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ADVERSE EFFECTS ARISING FROM CONSERVATION TREATMENTS ON ARCHAEOLOGICAL SITES: THEORY, PRACTICE AND REVIEW.

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Introduction

Conservation and restoration of archaeological sites developed significantly in the second half of the twentieth century, with greater emphasis in recent decades, which has led to a considerable number of interventions.

Methodology of intervention has changed significantly since more interventionist measures are performed against the current criteria of minimum intervention, although what actually occurs today is a difficult balance between innovation (experimental application of new techniques and products) and minimum intervention. The debate, in the case of archaeological sites, has focused on the actions traditionally more aggressive: cleaning, consolidation or reintegration, as this is where most notable has been the restorative action throughout history.

The restoration, like everything else, has been subject of trends, in relation to the appearance of new products and technologies, and today remains a discipline that widely develops experimental practice. It certainly brings great benefits and constant renewal of criteria and methodologies, but also risks by introducing new compounds that may interact negatively with original substrate, although their effects cannot be checked in the short or medium term. The lack of knowledge of the causes of decay arising from previous interventions has generated a series of continuous protection and consolidation treatments at different periods.

Restorers currently must deal with decayed areas where the products, methodology or techniques used, have caused a negative effect on the original material. This paper attempts to explore the general study of effects and alterations arising from restoration treatments, as well as reviewing of scientific publications related to this issue.

Theory and practice in conservation interventions on archaeological sites

Current theoretical criteria of intervention such as minimum intervention, discernibility of restoration elements or maintenance of authenticity actually depends on the interpretation of the technician in charge. Others, like reversibility of treatments, are almost impossible in practice; the application on site of any product on a porous material (stone material, as well as plaster, mosaics or wall paintings, the main elements in archaeological sites) will always leave some remains interiorly, although it might be apparently eliminated in surface. Material compatibility seems to be the most reasonable and respectful approach, yet with significant limitation in practice, as we will see in following paragraphs.

Moreover, when planning a restoration project it is essential to document and study previous interventions on the site and check the current status of those areas. However this is not as easy as it could seem at first sight; there is a remarkable lack of documentation when speaking of interventions on archaeological sites, documentation is disperse or imprecise, and frequently non-accessible. When some treatments have become a source of degradation it is crucial to know detailed data about the intervention: methodology of application, exact location, products and techniques used, solvents and proportions, etc. This kind of accurate data is rarely given and thus monitoring and subsequent evaluation is unreliable and often nonexistent.

In this sense the use of modern technologies, such us GIS platforms, are extremely useful and pragmatic, and still little exploited as documentation and analysis system in conservation projects. It allows to integrate all kind of information in one unique digital platform, data from archaeological excavations, conservation interventions, tables, graphics and photographs (including 3D imaging), etc. with the advantage of been all georeferenced. The implementation of integrated data is highly recommended, it is very common that different groups or disciplines acting on the same site generate each own report, duplicating not only information, but also efforts and costs, also hampering access to all useful information for future management and preservation.

When selecting restoration products it is necessary to be critical at the time of considering most suitable product, methodologies and compatibility with substrate. It is risky to establish general assessments about the application of one or another restoration product; what seems to be suitable in theory might become inefficient in practice. Thus, the use of ethyl silicate could be suitable and effective in a particular site, and completely opposite in other, even considering similar material and climate conditions. This seems to be an obvious statement, but it is not always taken into account, or because there might be a wrong identification of degradation agents, which ends up at the same point of conservation degree.

Another mismatch between theory and practice is the fact itself of intervening, after studying former restorations, reviewing current products and methodologies, it might be reached the conclusion that the best way to act is not to act, leave it as found it (performing minimal preventive conservation measures) or reburying archaeological remains. It has been repeatedly demonstrated that sometimes, in particular cases, it is better not to touch. Nevertheless it is true that in archaeological sites the authenticity of the whole assembly depends on the preservation of each singular element, as they provide historical information by themselves, therefore punctual interventions are necessary. In the case of historical building in use must prevail security requirements and functions of its constructive elements, over material authenticity.
Restoration theories have changed in time and space and will keep on changing in the future,

but what really matters, what definitely give us the information to assess the correct treatment, is the field and laboratory practice of each case, deep knowledge of our case study and a right previous diagnosis and identification of degradation agents.

Review: effects of consolidation treatments on stone material

The study of the effects and changes resulting from restoration treatments have been developed in recent years; most studies have been conducted in laboratory using artificial aging tests, some others, much rarer, evaluated on site the durability and effectiveness of these treatments after several years of application (Rossi-Manaresi 1981, 1995, Fassina 1995, Stadtbauer et al. 1996, Hansen et al. 2003, Wheeler and Goins 2005, Favaro et al. 2006, 2007, Laurenzi Tabasso and Simon 2006, Varas et al. 2007, Nimmrichter and Linke 2008).

Treatments performed over three to four decades provide little information about the behavior of the products used, as there is little documentation on their characteristics, application techniques, the state of the stone before intervention, and so on (Laurenzi Tabasso and Simon 2006). Anyway the alteration processes have a slow performance, meaning that it would be necessary to wait long in order to get information for studying on site the effects of these products, therefore laboratory tests are yet a key factor to arrive at the choice of the most appropriate treatment (Alvarez de Buergo 2008).

Many of these studies have focused on carbonate rocks, being especially alterable. Besides, consolidants and water-repellent products take numerous studies and publications, as well as cleaning systems.

Since the literature in this area is very large, this paper attempts to address those studies focused primarily on consolidating treatments, as they are widely used in archaeological sites and a field of continuous innovation.

Some of the known drawbacks for general use of consolidants are following listed (Fort and Pérez-Monserrat 2012):

- Changes in the material properties, due to modification in its internal structure
- Modification of the surface characteristics, mainly aesthetic changes, such as color or brightness, but also texture and roughness
- Increased sensitivity to acidic or alkaline substances
- Corrosive reactions
- Degradation arising from differences in thermal expansion coefficient between substrate and product (synthetic polymers)
- Generation of subproducts, mainly salts
- High toxicity
- Irreversibility

Until late nineteenth century natural products of animal and vegetable origin were used, like waxes, shellac, etc. (Fort 2007). The sixties saw the extensive boom of synthetic products, although adverse effects were early seen; different researches came out in order to improve the quality of these products, as well as limiting their disadvantages and unintended effects. Nowadays it is much about promoting compatibility standards, often adapting traditional or natural materials to restorative practice. Under this premise, researchers started developing inorganic materials and silicates for consolidating and protecting purposes.

Organic consolidants

Traditionally natural materials, like waxes or organic resins, have been used as protective and repairing products. However it is in the sixties when interventions on archaeological heritage are intensified coinciding with the emergence of synthetic polymers. These products, made for industrial purposes, are resins derived from petroleum synthesis. Besides its consolidating function, they have been used as protective products given their hydrophobic capacity, precisely because of its organic composition.

Its action is based on the penetration of the polymer in the pore system of the material when, after evaporation of the solvent, the particles form three-dimensional networks surrounding loose particles (grains) of the stone.

The big disadvantage in the application of these products is their low penetration capability, due to its high viscosity. The dissolution of the solute requires evaporation of the solvent in the polymerization process after the application; this stage usually involves some solute migration to the surface; therefore the polymer is deposited in a thin surface layer. Acrylates and methacrylates cause a drastic reduction of the water vapor transmission in the porous system of the stone material, creating waterproofing barriers which can generate mechanical damage by crystallization of salts in this barrier that separates the inner bulk and the consolidated surface (Figure 1).

It should be taken into account, as a starting point, that it is about organic compounds applied over inorganic material, therefore, unlike other consolidants, not strictly meet compatibility.

The photodegradation or photooxidation is one of the biggest problems when referring to the case of archaeological sites, particularly exposed to extreme weathering. In recent decades several research projects were developed in order to understand the processes of degradation of these materials in the field of cultural heritage.

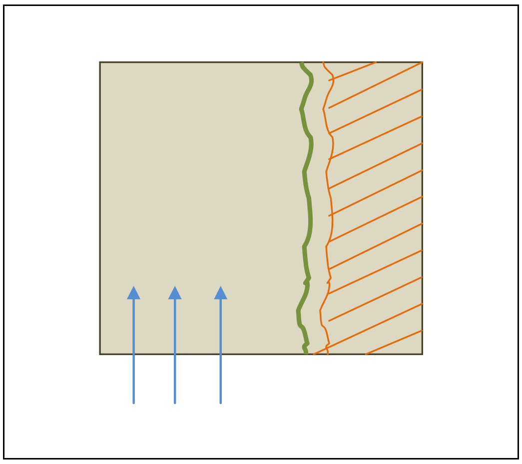

Figure 1. Capillary moisture may cause the crystallization of salts (→) on the barrier line (▬). Waterproof surface prevents evaporation outward and can cause total detachment of this layer.

The photodegradation process of acrylic resins implies physical and chemical alterations (Melo et al. 1999, Chiantore and Lazzari 2001), mainly due to prolonged exposure to ultraviolet radiation, as a consequence, chain scission results (responsible for maintaining binding of monomers), cross-linking and finally accompanied by a generation of volatile compounds such as methanol, carbon dioxide, carbon monoxide, methyl formate, methane or hydrogen. Moreover, acrylic polymers, as a consequence of photodegradation, may suffer yellowing; a chromatic effect derived from the formation of conjugated double bonds resulting from chemical reaction (Allen et al. 1992).

Different researches showed similar results when assessing some commercial products, based on the application on various stone types' samples, artificial aging tested. Those common alterations are:

- color and brightness changes,
- loss of mechanical (adhesive) and protective (hydrorrepellence) properties
- completely degradation until total removal of the layer,
- it has been proved impossible to completely remove the remnants of the resin (irreversibility).

Another harmful effect mentioned in the literature is related to biological degradation of the synthetic polymers due to their organic nature (Nugari and Priori 1985). All polymers are potential substrates for the growth of heterotrophic microorganisms, including bacteria and fungi (Ji-Dong 2003). The microorganisms attack can completely decompose the polymer structure reaching full mineralization. As a general rule, the more similar the polymer structure to the natural compounds, more likely they will be subjected to biological attack. Besides, producers usually incorporate additives, which, in many cases, contain compounds that serve as carbon and energy source for microbial growth. Biodegradation will be faster when temperature and moisture conditions are favorable, as in the case of archaeological sites, much more accentuated when they are found in tropical environments, as many sites of Central America.

Thermoplastic resins like Primal / Acril 33© or Paraloid©, have had widespread use since the seventies until today. Some of these alterations are visible soon after application showing dark

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and hard crusts in the material surface (Doelme and Price 2010), but also whitish veils due to a faulty drying phase. That is the case of many Mexican archaeological sites where the use of these products was especially extended in the seventies and eighties for the consolidation of mural paintings (Saenz 2012). The climate conditions in these sites are extreme, with high level of humidity (from capillarity and precipitations), daily temperature fluctuations and biological growth. Since the nineties these alterations have been documented in important archaeological sites such as Cholula, Plaza Oeste in Teotihuacan, or Cacaxtla, in Tlaxcala (Anonymous 2012), all of them located in Mexico. In the case of Cholula, the painting of *Los Bebedores*, treated in the seventies, has shown mechanical damages and superficial changes. Between 1994 and 1998 a study with the support of the Getty institution was carried out for further knowledge of the effects and damage resulting from the use of these products, and thus to propose new conservation solutions (Saenz 2012).

In Cacaxtla, professionals from different disciplines (archaeologists, engineers and chemists) have addressed the problem of how to remove synthetic polymers from mural paintings (the conservation project of both sites is included within the National Program for Conservation of Prehispanic Mural Painting, developed by the INAH since 2010).

Paraloid© has been specially appreciated and used by restorers as adhesive, consolidant and coating product. Between the different products commercialized under this name the B-72 seems to be more stable against photo-degradation (Figure 2). According to studies by Chiantore and Lazzari the photo-oxidative stability of acrylic/methacrylic resins is higher in resins containing only ethyl and methyl esters, against those ones containing long alkyl side groups, such as butyl or isobutyl (Chiantore and Lazzari 2001). Samples of different products were tested by artificial aging tests, monitoring the reaction by using FTIR and UV–Vis spectroscopy, and size exclusion chromatography.

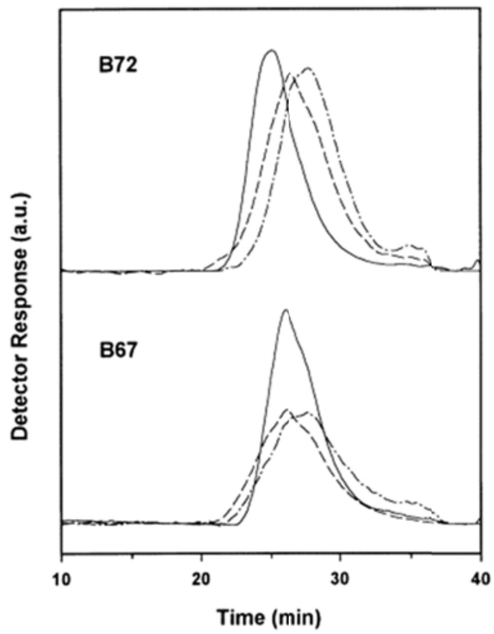

Figure 2. Chromatograms obtained from samples of Paraloid B72 and B67 before test (solid line), and after expose them to 150°C in cycles of 115h (dashed line) and 200h (dash-pointed line). It shows the weight losses of each sample (Source: Chiantore and Lazzari 2000).

Vinyl resins, such as Polyvinyl acetate (PVA, used mostly as an adhesive), can cause mechanical damages due to different thermal expansion coefficient and consequent contraction-expansion movements caused by fluctuations of temperature and humidity, finally decaying by flaking and peeling. Between 2002 and 2005 the Department of Conservation and Restoration of the University of Barcelona conducted a research project for the study of damages caused by aging of polyvinyl acetate. PVA was used as an adhesive, coincident with the rise of plastics in Spain during the seventies, for the transfer of mural painting on a new support, replacing traditional calcium caseinate support (Campo Francés et al. 2005). Unlike calcium caseinate, PVA suffered the stress generated between the last one and the organic glues used for striping the paint layer (the use of organic glues has been constant for the facing process due to its ability to grip the gauze and its high reversibility), due to the contraction-expansion movements caused by fluctuations in temperature and humidity, as it was mentioned before. Mechanical damage is manifested by the separation of the paint layer and blisters where the adhesive was accumulated. These changes will be even more evident in the case of murals or mosaics when replaced in their original place after restoration treatments, where environmental conditions are difficult to control.

Regarding epoxy resins, the biggest problem is their low penetration and the resulting chromatic alterations, yellowing and darkening, as well as the formation of hard crusts in surface. Selwitz (1992) maintains that the vast majority of negative effects are not due to the product itself, but rather to the application method and its high viscosity. This product has been widespread used for the adhesion of stone material fragments. In the case of the Roman Theater of Mérida (Spain) it was employed from the fifties until today, particularly for the reconstruction of decorative marble fragments in the Front stage. Some of these fragments are now falling down (Figure 3) due to the loss of mechanical properties of the epoxy resin, related to the permanent exposure to solar radiation.

Figure 3. Marble fragment from the basement of a column in the Front Stage of the Roman Theater in Mérida. The degradation of the epoxy resin is visible in both sides of the fracture. (Source: *Consorcio de Mérida*).

The method of application is also crucial, especially when speaking of stones with low porosity, such as granite or marble, showing that brushing may not be the most appropriate method, forming a thin surface layer (Ferreira Pinto and Delgado Rodrigues 2008). Other variables like moisture of the substrate, temperature or wind exposure must be taken into account when applying these consolidants.

Inorganic consolidants

Inorganic consolidants seem to be most appropriate, at least more compatible, because of their similarity with the inorganic components of the stone, besides the fact that they resist better the action of outdoor exposure. However, their mechanical properties are significantly lower than those of the organic products and it is difficult to achieve good penetration of the treatment. In addition there are some limitations in its use; aqueous dispersions in many cases require a large number of applications for a consolidating effect which involves movement, redistribution and processes of dissolution and recrystallization of salts, as well as hydrolysis of clay components. In other cases the application of these products entails the formation of secondary by-products.

One of the most used consolidants is calcium hydroxide or lime water, mainly for mortar and limestone. Lime is usually deposited on the surface forming a thin layer which hardly penetrates the material. There are certain differences between this layer and the original substrate surface in aspects such as grain size, texture (heterogeneous) and crystalline phase, resulting in different degrees of dissolution, which affects the durability of the treatment (Hansen et al. 2003) becoming powdery and weak.

The low solubility of calcium hydroxide force to repeat successive applications with the consequent contribution of water and the above mentioned disadvantages. The pH of the solution is high, which may affect pigments and sensitive compounds to alkaline media. It should be add that lime slurries often leave visible white stains after application.

The calcium hydroxide reacts in the presence of CO_2 and moisture to form calcium carbonate, much more stable and insoluble. This reaction is slower and more complex than traditionally been considered, due, among other variables, to the difficulty of CO_2 to penetrate into the object, so the carbonation reaction is usually incomplete and so it is the consolidation faculty. Several studies have attempted to limit this drawback, favoring the reaction of CO_2 by introducing carbamates into the solution (Baglioni et al. 1997). Another alternative, currently subject of many researches in the field of conservation, is the use of nanoparticles, which facilitates the reaction by having higher dispersion inside the porous system (López-Arce et al. 2010, Campbell et al. 2011).

Barium hydroxide is more soluble in water than the former and therefore does not require so many applications to be effective. Some authors emphasize the positive effects of this treatment - durability, compatibility, similarity in the coefficients of thermal expansion, minimal changes to the original appearance (may cause bleaching), maintenance of hydric properties of the material, compatibility with other consolidants and effectiveness in transforming the barium sulfate gypsum (protective character) - although in practice its use is currently limited and many cases have proved it ineffective. As in the previous case some variants have arisen trying to limit the disadvantages of the treatment, one of the best known is the addition of urea to barium hydroxide in order to facilitate precipitation of barium carbonate (Hansen et al. 2003).

Barium hydroxide has been traditionally used for the consolidation of mural painting and lime mortar. Its application is delicate and has some disadvantages. Some of them are more related to the use of incorrect methodologies of application. Experimental studies are still lacking in this regard. According to Matteini (2008) there is no reason to reject it when treating marble, limestone and even sandstone and clay material.

Other products within this group, less used than the above mentioned or no longer in use, are fluorine-based products such as hydrofluoric acid or mixtures as fluorosilicates. The damage caused by fluorine-based products is related to the formation of hard crusts that use to end up falling off; for this reason there is a wide consensus in rejecting its application (Losada Aranguren 2003).

Silicates-based consolidants

The family of silicates was first used early in restoration, the first treatments with alkali silicate (discovered by Fuchs in 1820) took place in Germany, France and England for the consolidation of the stone, and continued until the late 20th century. Alkali silicate fell into disuse in the eighties after finding that stimulates the accumulation of salts as they provide Na and P, effects early described by Arnold and Zehnder in 1989 and 1990, respectively (Franco et al. 2002). However silicates have proven to have effective strengthener capacity, and industry has diversified with the elaboration of new products; ethyl silicate, methyl silicate, lithium silicate, sodium or potassium silicates are some examples.

Among the most important advantages to highlight is its great penetration capacity (avoiding formation of hard crusts on the surface) and material compatibility. It may confers remarkable mechanical strength to the material creating strong links after polymerization process, which, however, has no adhesive capacity above 0.1 mm.

Currently ethyl silicate is widely used in conservation of stone material, and particularly in the conservation of archaeological sites. Its effectiveness depends on environmental conditions and methodology of application, nevertheless in a few years loses its effectiveness, and so it is convenient to carry out some monitoring and maintenance actions.

Overall consolidants with silicates can cause discoloration, darkening and brightness changes. Its application involves a risk caused by preferential absorption of some areas over others, since stone is a heterogeneous material, which can lead to mechanical damage by differential internal tensions. It also decreases the water vapor transmission, although in lesser extent than synthetics.

We mentioned its high efficiency as cohesive consolidant, but we must emphasize the significant dependence on the conditions of application and expertise of the operator to ensure its effectiveness. It will not be effective if the material is not absorbent enough or if the temperature and humidity conditions are adverse; ideal conditions are between 5ºC and 25ºC, and 40% to 80% RH respectively (although these figures may vary slightly according to each manufacturer). It is also necessary to cover the surface on which it is applied for several days after application to slow down the evaporation of solvent. Furthermore its effect is slow (about 40-50 days) and irreversible (it modifies the pore system), but effective for a limited period.

Studies carried out by Fort et al. (2000) on granites and limestone from Royal Palace of Madrid, Spain, showed that siloxane-based treatments with organic solvents where the most effective among others (such us methacrylates and microwaxes) for the protection of the stone against the action of water. Nevertheless, siloxane-based treatments experiment the most significant chromatic changes after exposure to wetting-drying, freeze-thaw and ultraviolet radiation cycles, being particularly strong in the case of limestone.

Conclusions

As we have seen there are certain limitations in the use of consolidating products for stone material and other inorganic and porous materials in archaeological sites, but also several limitations when evaluating the effects of these products on a specific case study. Too many variables must be taken into account when facing the selection of a conservation treatment; climate conditions, state and properties of the substrate, methodology of application, uses and functions of the site, future conditions of preservation, previous interventions, etc. Although this might seem viable in theory, it is hard to manage in practice. In many cases interventions on archaeological heritage are short campaigns or emergency plans where there is neither time nor the means to develop a comprehensive conservation plan, or simply no resources to conduct preliminary analysis, evaluation and monitoring post-intervention. It is in these cases where practical knowledge and review of these limitations of treatments is decisive in order to avoid more damages than benefits. In this sense some treatments, considered already traditional and widespread used, are much more complex in practice than usually assumed regarding to preparation and application. It is just a matter of adaptation of the right treatments in the right context, but it requires precise and deep knowledge of the material, its state of conservation and the restorative product, as well as the interaction of all of them.

We have now the chance to study the behavior of these treatments on sites where interventions have been carried out several years ago, even decades, in order to collect information from natural environments, and complement it with laboratory outcomes. Some of the factors that should be measured have been already mentioned: compatibility with substrate, strengthening capacity, depth of penetration, changes in surface properties (compared to inner material or to untreated surfaces), effect on porosity and permeability, durability of treatment, biological resistance, effects on appearance, ease of application, and health and safety impacts (Fidler 2004). This results in the measurement of specific parameters, such as color parameters, brightness, pores size distribution or water vapor permeability (Fort et al. 2005).

The development of portable and non-destructive analytical techniques is nowadays a great advantage in order to monitoring the behavior and evolution of these treatments, but also to evaluate past treatments.

The study of the mid and long-terms effects of conservation treatments is an open field for further research (Laurenzi Tabasso 2004), deep knowledge is required when referring to process of chemical reactions between the different components of the treatment and the original material; or the so called problem of retreatability (the interaction between two different treatments over the same surface).

Scientific research in the field of heritage conservation has enjoyed considerable growth in recent years, highlighting the development of analytical techniques for the diagnosis phase and those related to the optimization of treatments. In many cases, beyond the release of new products, it is focused on improving properties of already known treatments. Certainly experimental practice is critical and shall also focus on archaeological remains preserved in situ, complemented, but not only, with laboratory tests.

In conservation of archaeological sites it is necessary, as in other scientific disciplines, continuous updating of knowledge, upgrade skills and be critical, since this is an area where much more specific research is needed in order to preserve it.

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