STONE DETERIORATION CHARACTERIZATION FOR ITS CONSERVATION

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RESUMO

A conservação da pedra é fundamental para a preservação do nosso património arquitectónico e monumental. Embora seja um dos materiais mais resistentes, deve-se considerar que existem muitos factores que podem contribuir para a sua deterioração. O presente trabalho sintetiza os principais factores de deterioração, tais como a poluição atmosférica, a presença de sais solúveis e a biocolonização. Uma breve resenha destes factores serve de base para salientar a importância de fazer o diagnóstico correcto da origem da deterioração observada. Só então se pode encontrar a solução mais adequada para resolver o problema.

PALAVRAS-CHAVE: tipo de pedra, deterioração, conservação.

ABSTRACT

The conservation of stone is fundamental for the preservation of our architectural and monumental heritage. Although stone is reputed as one of the most resistant materials, there are many factors that contribute towards its deterioration. This paper aims to summarize the main deterioration factors, such as air pollution, the presence of soluble salts, and biocolonization. A brief discussion of these factors serves as the basis to introduce the importance of a correct diagnosis regarding the origin of the observed deterioration. Only then, can the most appropriate solution be found to address the problem.

KEYWORDS: stone nature, deterioration, conservation.

1. INTRODUCTION

Stone conservation is fundamental for the preservation of our architectural and monumental heritage. Stone has always been considered as one of the most resistant building materials, but this is not always the case, since there are many varieties, some more resistant than others, depending on their origin and formation. Consequently, each building, each monument is really unique, and to preserve it requires first a thorough condition survey, based on a careful observation and analysis, so as to be able to correctly identify its deterioration problem, and carry out a value analysis, to find the most appropriate solution for the specific object.

This paper aims to present a brief introduction to the most common deterioration factors so as to identify and evaluate the most important points that should be taken into account when carrying out a condition survey of the building or monument. It is not always possible to carry out all the analyses that would be desirable to confirm the observed problems. Therefore, it is critical that in a first evaluation, the type of stone and the main deterioration problems be identified so as to reduce to a minimum the number of required analyses. A correct diagnostic is fundamental for determining the best conservation method to be used, while also taking also into account the overall objective of the intervention.

2. DETERIORATION FACTORS

Stone is susceptible to deterioration by various agents, the most important ones are air pollution, the presence of soluble salts, and biocolonization, apart from freeze-thaw issues as found in colder regions. All these deterioration mechanims have one common factor: the presence of water (CHAROLA y WENDLER, 2015, p. 55). Many studies have been undertaken to elucidate these mechanisms and to understand how each individual factor acts by itself, or in conjunction with others. While science has made great advances in this area, the practical application of this knowledge has lagged behind. Many conservation interventions failed because the actual problem was not correctly diagnosed. A correct diagnosis of the problem is required to identify its origin so as to allow finding the best solution to it. Only then, can an appropriate conservation intervention be designed.

2.1 Air Pollution

Air pollution became very important in countries where the industrial revolution brought with it the great technological advances. The subsequent pollution problems have been well described in the works of Charles Dickens (1812-1870) for the case of London. The black crusts that formed on the surfaces of the buildings and monuments are the physical evidence of the problem. The first attempt to eliminate them using a grit (i.e., sand) blasting technique, was carried out in Paris around 1955. Unfortunately, most buildings were constructed from a relatively soft local limestone and the amount of damage induced was only realized later. Around 1960, the origin of air pollution was recognized but appropriate measures to control it were only implemented in subsequent decades (BABOIAN, 1986; ROSVALL and ALEBY, 1988).

To understand the air pollution problem it is important to differentiate dry deposition, i.e., when it is not raining, from wet deposition, the so-called acid rain. Dry deposition occurs in proximity to industrial and/or urban areas and generally is far more important than wet deposition. Gaseous pollutants, such as sulfur oxides (SO_2 and SO_3), generally referred to as (SO_x), originate from various industries; while nitrogen oxides (NO y NO_2), simplified to (NO_x), are emitted by vehicular traffic. These, together with air-borne particles and aerosols are accumulated on the surface of buildings forming a deposit. Their concentration in the air, molecular diffusion, and atmospheric turbulence; as well as the nature and roughness of the stone in question, will determine the amount deposited. A critical factor is the time-of-wetness of the stone, i.e., how much humidity does the stone surface store, from moisture condensation or after a rain event, since water will facilitate deposition as well as the reaction between pollutants and material.

On the other hand, wet deposition, during rain or fog, is less important in urban areas. But it can be critical for rural areas. The reason for this is that rain is normally acid (pH ~ 5.6) from the dissolution of carbon dioxide and subsequent formation of carbonic acid. Pollutants transported by rain originate from far away pollutant sources and, because their concentration during the initial rain fall is high, the acidity can reach low pH values (pH ~ 3). However, with on-going rain the pollutants are washed out, and the rain returns to its normal value.

An important point for the deterioration process are the hydrodynamics of the rainfall on the monuments, as originally identified by GUIDOBALDI (1981), and this is also related with the three characteristic deterioration patterns that develop on limestone and marble depending on how water wets them (CAMUFFO, 1990): white areas, where the surface is eroded; black areas, with no run-off but where condensation or percolation occurs; and, gray areas, with no run-off, condensation or percolation. The latter only collect a surface layer of dust but they are not chemically corroded.

Black crusts are the result of the reaction of sulfur oxides with the calcite, calcium carbonate ($CaCO_3$), present in calcareous substrates, such as limestone, marble, calcareous sandstones and lime mortars, following a typical acid attack in the presence of water. The resulting formation of gypsum ($CaSO_4.2H_2O$) incorporates into it solid particles, such as fly ash, carbon, dust, etc., turning the deposit black. Much has been published on this subject, such as BRIMBLECOMBE (2014); CAMUFFO (2013); SABBIONI (2003); CHAROLA y WARE (2002); CHAROLA (1998), y CAMUFFO et al. (1982).

2.2 Soluble salts

Soluble salts, such as sodium chloride (NaCl), sodium sulfate (Na_2SO_4), and sodium or potassium nitrate ($NaNO_3$, KNO_3), can be considered the factor that in general induces most damage to stone and that can, in some instances, induce the fastest deterioration. Soluble salts are ubiquitous, for example, NaCl can be found in suspension in the atmosphere in marine environment, while Na_2SO_4 is found in desert areas, and KNO_3 is found in bat guano deposits. Being highly soluble they easily dissolve in water (even in deserts there is enough water for some dissolution) and in solution they can migrate and by capillarity enter the stone pore system. Once in the stone, water will tend to evaporate at the surface of the stone, leaving the salts behind forming efflorescences and subflorescences, as well as flaking and sanding (AMADORI et al., 1990). Repetition of this cycle results in the slow accumulation of salts within the porous material. Another point to be considered is that the solubility of less soluble salts, such as gypsum, and even calcite—approximately 100 times less soluble than gypsum—, increases significantly when in presence of salts that do not have a common ion with them, such as NaCl or KCl.

To illustrate the point, we can consider a stone monument and its base in contact with the ground. If the soil around it is moist, from rain or groundwater, any soluble salts present will dissolve, and the solution will rise by capillary action entering the base of the monument. The different salts that are present will migrate to various heights as a function of their solubility as described by Andreas Arnold (1982) and crystallize in various habits depending on the environmental conditions during water evaporation (ARNOLD and ZEHNDER, 1991).

The issue of salt deterioration is particularly complex, as not only does the crystallization of salts, either as anhydrate or a hydrated salt induce stresses during this process, but changes in relative humidity will induce further recrystallizations from hydrate to anhydrate, or vice-versa. The reason for this process is the hygroscopicity of soluble salts, which can be defined as the adsorption of water vapor, i.e., moisture, from the air. While most materials are hygrospic, highly soluble salts are particularly so, adsorbing moisture to a degree that turns them deliquescent, i.e., they dissolve in their own adsorbed moisture. This can be explained considering that the water vapor pressure over a salt solution is lower than that over pure water, and will decrease with increasing salt concentration. The minimum is reached when a saturated solution is formed. This point is called the deliquescent relative humidity (DRH). Each soluble salt has a specific DRH, for NaCl this is 75% RH at 20ºC; if the ambient humidity increases above 75% RH, the NaCl starts absorbing moisture and eventually deliquesces. If the ambient RH decreases, the salt in solution will start crystallizing out. But if this salt is in solution with $NaNO_3$, whose DRH is also about 75% RH, there is no longer a single DRH value but a range of them, between ~75% and ~67% RH, depending on the concentration of each salt in the mixture (STEIGER, 2005).

Damp walls in buildings may very well be the result of hygroscopicity of the soluble salts present in them. In general, the first diagnostic in these cases is rising damp, but in general it is forgotten that the maximum height that rising damp will reach is about 1 m, the general case being between 15 to 25 cm. Any moisture found above 1 meter height can be attributed to the hygroscopicity of salts that accumulated over time in the walls of the building (CHAROLA y BLÄUER, 2015; LUBELLI et al., 2006a).

Another point that has to be considered is that if the stone in question contains clays, particularly expansive ones (from the smectite or montmorillonite group), these will adsorb moisture and expand, thus inducing yet another deterioration mechanism, i.e., expansion-contraction. This mechanism is practically reversible when only water is present, but if salts are also present, the cycles are no longer reversible and the expansion increases significantly with each new cycle (SNETHLAGE and WENDLER, 1997; LUBELLI et al. 2006b).

From the vast literature about soluble salts, the following are useful for obtaining a general perspective on the topic: SIMON and DRDÁCKÝ (2006); DOEHNE (2002); CHAROLA (2000); GOUDIE y VILES (1997); BEHLEN et al. (1997); PÜHRINGER (1983).

2.3 Biocolonization

Biocolonization is yet another deterioration factor that impairs stone materials; however, it is not usually as critical as those induced by soluble salts or air pollution, nonetheless the increasing climate changes may well turn it into a more serious issue in the future. Biocolonization is the growth of microorganisms and plants on the surface of materials (e.g., stone). These can induce soiling, discoloration, patinas, and fouling, as well as some chemical attack, especially on limestones and marble. Biological growth on stone is dependent on both climatic and microclimatic conditions, and the bioreceptivity of the substrate depends upon its nature, i.e., mineralogical composition, petrographic properties, surface roughness and porosity; while the presence of water is fundamental (MILLER et al., 2006; CANEVA et al., 2004; WARSCHEID and BRAAMS, 2000).

A frequent question is how this biocolonization occur. Microorganisms, spores, pollen and other biological material is also present in the air. Their deposition on surfaces, will follow a pattern similar to that of air pollution particles. Once deposited, microorganisms secrete extracellular polysaccharide substances (EPS) that will form a coating, or biofilm that protects them from the environment (GORBUSHINA, 2007; KEMMLING et al., 2004). This protective layer retains moisture so that environmental changes are lessened. Not all organisms will be on the surface though, some of them may actually penetrate into the stone, especially if translucent minerals, such as quartz or calcite, are present which allow light to reach deeper into the stone. Microorganisms that penetrate into stone are called endolithic microorganisms. They may dissolve carbonate stone and create microcavities within it (DePRIEST and CHAROLA, 2007). Endolithic biocolonization, especially on white limestone, may turn it visually grey. Once a biofilm is established, the colonization of the stone surface may be followed by that of higher order organisms. The microorganisms in the biofilms, bacteria, fungi and algae, may then provide the nutrient base to allow the development of lichens, followed by mosses, liverworts, and ferns. Subsequently, grasses, bushes, and trees may develop; which may lead to mechanical damage by root growth. A simple description of this process can be found in CEDROLA and CHAROLA (2009).

While biodeterioration at the incipient stage is not very damaging, resulting mainly in soiling and staining, once higher plants develop, as is the case in many archaeological sites in tropical areas, the damage induced may be significant. The soiling and staining of initial biocolonization may be an aesthetic issue for monuments and elimination of this growth may be necessary; this appears a fairly easy task but it has to be considered that biological growth will return and may develop resistance to the biocide(s) applied, or more aggressive organisms may develop. Elimination of higher plants should be carried as soon as ferns and grasses grow. In archaeological sites, where trees have already developed, their eradication has to be considered within the context of the site and its value. The following publications address the various issues discussed in more detail: CANEVA et al., (1991) CAMERON et al. (1997); KUMAR and KUMAR (1999); CIFERRI et al. (2000) KOESTLER et al. (2003); CHAROLA et al. (2011).

3. DISCUSSION AND CONCLUSIONS

The deterioration topics briefly discussed previously serve as an illustration of the complexity of deterioration mechanisms and the fact that in many cases, they may be misdiagnosed. For example, a grey coloration on a white limestone may be the result of a "grey" area from air pollution, or the result of an endolithic biocolonization. To differentiate them, it is critical to observe the location of these areas and whether rain washes over them or not. Therefore, close observation of the building is fundamental for its evaluation.

When considering a conservation intervention on a monument or a historic building, it is critical to identify the deterioration mechanism that may be affecting it, in other words, the diagnosis of the problem. But equally important is to consider its "value", historic, artistic, etc. This requires that as much background and historical information be obtained as possible. Likewise, documentation of the "present" condition of the monument, i.e., the condition survey, is essential. Both of these, the historical information and the condition survey, are the first step required for developing a conservation strategy. The subsequent step is the diagnosis of the problem, to identify the deterioration mechanism so as to determine the most appropriate conservation approach to be taken and considering that in most cases there may be several ways to solve the problem. In conjunction with the diagnosis, the objective of the conservation intervention needs to be defined, especially in the case of buildings that will continue to be used as such. Therefore a consensus has to be reached between these sometimes contradicting values. For this purpose, what is called a "value analyses" should be carried out, between all parties involved in the process: historians, architects, scientists from the different disciplines, geologist, biologists, chemists, physicists, conservators and the "owner" of the object in question. The value analysis also considers the costs and benefits of all the possible solutions, and based on these, the most appropriate one can be chosen.

As human beings we have limitations: in many cases, especially if we are familiar with a building, as for example maintenance personnel, we “see” the building, but we do not “look” at it unless a major change occurs. So looking at the problem, and observing it at different times and conditions, will help to obtain a correct diagnosis. In most cases, problems are easily solved if addressed as soon as they appear: a gutter that needs cleaning, a leaking pipe. These minor problems need to be dealt with immediately to avoid the increased damage that will develop over time; if delayed, the solution will be more complex, difficult, and expensive to address (SESTINI et al. 2013). The most critical point is finding the balance between problem—possible solution—maintenance of the monument or building in question.

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