

THE SURFACE CONSERVATION PROJECT OF THE ACROPOLIS MONUMENTS: STUDIES AND INTERVENTIONS

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ABSTRACT:

The deterioration of the Acropolis monuments' surface can be attributed to a combination of mechanical, physical and chemical factors. The current conservation project carried out by a team of conservators and marble masons aims to the consolidation and the protection of the marble surface. The methods and the materials used are presented in this paper. A special research project was the cleaning of the Parthenon West Frieze by means of a prototype laser system designed and developed for this purpose. The atmospheric depositions and encrustations were removed in a controlled and safe way while precious details and traces of colour and ancient tools were revealed.

1. THE DETERIORATION

The Acropolis monuments are constructed of Pentelic marble with low porosity but in the case of deteriorated marble it comes up to 2,1%. Besides calcite, which is the main constituent of marble, quartz, iron oxides, clay minerals and ferrous sulphate may be found either as interspersed areas or in the form of veins. The deterioration of the marble is attributed to a combination of mechanical, physical and chemical factors along with the atmospheric pollution, the microclimate and the microstructure of the marble. Multiple cracks are related to aluminosilicate inclusions, the destructive ancient fire (3rd Century A.D.), the earthquakes, the explosion of 1687 and the presence of iron clamps and dowels (Korres, 1983). The isolated or combined action of the acid rain, mechanical and biological factors affects the marble surface and leads to damages like sugaring, cracking, flaking, detachment of fragments and the reduction of the monochromatic surface layers. A layer of gypsum formed by the reaction of sulphur dioxide covers the areas not exposed to the rainwater. The exposure of monuments to atmospheric pollutants and suspended particles modifies their colour in places which are not washed by rainwater. Deposition of dust and soot particles, in conjunction with the phenomena of calcium carbonate recrystallization, create loose deposits and black crusts. The presence of various microorganisms (biodeterioration) affects the marble and the long-term effectiveness of the conservation materials. Mortars based on Meyer cement (composed of magnesium oxide and magnesium chloride), used in previous conservation campaigns also contributed to the surface deterioration.

2. THE CONSERVATION PROJECT

The current conservation work focuses on the marble surface of the architectural members either in situ or after they have been dismantled and has, since 1986, constituted a separate project, conducted and coordinated with the structural restoration projects. The works executed today on a broad scale on all the

Acropolis monuments (the Parthenon, the Propylaia, the Erechtheion and the Temple of Athina Nike) can be divided in rescue and systematic interventions. All the materials used are inorganic, reversible and compatible with the marble. The rescue interventions include the preconsolidation of the deteriorated surface and the "facing" of friable areas with Japanese paper, gauze and methylcellulose adhesive (Figure 1). Wherever the marble exhibits sugaring, the surface is consolidated by being sprayed or impregnated with a solution of lime with the addition of calcium carbonate for the faster carbonation of the material. It is noted that about forty sprays are adequate for surface consolidation. The cracks and the interior gaps are cleaned using air or deionized water and hydrogen peroxide.



Figure 1: Consolidation of the surface



Figure 2: Injection of grouts



Figure 3: Reattachment of fragments

They are then filled by injecting according to the strength required, cement, cement-lime or hydraulic grouts of high injectability consisting of white Portland cement, fine-grained pozzolana (Santorin earth) and water in a ratio of 75:25:80 (Figure 2). The grout is stirred in an ultrasonic agitator and applied to the cracks through small tubes. The large fragments that had become loosened or detached from some blocks, are reattached with white cement and reinforced with titanium dowels wherever this is considered necessary. When small flakes are to be attached, a mortar of reduced strength is used consisting of cement and lime with the addition of calcium carbonate in order to accelerate the hardening of the mortar (Figure 3). For shallow cracks as well as after attachments or injection grouting, the joint is sealed with a mortar made of cement, lime, quartz sand and iron oxides as pigments for the chromatic harmonization with the ancient marble. The mortar is in a ratio of 1:3 binder to aggregate. The brass pins are removed and replaced, if needs be, by new pins made of titanium. The old mortars were removed using masons' and dentist's tools. The whole process is well documented through a series of photographs and graphic mappings before, during and after treatment of individual areas.

3. RESEARCH PROJECTS

Interdisciplinary collaboration with scholars in other fields – geologists, biologists, physicists and others had fruitful results in the improvement of the conservation methods and materials and the solutions of many problems. Among others:

1. Through research carried out at the National Technical University of Athens, using the model of galvanic cell, the mechanism of the marble sulphation was determined. It was found that the gypsum layer formed preserves details of the surface, therefore it must be preserved rather than removed. Furthermore a method was developed for consolidating the details by the inversion of gypsum back into calcite, which is the main component of marble (Skoulikides, 1983).
2. The method of increasing the mechanical resistance of lime by adding crystallization seeds was developed (Skoulikides, 1991).
3. A new material for protecting the surface from atmospheric pollution was designed. It is based on n-semiconductors and has already been applied successfully on the Acropolis. The artificial patina applied on the new marble used during the restoration is based on the same material with the addition of iron oxides (Skoulikides, 1992).
4. Biocides suitable for the fragile marble surface have been found to cope with the biodeterioration phenomenon.
5. An innovative laser methodology was developed for the cleaning of the marble surface (Frantzikinaki, 2004).

4. THE LASER CLEANING OF THE PARTHENON WEST FRIEZE



Figure 4. The Parthenon West Frieze on the monument

The Parthenon West Frieze, thought to be sculpted by Pheidias during the period 442 – 438 B.C. It was placed above the architrave of the opisthonaos and consists of sixteen blocks depicting the beginning of the Panathenaic procession which is the start of the Athenian cavalcade. The first two blocks are among the parts dismantled by Elgin, now in the British Museum. The fourteen blocks remained *in situ* until 1992 – 93 when they were removed during the restoration carried out on the temple. Two monochromatic surface layers are preserved and cover the 33 % of the sculptured surface of the West Frieze. These layers are distinguished as a) the lower orange-brown layer with a thickness of around 30 – 100 μm is well-adhered to the marble surface (Galanou, 1994). Its main components are calcium oxalates, calcium phosphates and iron oxides and it is described as the “epidermis” (skin) or “patina” encountered on many Classical and Roman monuments and b) the outer beige layer covers the epidermis and is described as the ‘coating’ (Kouzeli, 1989). According to this analysis, it is a thin artificial layer (about 80 – 120 μm thick), composed mainly of calcium carbonate. Both of these surface layers preserve original tooling traces and relief details which are observed to indicate the original surface. Thus, they document and are characterized as part of the original historic fabric and were not to be removed during the cleaning process. The presence of sulphur dioxide (in the atmosphere) led to the formation of a gypsum layer, which up to a certain thickness preserved details of the relief and it was important that it was not removed during the cleaning process.

The deposition of soot and suspended particles covered the surface in places, not directly exposed to rainwater. Observations indicated that the formation of black crust increased significantly after the 1950s as a result of rapid industrialization in Athens. The layers of the deposits varied in thickness and composition, and they were classified in the following categories: loose deposits up to 100 μm thick consisting mainly of gypsum, calcite, organic compounds and traces of other minerals and metals, homogenous compact crust with good adhesion to the surface, up to 150 μm thick and dendritic black crust of significant thickness consisting of recrystallized and reprecipitated calcium carbonate in dendritic formation and a mixture of gypsum, aluminium silicate compounds and other atmospheric and mineral particles (Figure 5).

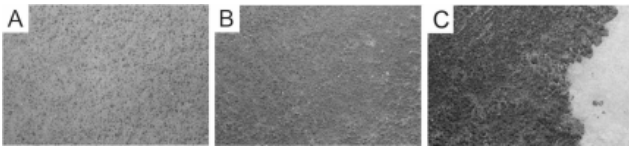


Figure 5. A. loose deposits, B. homogenous compact crust C. dendritic crust.

4.1. Evaluation of the cleaning methods

Following an assessment of all the currently known cleaning techniques, four were deemed to be the most promising for further study. These were a) application of absorptive poultices, b) microblasting, c) inversion of the gypsum layer into calcite and d) laser cleaning (Skoulikides, 1994). A research project was then implemented in order to provide a comprehensive comparative study of the four cleaning techniques. The evaluation of the four cleaning methods was conducted by gradually approaching the real conditions of the West Frieze. Preliminary applications of the cleaning methods were initially undertaken on newer marble complements dating from the 1960s (attached on the West Frieze blocks in order to replace missing parts) and which had been exposed to the same atmospheric pollution as the ancient surface. The cleaning tests were completed on representative surfaces of sculptures and architectural members of the Acropolis monuments and finally on the West Frieze itself. Quantitative and qualitative tests were conducted to evaluate the effects of the four cleaning methods both on the substrate and the black crust before and after cleaning, for example: colorimetric measurements for the recording of the chromatic variations, observations of thin cross-sections under a polarizing microscope so as to examine the stratigraphy of the substrata and the deposits, stereo microscopic observations, XRD and SEM-EDAX analyses to assess the composition of the crust before and after cleaning and finally artificial ageing tests.

Throughout this research project, it was noted that the efficiency of the applied cleaning methods might be dependent on the thickness and the formation of the encrustations as well as on the type of substrate.

Laser cleaning was investigated in collaboration between the Acropolis Restoration Service (YSMA) and the Institute of Electronic Structure & Lasers, Foundation for Research & Technology (IESL-FORTH). Following experiments laser cleaning was selected as the method which met all the criteria for safe and effective cleaning (Amoroso, 1983). It was also proven to efficiently remove all types of encrustation without leaving any by-products on the stone surface. The laser cleaning methodology offered unique features such as high selectivity and precision, while the developed prototype laser system was proven to be fully controllable and ergonomic.

4.2 The laser system developed for the cleaning process

After experiments to all the possible substrates and encrustations present on the surface of the Acropolis monuments, the IESL-FORTH research team suggested combining the action of the two discrete laser ablation mechanisms. This was accomplished by the simultaneous use of two laser beams of different wavelengths, whose pulses were temporally and spatially overlapped. According to this scheme, a prototype hybrid laser system was developed by the IESL-FORTH (EP1340556A2) which in its initial state was tested successfully on the Acropolis site (Figure 6). The laser system developed was a Q-switched Nd:YAG system emitting at the fundamental (1064 nm) and the third harmonic (355nm), with

the option of using the two laser beams individually or in combination and in various ratios of energy densities. This made possible to combine different cleaning methodologies to adjacent areas of the surface to be cleaned with no profound colour or structural differences.



Figure 6. The laser system

4.3 Laser cleaning of the West Frieze

In terms of the substrata and the crust morphology, the following cases could be distinguished on the West Frieze surface: loose deposits of soot and suspended particles on the marble substratum, homogenous compact crust with good adhesion to the marble surface, dendritic crust on the marble substratum, loose deposits on the monochromatic surface layers, homogenous compact crust on the monochromatic surface layers and dendritic crust on the monochromatic surface layers.

Cleaning by means of infrared radiation is based on the differential absorption of the radiation by the calcitic substrate and the intermediate gypsum layer. The energy threshold for the removal of the superficial layer is significantly lower than that required to remove the substrate material. In particular the energy threshold for the removal of black crust is about 0.8 J/cm² while for the Pentelic marble was estimated to be 3.5 J/cm² (Marakis, 2003). This ensures the selective and self-limiting removal of the encrustation without the slightest damage to the marble or the gypsum layer. Moreover, the cleaning depth is controlled by varying the number of pulses.

It has been observed that in certain cases (i.e loose deposits and thin compact crust on marble substrate), surfaces cleaned by infrared radiation only, may appear discoloured, towards yellow hue (Skoulikidis, 1995). It should also be mentioned that no discolouration could be noticed when infrared radiation was used to remove encrustation from monochromatic surface layers (Pouli et al., 2005). On the other hand the use of ultraviolet radiation alone may result into greyish discolouration on all substrates and into non-homogeneous cleaning, which gets very significant in cases of relatively thick encrustation (Papakonstantinou, 2003).

The simultaneous action of the two wavelengths remove the deposits in a controllable way, with no discoloration or surface damage phenomena as proved by physicochemical analyses performed on architectural members of the Parthenon during preliminary cleaning tests. During these preliminary cleaning tests laser parameters such as the energy fluence values for each case of crust and substrate as well as the appropriate number of pulses for a desirable depth of cleaning were determined in detail. A series of tests have also been performed in order to decide the optimum ratio of ultraviolet to infrared energy densities towards a satisfactory cleaning result ($F_{UV}/F_{IR}=0.2$ up to 0.33).

The cleaning efficiency (rate and degree of cleaning) is enhanced by applying a thin film of water saturated with calcium carbonate during cleaning with the use of infrared radiation. The water, strongly absorbed by the dirt deposits, penetrates into the micropores of the black crust and when laser irradiated enhances the ejection of the encrustation material through its rapid heating and vaporisation (Cooper, 1998). The presence of calcium carbonate helps the consolidation of gypsum layer on the marble surface. In cases where cleaning is achieved through the combination of ultraviolet and infrared radiation the use of water is not recommended as it may result into non controllable and thus in-homogeneous cleaning.

4.3.1 Marble substrate

The combination of the infrared and ultraviolet radiation at relatively low energy fluences ($F_{IR} = 0.3 - 0.5 \text{ J/cm}^2$ and $F_{UV} = 0.08 - 0.2 \text{ J/cm}^2$) on loose deposits was successful without any discoloration to the underlying marble surface (Figure 7). However, in some cases, where the substrate is non-homogeneous due to deterioration, loose deposits remain among the marble crystals. In these cases, infrared radiation alone at higher densities about $0.6\text{-}1 \text{ J/cm}^2$ was applied selectively on the non-cleaned areas.

Combination of the infrared and ultraviolet radiation at relatively higher energy densities ($F_{IR} = 0.4 - 0.8 \text{ J/cm}^2$ and $F_{UV} = 0.1 - 0.3 \text{ J/cm}^2$) is also used for homogenous compact crust, with good adhesion to the marble surface.

Application of the combined infrared and ultraviolet laser beams on dendritic black crust had no result at low fluences. When the fluence increased significantly, the cleaned surface appeared rough and non-homogeneous with visible remains of the black crust. Most acceptable results were obtained with infrared laser pulses at high-energy fluences in the range of $1\text{-}1.8 \text{ J/cm}^2$.

It should be mentioned that in all cases discoloration towards yellow, possible outcome of the application of infrared radiation alone, can be eliminated by application of the combination of infrared and ultraviolet radiation at lower fluences than the ones used for cleaning.

4.3.2 Monochromatic surface layers

The use of ultraviolet radiation or any combination of ultraviolet and infrared radiation, causes discoloration to the underlying monochromatic surface layers. The use of infrared radiation alone at 0.5 to 0.9 J/cm^2 results macroscopically, into acceptable cleaning of loose deposits and the homogeneous compact crust. To remove thick dendritic crust it was necessary to significantly increase the fluence of the applied radiation (sometimes up to $1.5 - 1.8 \text{ J/cm}^2$). Repeated wetting with water, saturated in calcium carbonate, is also required in all cases of crust.

4.3.4. Conclusions

The cleaning process revealed the precious details of the sculptures and traces of ancient tools and colours (Figure 11,12).

Once they have undergone conservation the West Frieze blocks were not replaced on the monument but were instead exhibited in the Acropolis museum. Copies made from artificial stone were put in their place on the monument.



Figure 7. Detail during the laser cleaning



Figure 8. Detail during the laser cleaning



Figure 9. Detail during the laser cleaning



Figure 10. During the laser cleaning



Figure 10. Ancient tools' traces



Figure 11. Ancient colour traces

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