surfaces showing decay, spalling and crumbling, with subsequent application of Japanese paper;
- Fixing of major fragments and spalls by epoxy resin injections;
- Brushing down of superficial deposits with soft brushes and/or local vacuuming;
• Consolidation by slow percolation of Rhodorsil 11309 (or RC90) solutions in toluene, alternated with prolonged pure solvent treatments to increase depth penetration;
• Removal of excess resin from the surface with low boiling point solvents;
• Deposit removal and discoloration reduction with aero-abrasive systems;
• Stucco work with a mixture of lime, rock dust and sand.

Macroscopic evidence showed that the most severely deteriorated area was the lower part of the monument, on which we focused for treatment evaluation. It must be noted that architectural elements had also been badly damaged, and that this had in fact occurred before restoration work began. Photographs taken before and after the intervention showed that no recent decay had occurred. The monument is oriented south and, except for some protected areas, is exposed to the rain. Before restoration, some deterioration forms such as spalling, scaling and crumbling were observed in the most exposed areas, while the sheltered areas were covered by thick black crusts. There was no evidence of rising damp along the entire base of the wall nor was there any discoloration. The surface showed several micro-cracks which sometimes evolved into spalls. Damp had given rise to a green biofilm on small portions of the east and west walls and particularly in the sheltered spots. In some areas, thin scales had become detached, revealing a powdery white layer underneath.

3. Sampling, analytical techniques and methodologies

After careful macroscopic observation based on the European guidelines CEN TC 346 for conservation of cultural property, several micro-flake samples were taken from many different areas of the monument, especially from the façade that was the most interesting area for evaluation purposes. Surface samples were collected by scraping off damaged layers, removing fragments of rock, and drilling dust at different depths (fig. 1b).

The following methodologies and analytical techniques were used:
i) Analyses of thin sections provided petrographic characterisation of stone and textural parameters;
ii) X-ray power diffraction (XRPD) was performed to establish the mineralogical composition of the bulk samples and the insoluble residue;
iii) A scanning electron microscope equipped with an energy dispersive micro-analyser (SEM-EDS) was used to examine the distribution and penetration depth of polymers in treated samples;
iv) X-ray fluorescence (XRF) calibrated with standard samples, carried out chemical analyses to determine element concentrations in bulk samples;
v) FT-IR spectra of the samples in the wave-number region 480-4000 cm\(^{-1}\) were obtained by the KBr method .
vi) A porosimeter measured total porosity and pore size distribution.
vii) Ion chromatography was performed to measure anion concentrations of sulphates, oxalates, nitrates and chlorides.

4. Results
4.1 Mineralogic-petrographic characterisation of stone

The samples were mainly composed of calcite; XRF shows average CaO values of 40.52%, although proto-dolomite, gypsum and traces of quartz and K-feldspar were also detected (Table 1). The XRD of the insoluble residue (17-19%) showed K-feldspar, goethite, smectite, illite, or mixed-strata smectite-illite, quartz and traces of probable chlorite.

Table 1. Mineralogical composition of samples from the façade and lower inner section of the Loggia Cornaro.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mineralogical Composition</th>
</tr>
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<tbody>
<tr>
<td>LC2</td>
<td>Calcite, Gypsum, Quartz, traces of Feldspar</td>
</tr>
<tr>
<td>LC4</td>
<td>Calcite; Quartz, traces of Feldspar</td>
</tr>
<tr>
<td>LC7</td>
<td>Calcite; Quartz, traces of Feldspar</td>
</tr>
<tr>
<td>LC8</td>
<td>Calcite, Quartz</td>
</tr>
<tr>
<td>LC9</td>
<td>Calcite, Gypsum, Proto-dolomite, traces of Quartz</td>
</tr>
<tr>
<td>LC11</td>
<td>Calcite, Gypsum, traces of Quartz</td>
</tr>
<tr>
<td>LC12</td>
<td>Calcite, Gypsum, Proto-dolomite; traces of Quartz</td>
</tr>
<tr>
<td>LC12b</td>
<td>Quartz, Calcite, Hatrurite, traces of Talc</td>
</tr>
<tr>
<td>LC13</td>
<td>Calcite, Quartz, Proto-dolomite, Gypsum, traces of Feldspar</td>
</tr>
<tr>
<td>LC17</td>
<td>Calcite, Gypsum, Proto-dolomite; traces of Quartz</td>
</tr>
<tr>
<td>LC18</td>
<td>Calcite, Gypsum, traces of Quartz</td>
</tr>
<tr>
<td>LC1 residue</td>
<td>K-feldspar, goethite, smectite, illite, or mixed-strata smectite-illite, quartz</td>
</tr>
<tr>
<td>LC13 residue</td>
<td>K-feldspar, goethite, smectite, illite, or mixed-strata smectite-illite, quartz</td>
</tr>
</tbody>
</table>

The monument is made of Nanto Stone, as identified by petrographic characterisation, composition and percentages of insoluble residue, and chemical analyses of bulk rock. Nanto Stone is a yellowish-brown, marly-arenaceous limestone of the Middle Eocene, outcropping near Vicenza and quarried along the slopes of the south-western sector of the Berici Hills. All the stone used for the Loggia Cornaro probably comes from the same quarry, although the different decay patterns observed in the lower and upper parts -built in two different periods- indicate that the layer of rock used was different. In particular, the upper part was probably built with stone from a higher stratigraphic layer, poorer in clay minerals due to the minor influence of the Alpone Chiampo graben, which was active during the depositional period of Nanto Stone (confirmed by SEM results on thin sections). Fig. 1a shows the two typical features of stone from the upper and lower parts of the façade, respectively. Numerous deep micro-cracks parallel to the outer surface were associated with higher quantities of clay minerals and caused the most deterioration.

4.2 Porosity and pore size distribution measurements

Fig. 2 shows measurements of total porosity of treated, untreated and quarry samples (Nanto Stone) and comparison of pore size distribution of the same samples.
Results reveal that the monument’s untreated stone had total porosity values of approximately 20.5 %, i.e., lower than today’s quarried stone (25.34±1.52%). The higher porosity of the Loggia samples may be caused by deterioration phenomena. A substantial decrease in total porosity was observed in treated samples of the façade, especially sample LC9, due to its semi-sheltered position. Sample LC8 had an even lower value, despite being sampled in an exposed area. The relatively high value of sample LC14, belonging to the upper part (which seemed well protected in previous tests) may be due to its more exposed position (explained by many nearby cracks). Pore distribution range results indicated that, after treatment, the micro-structural characteristics of the stone changed with respect to those of untreated and quarry specimens. A shift towards smaller pore radius was observed in treated samples (more visible in samples LC8 and 9), perhaps due to film formation on coarse pore surfaces. Here, increased micro-porosity in treated samples was observed. Average pore diameters were also smaller, indicating accumulation of consolidation materials in the stone pores.

The pore size distribution of quarry samples is unimodal and mainly centred on smaller pores, while samples from Loggia Cornaro have bimodal pore size distribution with the first peak on micro-pore intervals and a second one in the range between 20 and 40 µm. These differences may either be due to deterioration, which increases the number of larger pores, or to the detection range of the porosimeter measuring pore radius >220 µm which, before treatment, could not be detected as the radii were too large. The formation of films reduced the radii, enabling us to identify them. The second hypothesis regarding the porosity observed in microscopic analyses of the Nanto Stone quarry samples seems less probable, although the formation of large pores due to decay...
processes is acceptable. Bulk density values showed an increase after treatment, indicating improved cohesion.

Mercury intrusion porosimetry was applied to examine changes in total porosity and pore distribution ranges of samples between treated surfaces and untreated and quarry samples. Consolidation materials aim to change the micro-structural characteristics of stone and possible modifications are very important, given the relationship between pore structure and the susceptibility of stone to specific forms of deterioration. A shift in pore size distribution towards smaller pore radii and a percentage reduction of large pores were observed in treated stone samples and attributed to consolidant deposition on pore wall surfaces (formation of films). According to some authors, reduction of fine pores is desirable.

4.3.1 SEM observations
4.3.2 SEM observations on bulk samples.

Samples were collected and examined, and the presence, distribution and morphology of polymers were analysed to assess the condition of treated surfaces and their condition.

Samples could be divided into two main groups:

i) Samples coated with a wide, uniform, thick layer of resin (confirmed by EDS) visible in both SEI and BEI images. The latter clearly discriminate between the inorganic substrate (light grey, due to its high average atomic number) and siloxane (grey, due to its low average atomic number). For example, Figs. 3 and 4 compare BEI and SEI images of the same area, respectively. As regards the morphology of the polymer surface, several cracks were noted.

ii) Samples coated with a wide, uniform but thin layer of resin. BEI images do not show this coating, although EDS analyses do reveal the abundance of Si on all surfaces. Only SEI images confirm the presence of thin coatings, because carbonate crystals have a smooth surface appearance due to the thickness of the surface layers (Figs. 5, 6).

The first group is smaller, as only 20% of all samples taken from semi-sheltered areas reveal a thick layer of resin.

Detailed examination of polymer surfaces revealed cracks (Figs. 7, 8) of various lengths as well as small particles. Micro-analyses of these materials showed S and Ca as main elements, clearly related to gypsum (Figs. 9, 10).

4.3.3 SEM observation on cross-sections

BSE analyses were carried out on cross-sections of surface samples. In all samples, the deterioration pattern of the Nanto Stone produced very long, deep, open cracks as well as micro-cracks, usually parallel to the outer surface. The frequent presence of clay minerals confirmed that expandable clays are among the most important causes of decay in this type of stone. In the examined samples, SEM discriminated between polymer and inorganic matrices, characterised, as previously described, by different average atomic weights, and provided an overall picture of the performance of the applied product. All sections revealed an outer layer of Si composition, i.e., polysiloxane, ranging in thickness between 10 and 100 µm. However this layer was not found in all samples, and its thickness and continuity on the surface
were often irregular (Figs. 11, 12). Although evidence of resin penetration inside the stone was found in several samples, only some cracks were filled. In some samples, the penetration path was visualised by means of X-ray maps on cross-sections of Ca and Si as markers of CaCO$_3$ substrate and silicone products, respectively. These images showed accumulation inside some pores and a higher content of silicic components on the outer resin layers (Figs. 13, 14). Examples of resin filling deep cracks are shown in Fig. 15.

Fig. 3. BEI image: thick resin coating on stone surface.

Fig. 4. SEI image: morphology of thick resin coating on stone surface.

Fig. 5. BEI images of surface with thin polymer layer. Sample LC17.

Fig. 6. SEI images: a smooth appearance of calcite crystals, due to polymer layer.
Fig. 7. BEI image of polymer cracks of sample LC 9

Fig. 8. SEI image of polymer microcracks

Fig. 9. BEI image of polymer and gypsum particles of sample LC 19.

Fig. 10. SEI image of polymer and gypsum particles of sample LC19.
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Fig. 11. BEI image of cross-section of sample LC18. Note external resin layer on stone surface. Resin penetrated in a crack under surface.

Fig. 12. BEI image of cross-section of sample LC16. Crack in depth filled with resin.

Fig. 13. BEI image of mapped area of sample LC18.

Fig. 14. SiKα map of sample LC18. Note superficial Si-rich layer.

Fig. 15. BEI image of mapped area of sample LC24.

Fig. 16. SKα map of sample LC17
In some sections the resin coating was found under layers of gypsum (Fig. 15, 16), and in others both gypsum and resin were found in the same areas. Cross-sections of treated specimens proved to be particularly good in detecting polymers. The technique distinguished polymer distribution from the inorganic matrix. Cross-sections are very useful in observing polymer and substrate relationships.

5. Conclusions

In situ evaluation was performed on the Loggia Cornaro four years after restoration work was performed, and conclusions are summarised below.

Firstly, a series of complementary techniques was used to establish the occurrence and distribution of treatments. The most immediate informative parameters used in performance evaluation are in situ water capillary surface absorption and polymer distribution inside the stone. Except for a few local variations, the absorption tests carried out on the Loggia Cornaro yielded results which are generally within acceptable ranges. Applying the test results, initial judgements can be made as to whether surfaces were treated or if previously treated surfaces are no longer waterproof.

A shift in pore size distribution towards smaller pore radii, and a percentage reduction of larger pores were observed in our treated stone samples and were attributed to the accumulation and penetration of consolidants in the stone pores (formation of films or precipitation as amorphous SiO$_2$).

Consolidant penetration depth and new formation of decay products showed that Si concentration generally decreases from the outer surface inwards. Si concentrations were very high on the surface and remained quite high down to a depth of 300 µm.

In the Loggia Cornaro, the evaluated penetration depth is more than 2 mm. Although this is an important factor, also the inside of pores and cracks that should be filled with polymers is.

This is a crucial problem, because although many polymer products available on the market can penetrate in depth, they cannot fill all spaces, and their function is thus compromised. As regards Nanto Stone, the occurrence of several empty fractures at different depths cannot be associated with the type of product used, but to deterioration patterns in the stone. This should be taken into account when planning conservation work. Results clearly show that consolidation of these fissures cannot be made directly from the surface, probably because the cracks are not contiguous. A special approach of indirect consolidation is required, whereby micro holes are drilled to provide specific access points to the stone interior.

Cross-sections revealed residual amounts of still active consolidants and protective coatings as well as small amounts of gypsum, which was probably ineffectively removed before consolidation. Cross-sections of treated samples proved to be particularly useful in detecting the type of synthetic products applied. Distribution and changes in structure and adherence to the substrate were precisely assessed.

Polymer applications certainly reduced the deterioration processes of stone materials, but could not stop them completely. Although decay caused by atmospheric pollutants was greatly reduced, the penetration of salt solutions may seldom be prevented, and this is precisely what causes disruption within the pore structure as a consequence of mechanical stress.
These results also show that areas of the monument affected by water leaks are subjected to spalling, and it is now time to plan new restoration work. The results obtained are still within acceptable values.

The test methods used are complementary and adequate for a complete overview of consolidant performance. They are useful in verifying the present state of conservation of artefacts and therefore helpful in assessing the performance of applied polymers in order to propose suitable conservation schemes.

All these considerations and results are very interesting in evaluating the performance of polymers applied to stone artefacts, because there is a clear decrease in their consolidant/waterproofing behaviour. We suggest that conservation work should be carried out in the near future by applying a new protective coating on the entire surface of the monument and by consolidating the stone in areas that are not in a good state of conservation. We do realise that this clashes with the difficulty and/or impossibility of removing them from the substrate for new restoration. When planning new restoration work, a number of issues must therefore be taken into account, such as the massive presence of insoluble polymers extensively distributed both inside and on the stone surface, the amount of insoluble material and the ongoing deterioration processes of the stone.

References