THEORETICAL AND TECHNICAL PRINCIPLES OF STONE CONSERVATION IN HISTORIC MONUMENTS

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ABSTRACT

The restoration of historic monuments is to preserve and reveal the aesthetic and historic value of them based on scientific principles. For this reason, it is essential to preserve the original materials during the process of restoration. The conservation problems of building materials in the historic monuments are among the subjects which have been investigated with an importance at the international level. It is necessary that, the conservative interventions which will specially be determined for each building, each material and each deterioration process must be determined according to theoretical and technical principles. The stone conservation processes can be provided by the sequence of operations such as diagnosis, cleaning, consolidation and protection. Diagnosis of deterioration is essential before any conservative treatment. In different deterioration cases; cleaning, consolidation and protection can be necessary in the order given or the selection and sequence of them can be determined according to the state of material. In this study, theoretical and technical principles of stone conservation in historic monuments were investigated, keeping in due consideration all previously published suggestions. The present study is an attempt to collect relevant concepts from several domains and expose them systematically.

Key Words : Historic monuments, Stone deterioration, Stone consolidation, Stone conservation

1. INTRODUCTION

The overview of the implementation of restoration and conservation activities in Turkey, obviously shows that the practices do not match the international principles. The restorations of historic monuments in Turkey are mainly centered around the renewal of deteriorated stones. The historical...
value of a building is only possible when the original ancient materials are preserved. However, this fact is not taken into consideration due to the approaches of conservation policy and technical difficulties in practice.

The conservation of stone in historic monuments is an intermittent process since the material exposed to the weathering environment. The deterioration of stone is a multiple mechanism that occurs as the result of any or all of physical, physico-chemical, chemical and biological processes. During the restorations of the historic monuments, instead of thinking of stone conservation as a single process, it should be looked upon as an ordered sequence of operations, under the four main headings of diagnosis, cleaning, consolidation and protection. Cleaning, consolidation and protection should be looked at individually, its particular problem should be diagnosed, then the necessary steps for conservation taken. This process should be looked upon as a maintenance operation to be repeated at certain intervals, instead of a once-and-all operation.

A conservative intervention not always includes all of last three treatments which are cleaning, consolidation and protection. Each intervention depends on the structural and mineralogical properties of stone, on its degree of deterioration and on environmental conditions. Their selection and sequence depends on the deterioration state of stone. For instance, if the stone is seriously deteriorated, even the mildest cleaning technique can be dangerous. In this case, firstly it must be necessary to consolidate the damaged surface.

The aim of this research is to determine the technical and theoretical principles at the international level. The available studies (Schaffer, 1972; Ashurst and Dimes, 1977; Amoroso and Fassina, 1983; Toracca, 1976, 1988; Tabasso, 1988) are valuable ones presenting general principles, philosophy and theories in detail. Additionally, numerous studies have been published presenting the results of researches related with applications (Rossi-Manaresi, 1976, 1981; Felix, 1985; Rodrigues, Henriques, Jeremias, 1992; Webster, 1992; Thiel, 1993; Fassina, Ott, Zezza, 1994). This research, which is realized with the urge of re-examining and underlying the essential principles, is aimed to introduce and review all the principles derived in other studies. Therefore, in this research, the theoretical and technical principles of stone conservation in historic monuments are reviewed with some reference to key studies of earlier date. Particular attention is given to basic theoretical and technical principles.

2. DIAGNOSIS

An investigation of the deterioration is essential before any treatment of stone. Variables in both the stone and the environment cause deterioration in different ways. Therefore the most suitable treatment must be determined for each case individually. A rational approach to the restoration and preservation of monuments must involve the following studies:

- It is very useful to gather as much data as possible, about the history of the monument, principally regarding previous restorations.
- The determination of the physical, chemical and mineralogical type of stone; i.e. of the chemical nature of the minerals composing the stone, the size, texture and degree of induration of these crystals in the sound (undecayed) stone, and the kind of chemical and physical modifications that have been produced by the decay processes.
- The survey of the amount and distribution of cracks and pores within the stone is essential because they cause the access of water and the onset of internal stresses.
- Measurement of the water absorption coefficient (capillarity) is necessary as water is a determinant factor in several deterioration processes.
- The survey of environmental conditions (temperature variations, average annual rainfall, frequency of frosts, relative humidity, air pollution level, salinity of soil, wind etc.) should be realized for the supplementary knowledge of the deterioration process.
- The analysis of biological factors should also be taken into consideration.

Application of treatment without diagnosis cannot further our knowledge or allow us to judge the success of our actions. Only a feedback of information on the practices employed will allow improvement in the classification of diseases and their respective remedies.

3. CLEANING

Cleaning is a necessary action in the conservation of stones exposed to the environment because it allows to remove from the surface dangerous products which are soluble salts, insoluble or soluble incrustations, soot particles present in polluted environments and sulphur dioxide oxidations catalysts, microorganisms, parasitic vegetation, bird or animal droppings and prepares it for the application of a consolidant or a protective agent.
As far as we know, the effect of weathering crusts on the preservation of the underlying stone is on the average bad. Even if the crusts do not cause deep deterioration, they still constitute a potential danger. When the way to the inside is opened through cracks and pores, the wetting-drying cycles of the surface push soluble material e.g. soluble salts, in thus causing deep deterioration to begin.

Therefore cleaning of soiled surfaces should always be carried out, unless a frequent and accurate inspection of stone conditions is possible. Many cleaning processes result in heavy loss of material from the surface, furthermore all cleaned surfaces will weather more quickly if cleaning is not followed by consolidation and protection. Actually, cleaning is a difficult process which requires extreme care and competence. If it creates new cracks in the stone surface or the deposition of soluble salts in the pores, cleaning opens the way to future deterioration processes. On the other hand, in the result of the cleaning process, it is essential to avoid any loss of the original surface and it is necessary to find out a good balance among the different parts of the building without spots at different degrees of cleaning. Moreover, if the stone is a carved one or in general it has a decorative function, cleaning must be carried out only by skilled and qualified persons.

The main requirements for cleaning processes for monuments are:

a) The choice of cleaning method should depend on the type of material to be removed, the condition of the stone surface and the type and extent of the surface to be cleaned.
b) The possibility to control the cleaning process, graduating the cleaning action at will.
c) That the cleaning process should not produce materials (e.g. soluble salts) which may cause future deterioration.
d) That the cleaned surfaces should be as free from cracks and other defects as possible.

3. 1. Cleaning Methods

The basic cleaning methods are as follows:

- Water-based methods.
- Chemical methods.
- Mechanical methods.
- Heat-based methods.

Water-based methods can be effective, if the soiling contains water soluble materials. However, the method is inadvisable if there is any risk of frost or infiltration of the walls. Among these methods, some of cleaning techniques available include:

“Sucking water” through porous stone from the outside to the inside (Ballestrem, Henau, Dupas, 1970). This is only possible for certain shapes of masonry pieces. However, if the deterioration of stone is serious and the amount of salt is important, the technique can be dangerous because of the rapid hydration of salts which can occur the spalling of fragments from the stone surface.

Water spray under pressure has a mechanical action and can lead to the detachment of little pieces of stone. On the other hand, water jets may cause deep penetration of water inside porous stone if large amount of water are used. This results in increased dampness of the masonry and may introduce or accelerate some deterioration process. Therefore, only for unimportant walls, a maximum pressure of 2-3 atm. is allowable. The stone must have a low porosity and low water absorption (Tabasso, 1988).

Water spray under very low pressure has a slower action, but it is necessary to use for a long time greater amounts of water. This can result in great and heavy penetration of water into the stone. Therefore, dissolution and transport of salts, microbial growth and spotting can arise as a consequence. If the low pressure water spray technique is used the water should be in minute droplets, and the total amount of water used should be kept to a minimumum (Hempel and Moncrieff, 1972).

Steam cleaning can also be dangerous for deteriorated stones due to the high temperature of the steam. The same disadvantages mentioned for water sprays can be remarked for the steam cleaning (Tabasso, 1988).

Water mists have a high efficiency in dissolving soot crusts on stone because the tiny droplets suspended in the air have a large specific surface and create a large interface when they are deposited on the stone. However, in the case of very porous or seriously deteriorated stones, this method can be dangerous.

Absorbent poultices are advisable for the extraction of water soluble salts without the risk of damage to the stone. It is slow and can be controlled.

Among the chemical methods, strong acids hydrochloric (HCl), sulphuric (H₂SO₄) and nitric (HNO₃) acids are the most dangerous and strong alkaline solutions are extremely dangerous. Acids erode irregularly the surface of stone and cause the
formation of soluble salts which may be absorbed in the pores and cause internal stresses. Hydrofluoric acid (HF) and ammonium bifluoride (NH$_4$HF$_2$) can also penetrate into the stone and react with the components of the stone; CaF$_2$ is formed as by-product. It has low solubility and can give a consolidation effect to the surface. These processes must be followed by washing in order to eliminate all the salts.

The use of strong alkaline solution (caustic soda or potash) is followed by a treatment with an acid to neutralize the alkali. This process cause the formation of soluble salts. Therefore, the cleaning is completed by washing water. It is clear that the use of strong alkaline solutions is unsuitable due to the difficulty of obtaining accurate neutralization and removal of salts.

Ion exchanging resins can be applied as a paste on the stone surface. They can dissolve either carbonates or silica and silicates. Their action is rather slow and can only take place in contact points between the wetted resin particles and the stone surface. When the paste is removed with a spatula, the dissolving action is stopped without penetration inside the pores without any further unfavorable reaction. Gelatinous solvent pastes are prepared by adding a jellying thixotropic agent to a weak basic solution to obtain a paste (Mora and Sbordoni, 1973). The solution remains in contact with the stone surface much longer than if it were sprayed or applied by brush and at the same time its penetration beneath the surface is reduced. The cleaning is completed by washing deionized water to eliminate all residue of the solution. However, it must be stressed that this method can not be used on very porous or deteriorated stone.

Mechanical method with dry or wet sandblasting contains the abrasive action of particles of sand sprayed under pressure at the surface of the stone. This technique may cause loss of material and produces new surfaces that being very irregular and full of cracks are frequently prone to further deterioration at an accelerated rate (Tabasso, 1988; Toracca, 1988).

Micro-sandblasting is performed by a special apparatus that ejects a very narrow beam of grit with a force that may be graduated according to the effect desired (Hempel and Moncrieff, 1976). The use of finer and softer powders such as alumina or glass microbeads, or of a powder obtained from the same type of stone to be cleaned reduces the abrasive effect. A combination of water mists and microblasting can be quite efficient and reliable process (Hempel and Moncrieff, 1976).

Heat based methods are based on direct flame and laser. The use of direct flame which cleans by burning the organic black material on the stone surface is dangerous for the thermal dilatations and stresses which can be provoked on the surface. When a laser beam is shot against a dark, dirty surface, it is absorbed, and its high energy vaporizes the components of the soot. This is very suitable technique but requires the long time for cleaning and the cost of equipment is very high (Lazzarini, Asmus, Marchesini, 1972; McStay, Enrique, Siddiqi, 1994; Copper, Emmony, Larson, 1995).

3. 2. General Evaluation of Cleaning Methods

It must be avoided the use of any kind of acid, alkaline substances, dry or wet sandblasting, mechanical cleaning with chisels, wire brushes, rotating grinders or polishers, water or steam under pressure.

In order to judge the merits of all these processes, both the ones in use today, and the new proposals, we must again stress the importance of accurate diagnosis and a feedback of information on results obtained. Only when these are thoroughly carried out can we begin to draw conclusions. In principle, it can be said that there are no cleaning methods which are guaranteed for efficacy or for safety, regardless of how they are applied. The selection of each technique requires several experiments. Another serious problem in the cleaning of monuments is the acute shortage of qualified personnel capable of applying the cleaning processes with the required sensitivity.

4. CONSOLIDATION

The aim of consolidation is to improve the cohesion of mineral constituents and the mechanical characteristics of the stone and to achieve the adhesion between the deteriorated and unaltered parts. Consolidation cannot be expected to be successful if there are major faults in the building (e. g. roofs, cornices, gutters etc.) causing deterioration in the masonry. Materials deposited by consolidating processes could only be expected to re-establish cohesion in the stone; any cracks arising from weathering processes or structural loads should be repaired by structural adhesives independently. Stone consolidation processes are only necessary where stone has lost its cohesion and is crumbling into fine dust. If the stone is strong, but eroded at the
surface, then a protective system is necessary; if the stone breaks down into hard splinters, chips, or flakes, then structural adhesives are required. Only a few agents can carry out the function of both consolidant and structural adhesive (epoxies or polyesters).

If stone consolidation is to be successful, deep impregnation is necessary (Wihr, 1976). The impregnation should be deep enough to connect solidly all incoherent material to the sound core of the stone, and full impregnation is necessary where there is no sound core. The basic concept in achieving satisfactory penetration is to keep the surface wet with a liquid consolidant for a sufficient time, and to delay evaporation of any volatile component of the mixture.

There are difficulties in controlling the distribution of the product inside the pores of the stone and in the choice what is the best treatment pore structure for each type of stone. Another important point is that the consolidants must not produce dangerous by-products such as water soluble salts.

### 4.1. Types of Consolidants

The consolidation of stone can be obtained with inorganic and organic products (Lewin, 1966; Riederer, 1972). The main differences between them:

The consolidation of organic materials is based on the precipitation of a newly product, either through a reaction with the component of the stone with carbon dioxide or through a hydrolytic process. The new product is weakly bonded to the original minerals and it is able to join very narrow cracks not longer than 50 μ. It cannot be possible to join detached parts by using inorganic consolidants. Inorganic materials generally last longer than organic ones but they are rather fragile and have a low elasticity.

If consolidation is provided through chemical reaction with components of the stone it is impossible to obtain good penetration because as soon as the reaction begins to take place, precipitation of the material inside the pores prevents the penetration of consolidant.

The consolidation of organic materials aims to introduce an organic adhesive between the grains that have lost cohesion. Organic consolidants are easily altered by U.V. radiation. They have a higher elasticity and improve the tensile strength of the treated stone.

Limewash and barium hydroxide can be used as inorganic consolidants. The precipitated products include calcium carbonate (Hempel, 1971) and barium carbonate (Lewin and Baer, 1974; Lewin, 1988) respectively.

Silicon based products are partly organic and partly inorganic consolidation materials. There are a large number of products ranging from alkaline silicates to silicone resins. With alkaline silicates, alkaline hydroxides are formed as a by-product which can be dangerous for the stone. Fluosilicates are Mg or Zn salts of fluosilicis acid (Sanpaolesi, 1966). The silica acts as a consolidant while some calcium and Mg fluorides are formed.

Silica esters (mainly ethyl silicate) have the advantage of good penetration and do not produce dangerous by-products. By adding an alkyl-alkoxy-silane to ethyl silicate, good water repellency is achieved, as the latter due to the presence of non-hydrolizable non-polar groups, forms a protective barrier against water. It must be noted that these are mainly recommended for sandstones or siliceous materials. Silicone resins have higher water repellency, good stability with acids and O₃, low variation of physical characteristics with temperature variations and good elasticity (Rossi-Manaresi, 1976a, Weber, 1976; Lewin, 1988).

Thermosetting and thermoplastic resins can be used for stone consolidation as organic materials. Thermosetting resins are applied as prepolymer mixed with a tridimensional stucture. The molecular chains are linked together with strong chemical bonds which reduce their flexibility and make them resistant to heat and to mechanical stress (Domaslowski, 1988). They are good structural adhesives. Epoxy and polyester resins are used for this purpose and they are mixed with solvents to reduce viscosity, delay the setting reaction and avoid filling completely the pores of the stone with resin (Marinelli, 1976). If epoxy resins are not diluted with a solvent, they are mainly inadvisable because their penetration is low and create an absolutely impermeable surface layer, forming shiny films which quickly become insoluble and which flake and yellow in time. The main problems are the difficult penetration and the low resistance to U.V.

The chains of thermoplastic resins are linked together with weak secondary bonds. Therefore they can be dissolved by specific solvents, and they are rather flexible and may be deformed by heat. In addition, thermoplastic resins do not penetrate easily in small pores because their molecules are very large. In contrast to thermosetting resins, thermoplastic polymers are more easily applied in...
solution with organic solvents which reduce their viscosity and improve penetration. Because of the creep phenomenon thermoplastic polymers are not resistant to prolonged stress and so they cannot be used as structural adhesives. Acrylic resins have generally a good resistance to the light and to chemicals but the water repellency are not very high (Wihr, 1988). In suitable cases, silicone and acrylic resins can be used together as the consolidant (Nonfarmale, 1976).

Better penetration is achieved by the use of low molecular weight substances that polymerize or set after the impregnation of the porous solid. Monomers of thermoplastic resins are extremely mobile, and deep impregnation may be easily achieved with them; they are polymerized by means of catalysts (Munnikendam, 1971) or gamma-radiation (Nadaillac, 1972). Thermosetting resins offer an easier technique. Polymers (Riederer, 1972) and epoxies (Domaslowski, 1971; Munnikendam, 1972) appear to be best because of their reliable cold-setting reactions.

4. 2. General Evaluation of Consolidants

It must be avoided to use sodium and potassium silicates and sodium and potassium aluminites which give rise to the formation of soluble salts as by-products, and also zinc and magnesium fluosilicates which have a low penetration and give rise to the formation of soluble salts as by-products, often due to the presence of zinc or magnesium sulphate impurities. There are wide differences of opinion as to which consolidation process is more suitable for any given situation. It should be remembered that all consolidation processes should be considered together with the subsequent protection treatment. It is generally accepted that inorganic processes based on the formation of calcium or barium carbonate are more suitable for calcareous stone, while silica-forming processes, are more suitable for siliceous material. Silica-silicone processes, and all organic consolidants, are considered applicable to any case, provided sufficient penetration is achieved (Hempel and Moncrieff, 1976).

The inorganic consolidants are more durable, however they do not cause a vast improvement in the mechanical properties of the stone. When inorganic consolidants are used, any improvement of weathering behaviour should be entrusted to the protective system, or else deterioration will start again.

Organic consolidants produce superior mechanical properties. Their main disadvantage is that they themselves are deteriorated by oxygen and light in the environment, which obviously occurs on the surface. This surface deterioration may be unacceptable if it causes a change in colour of the treated object, or the formation of surface cracks. The application of thermosetting resins (epoxies and polyesters) to porous stone may cause the formation of an impervious crust over a porous core, which might cause problems if water gains access to the untreated porous core.

5. GAP FILLING

After cleaning and consolidation processes and before final protection, it is necessary to obtain a smooth surface without open cracks and holes. Consolidation materials cannot fill cracks larger than 0,1-0,2 mm. Therefore, it is necessary to use a suitable adhesives or fillers to fill larger gaps.

The filling material should be compatible with the original one; its strength and its thermal expansion coefficient should be similar to those of the original stone. The porosity of filling material should be similar to or higher than the porosity of the stone to allow the evaporation of water and salt solutions. In addition they must have similar aesthetic characteristics with the stone.

Fillers are prepared by mixing a binder with an inert material (silica, glass powder, powder ground from the stone to be repaired). Hydrated lime mixed with a calcareous filler (crushed marble or travertine are the best) is a suitable filling compound for limestone or marble.

Cement should not be used as a filler because it can be rich in alkaline substances and sulphates which lead to the formation of harmful soluble salts. In addition, cement is usually less porous than many kinds of stone. Therefore, a movement of water can be inside structure, and evaporation of the water and crystallization of salts occurs in the more porous areas. Moreover, the differences in thermal expansion between cement and stone can cause cracking and mechanical damage.

Synthetic resins which are acrylic emulsions, silicones or polyester and epoxy adhesives can also be used as binders. Epoxy resins are the most advisable as binders because of their high adhesive power and their mechanical characteristics (Domaslowski, 1988). However, epoxy resins are altered by the action of light and atmospheric agents, undergoing oxidation which causes yellowing and surface fragility. It is better to use those resins in the deepest parts of the cracks and they should be
covered on the surface with a more light-stable product, for instance an acrylic resin. Acrylic resins (thermoplastic materials) can also be used as binder with fillers like crushed stone, crushed marble, glass powder.

6. PROTECTION

After cleaning and/or a consolidation treatment, if stone remains exposed to the same deterioration factors, previous deterioration processes will start and continue. For this reason the aim of protective treatment is to reduce the probability of deterioration processes. Protection can be achieved either by modifying environmental conditions or by applying a suitable product to the stone, or by both of them.

6.1. Environmental Protection

The basic points of the environmental protection of stone are complete revision of water disposal systems in building, control of rising damp in masonry, climatic provisions tending to eliminate condensation from the surface to be protected. It is possible to control the influence of environmental factors with various protection systems:

- Installation of transparent screens.
- Non-transparent temporary shelters during the most dangerous periods of the year.
- Heating with warm air to prevent condensation.
- Installation of sheds.

However, all of these methods must be carefully considered to avoid introducing a new deteriorative environment. In the first system, if the interior is not artificially conditioned, the “greenhouse effect” can prove to be very dangerous for the stone. In the third case, if applied to stones affected by rising damp where suction of water occurs, salt crystallization could take place. The method of external sheds give protection against rain but not against condensation.

If this method is adopted, a surface protective film should be applied on the stone. If mortar was used between stones, the joints must be kept in good condition by repointing them periodically with a suitable material. It is important that the repointing mortar, besides being porous and free from soluble salts, should not be exceedingly strong. For this reason, mortars made of thermosetting resins (e.g. epoxy resins) are not advisable for this application (Toracca, 1988; Tabasso, 1988).

6.2. Surface Protective Treatments

The application of surface protective films on the surface of stone aims to reduce the deterioration process. The presence of a protective film can reduce the penetration of water, acid or saline solutions and gaseous pollutants. However, a protective film must be applied to a clean and sound surface. Therefore, if necessary, it should always be applied after cleaning, consolidation and gap filling.

The main requirements for protective material are:

- That the protective material should be a good reversibility.
- That it has good vapor permeability to allow evaporation from the core of the stone should some water reach it.
- That it should be good resistance to the U.V. radiation to withstand long exposure without change of colour and loss of effectiveness.

In the past, such materials as wax, paraffin, linseed oil, tallow (Rossi-Manaresi, 1972) and pigmented paints (Campoli, 1971) have been applied to stone masonry for protective purposes. Of the old materials, waxes and paraffin wax appear as possible choices, together with their modern counterpart microcrystalline wax (Plenderleith and Werner, 1971). Salts of fatty acids such as aluminium stearate, and silicones are modern treatments which may be possible choices (Toracca, 1976). Silicones dissolved in solvents appear to be preferable to the water soluble types (Gerard, 1972; Mammillan and Simonnet, 1972). Polysiloxanes (silicone resins) (Marchesini and Bonora, 1988) and alkyl-alkoxy-silanes or their mixture with acrylic resins are commonly used. The use of all thermosetting resins does not appear advisable since removal, when necessary, would be difficult, and because some of them discolour. Thermoplastic resins appear to have more suitable properties, while acrylic resins are in use for the surface protection of marble carvings (Mora, 1971).

The most important properties required for protective films are aging resistance and optical properties, mechanical requirements are less important. Indeed, mechanical strength may be undesirable if the film creates an impervious surface on porous stone, preventing the release of any water which may gain access to the core of the stone. In this respect, the use of soft film forming materials is to be preferred, however these create a wet appearance to the building, and attract dust.

7. CONCLUSION

All the conservation processes discussed here have a limited useful life, therefore periodical inspection is essential. Maintenance of stone should upkeep the protection system so that no attack takes place in the
bulk of the material. In order to realize the operational process described here a modification of the conservation services currently available is required. It is necessary to make equipment available for the inspection and control of monuments together with the skilled personnel required. In addition, the establishment of an conservation policy is essential. Although the establishment of this policy is above the level of the specialist in stone conservation, it is his/her duty to apply pressure to ensure that such a policy is introduced. Thus the mistakes being made at present will be avoided.

8. REFERENCES


