

Biodeterioration: Risk Factors and Their Management

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ABSTRACT

Historic stone structures are subjected to many damage factors: geological, hydrological, and meteorological factors, pollution loading, human interaction, biological succession as well as cleaning, restoration, and conservation efforts. Under those related to biodeterioration fall biogeochemical and biogeophysical risk factors caused by (a) microbes (including bacteria, algae, fungi, and lichens) enmeshed in gel-like biofilms; (b) higher organisms (mosses, plants, insects, and mammals); and (c) detrimental effects of protective treatments (biocides, direct cleaning, or treatments). All of these factors may damage the stone directly or by synergistically enhancing nonbiological deterioration. What do we know about the rate(s) of damage of these factors? How variable are the rates? Can we estimate a range of risk for them without clear-cut rates of damage? This chapter will discuss what is known or surmised about biodeterioration risk factors and attempt to assign their relative place in the overall scheme of historic stone deterioration.

Management of biological risk factors implies that their relative importance in the overall deterioration of a stone structure has been assessed appropriately. Is this possible with current knowledge? What further practice-related research needs to be performed? Do we know enough about the rates of these factors to recommend treatment? If so, what is the range of treatment that should be recommended? If a biocidal treatment is recommended, how do we assess its effectiveness? How often should it be repeated? How do we assess the cost-benefit relationship between the biodeterioration factor and the treatment?

INTRODUCTION

Biodeterioration of stone materials is an area of research that has been receiving increased interest over the past 15 years in the field of conservation of cultural heritage.

Biodeterioration encompasses the human factor also (see Charola et al. 1993) which has a severe impact on buildings and monuments. Understanding the impact of microbial deterioration on building materials is quite complex. Simplified, single organism studies have clearly shown the potential physical and chemical impact that microbes can have upon building materials (see biodeterioration bibliography, Koestler and Vedral 1991). What is unclear in these studies is how to assess the relative importance of biodeterioration effects versus other environmental damage factors, e.g., air pollution, acid rain, wind abrasion, salt efflorescences. A previous Dahlem workshop helped define this problem and suggested an experimental approach to assess the co-association of physical, chemical, and mechanical damage factors (Koestler et al. 1994).

Is it possible to devise a risk-assessment scheme that would permit field assessment of a given number of parameters and fit these into a protocol that then reliably guides conservation of the building? What are the important parameters that need to be measured?

First, though, one must review biological interactions with stone building materials.

WHAT DO WE KNOW ABOUT BIODETERIORATION OF STONE MATERIALS?

Three general stages, extrapolated from Characklis (1990), of biodeterioration on stone can be envisioned: transport and deposition; interaction with the substratum; and detachment of biogenic crusts from the stone and reinfection.

Transport and Deposition

Microbial colonization of stones requires preconditioning of the surface with dust and pollutants transported by wind, aerosols, plants, and animals. The deposition rate of chemoorganotrophic bacteria on exposed stone surfaces may reach 10^6 cells per m^2 per day; however, many of the airborne bacteria are different taxa than the colonizing bacteria normally found in surface layers of rocks (Eckhardt 1983, 1985; Warscheid 1990). Adhesion of the microorganisms is regulated biologically by the microbial cell structure (e.g., fimbria and pili) and their surface charge. It is physically controlled by the stone surface structure, which partially determines the availability of water, oxygen, nutrients, niche possibilities, and thus the survivability of the microbes. Subsequent formation of surface-covering biofilms increases the stickiness of the mineral surface and improves the living conditions for the microflora by increasing water retention and enhancing deposition of nutritive aerosols and microorganisms from the atmosphere. The precursor function of the microbial biofilm has to be considered as the most important phenomena for biodeterioration impacts on stones. (See Characklis and Wilderer [1989] for a general introduction to biofilms.)

Interaction

Within this term the classical biogeochemical and biogeophysical impacts are subsumed (Table 3.1). Their potential relevance to deterioration of stones derives from laboratory analysis and estimation of rates under natural conditions. The description of reaction patterns refers not only to microbial deterioration mechanisms themselves, but also to measurable changes of the material in question. Biogenic pigments lead to an increase of absorption of light energy and would increase temperature variations. The mineral lattice would be weakened by gel-sol-regulated movement and wetting and drying of slimy biofilms in fractures and in the pore system as well as the corrosive action of biogenic acidic products. In addition, the biofilm alters capillary water uptake and gas diffusion in the stone material and increases the deposition rate of acidic and nutritive aerosols impacting (bio)deterioration processes.

Detachment

During the development of surface-covering biofilms a succession of microorganisms occurs, beginning with the producers and basic mineral-degrading microorganisms and advancing to secondary consumers. Thus, the complexity of the stone-colonizing microflora changes over time. The final stage in the biodeterioration of stones is a loss of the weathering crusts. The cycle then continues with reinfection of the freshly exposed stone surface (Warscheid 1990).

TABLE 3.1 Biodeterioration mechanisms on stones.

Biogeochemical Influences
<ul style="list-style-type: none"> • Acidolysis: chemolithotrophic processes (sulfuric acid, nitric acid) • Complexolysis: chemoorganotrophic processes (organic acids) • Redox processes on cations and anions (e.g., iron and manganese oxidation) and selective cellular enrichment • Phototrophic processes (accumulation of organic nutrients, supply of oxygen) • Discoloration by biogenic pigments (e.g., melanin, chlorophyll)
Biogeophysical Influences
<ul style="list-style-type: none"> • Alteration of the porosity/pore size distribution caused by the contamination of microorganisms linked with changes in the vapor diffusion inside the material caused by extracellular polymeric substances (EPS) and excretion of surface-tension-reducing compounds • Biofilms in the function as "pollutant-absorber" and thus precursor for the formation of crusts • Enhancement of salt migration • Alteration of the aerobic/anaerobic environment

The rate and extent of biodeterioration are influenced by many parameters that in themselves are not constant. Hence, the length of the three periods — transport and deposition (induction), reaction (exponential), and detachment (plateau) — may also vary. No formula has been devised that permits establishment of the biodurability of different stones. It is believed that a durability scale of stones will not be a linear time-related process, but rather that it may be some complex relationship of co-association factors (Koestler et al. 1994).

WHAT ORGANISMS ARE INVOLVED?

A large variety of microbes and higher organisms may grow on and in the stone. Among the microbes are: bacteria, algae, fungi, and lichens. Among higher plants are: mosses, ivy, bushes, and trees (see, for example, Bock and Sand [1993]; Koestler [1991]; Koestler and Vedral [1991]; for more recent references check McCarroll and Viles [1995], lichens; Palmer [1992], techniques; and Urzi and Krumbein [1994], general.) Each general group has many subgroups that may specialize in particular types of stone surfaces and require specific types of environments. For example, among lichens, specialization is common and definitive enough that surface surveys of lichen coverage of the stones' surface can be used to predict the environmental conditions that each area incorporates, e.g., moisture, insolation, salt. However, their presence may only become evident if discoloration of the surface occurs, lichens' coverage becomes sizable, or higher plants (e.g., moss, ivy, or bushes and trees) start growing on the surface. By the time the visible stage is achieved, potential significant alteration of the stone may have occurred.

WHAT ARE THE ORGANISMS DOING ON/IN THE STONE?

Microorganisms act singly or in co-association with other microbe(s), or with physical and chemical damage factors, to deteriorate stones. They may alter the stone physically or chemically in a variety of manners (Griffin et al. 1991; Koestler et al. 1994). One late 19th century study of biodeterioration of stone by lichens (Bachmann 1890) reported on the effects of lichens on calcite-rich stones. In Bachmann's study it was found that the hyphae penetrated the calcite crystals without any regard for crystal planes. This is the same kind of phenomenon Koestler et al. (1985) described with aid of the scanning electron microscope for fungi on calcitic and dolomitic stones. Other studies have dealt with bacteria, fungi, algae, and lichens (see reference citations in the previous section) and have shown physical as well as chemical deterioration attributable to microbes.

Biodeterioration of stones has sometimes been assumed to be a secondary degradation process, occurring after inorganic agents have enriched and conditioned the surface with inorganic and organic materials. Recent biodeterioration investigations,

however, have stressed the fact that even in the early stages of stone exposure, primary biodeteriorating effects can be clearly defined (Warscheid and Kurozckin 1997). This is especially true with the phenomena of surface-covering biofilms formed by microorganisms as a protection against harmful environmental impacts, such as desiccation, and osmotic or temperature variations.

The classical biogeochemical impacts of biocorrosion and biooxidation may weaken the mineral structure of stones and abet subsequent chemical problems, e.g., enrichment and crystallization of salts. Other effects to the stone may occur as a consequence of biofilm-related impacts; these include visual discoloration and staining of stone surfaces from biogenic pigments and mechanical stresses to the mineral structure caused by the presence of extracellular polymeric substances (EPS).

Mechanical stress created by EPS of the biofilm occurs as a result of shrinking and swelling of the colloidal biogenic slimes between the mineral grains and inside the pore system, and, as shown by Koestler et al. (1985), within the mineral grains. The consequent alteration of the pore size distribution may cause changes in the circulation of moisture and further enhance chemical dissolution of the stone. Furthermore, it has been shown that the presence of early biofilms on exposed stone surfaces accelerates the accumulation of atmospheric aerosols and particles (Wittenburg 1994); in this way, microbial contamination acts as a precursor for later formation of detrimental crusts on rock surfaces caused by the acidolytic and oxido-reductive biocorrosion on the mineral structures mentioned above (Warscheid and Krumbein 1994).

Considering this complex background, the definition of rates and extent of biodeterioration processes on stones seems to be a difficult undertaking. All the more so considering the variety of microbial impacts such as exponential (growth rate), seasonal (climatic changes), impulsive (atmospheric influences), or dose law (nutritive parameters) dependencies.

BIODETERIORATION RISK FACTORS VERSUS OTHER RISK FACTORS

In conservation practice, the assessment phase for any project attempts to consider the complete range of possible deterioration factors; this is obviously tempered by the time, experience, and money available for each project. During the condition survey, in general, only simple and quick measurements can be undertaken; occasionally, laboratory assessment of some parameters is economically feasible. The more usual case though is that the scientific investigative phase is of a very limited nature; therefore, if science is to have an impact upon the final treatment outcome, a simplified field assessment of parameters must be devised.

Among the nonbiological factors causing stone deterioration are chemical and physical factors of wet and dry deposition of pollutants and salt crystallization (Charola 1988). The rate of dissolution of calcite, for example, is dependent upon the pH of the water filling the pores and interstices of the stone. Below pH 4, the

dissolution is transport controlled and the rate will be proportional to the hydrogen ion activity, between pH 4 and 6, the rate of dissolution seems to be controlled by surface kinetics (Charola 1988). Microbes can affect the pH of the moisture surrounding stone, thus affecting the chemical rate of dissolution. Therefore, any consideration of biological effects on stone must consider not only the direct interaction of microbes with the material, it must also take into account the alteration of the environment, which may enhance other chemical and physical deterioration factors.

Where do we draw the line between biodeterioration risk factors and chemical and physical factors? What are the parameters for biodeterioration? Can we just provide a rapid identification scheme for those microbes believed to be the most deleterious? Do we know enough about the biodeterioration capabilities of stone-inhabiting microbes to rank their relative importance?

EXAMPLES OF QUALITATIVE AND QUANTITATIVE RATES OF BIODETERIORATION

An example of what can be considered rapid biodeterioration is given by Koestler et al. (1985). In this study, monocultures of fungi and bacteria were grown on samples of calcitic and dolomitic limestone for five weeks. At the end of this period the stone samples had an extensive fungal growth. Examination of the samples with scanning electron microscopy clearly demonstrated a severely etched surface and fungus hyphal penetration into single crystals of the stone. The fungi were able to penetrate 1–2 mm into the single crystals in five weeks. Bacteria were found associated with production of precursors to salt formation minerals (air-dried gypsum crystals only appeared on bacteria-infected stones).

An example of a much slower rate of attack is seen in another experiment. This one used mixed cultures of fungi, algae, and bacteria on medieval stained glass (Koestler et al. 1986). After six months, an extensive coverage of biofilm and organisms was observed on the two types of glass tested (a Na-rich and a K-rich glass). The K-rich glass had only a few circular pits attributable to the microbes while the Na-rich glass had more apparent dissolution and some apparent physical damage. The physical damage was manifested by “spalling” of a fine surface layer of glass, believed to be caused by drying of the biofilm. Another interesting aspect of this study was that the water controls had more damage than the biofilm-covered experimental samples did. This implies that the biofilm actually protected the surface to some extent from the more damaging water attack.

The concept of reducing other environmental damaging effects by a biofilm may also be applicable to stone. However, in the case of lichens, McCarroll and Viles (1995) present evidence that implies a greater rate of deterioration of stone covered with lichens than those not covered. In mortars and renders, Charola and Koestler have repeatedly observed (see Figures 3.1–3.3, and Charola et al. 1985, 1986) that an extensive fungal-hyphal network may permeate the material. After permeation, the

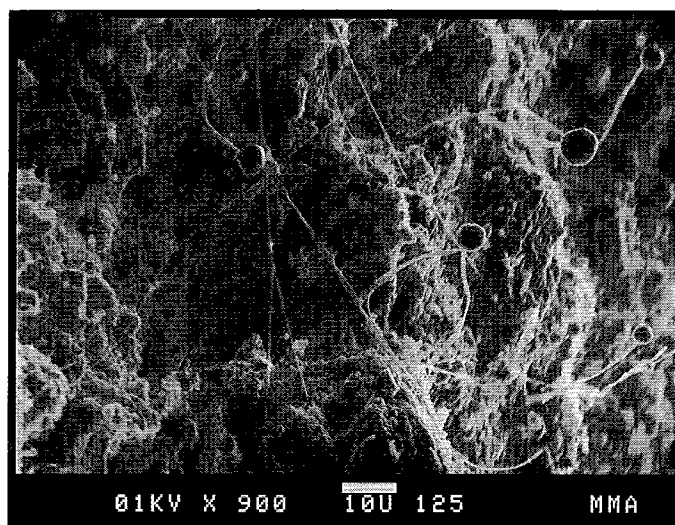
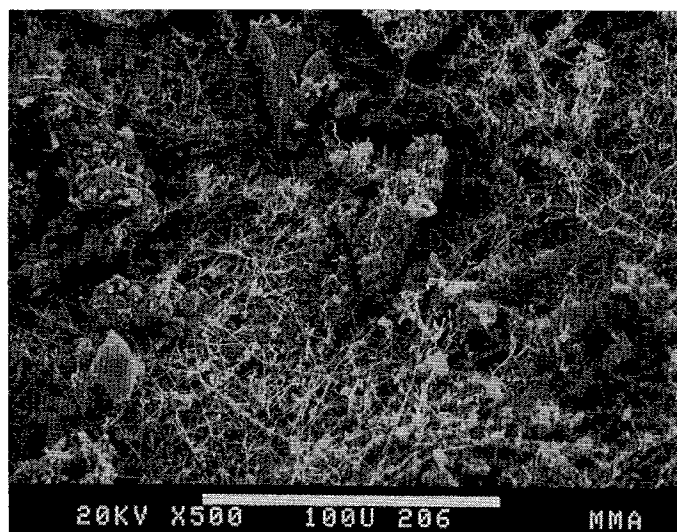
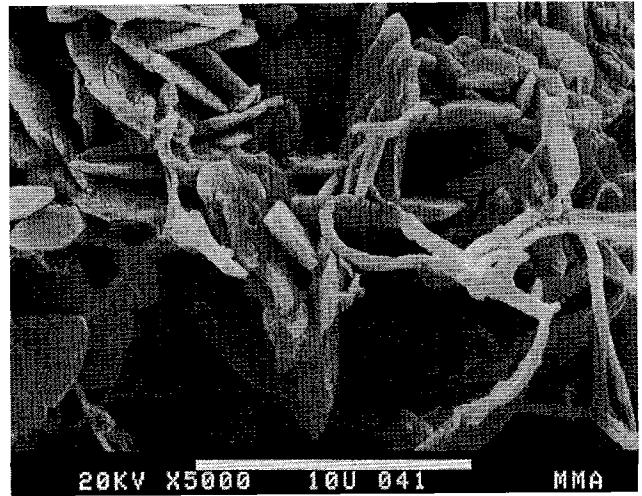


Figure 3.1 Scanning electron microscope image (900× magnification) of fungal-infested mortar (ca. 1500s) from the north sacristy of the Church of Saints Hermès and Alexandre at Theux, Belgium (Photo by Charola and Koestler).

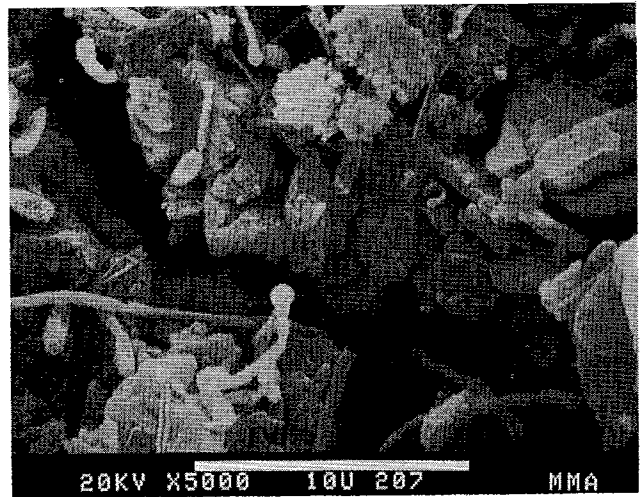


Figures 3.2 Scanning electron microscope image (500× magnification) of decorated render (ca. 15–16th century) from Venice (Fondamenta S. Giobbe), showing the extensive fungal network throughout the render (Photo by Charola and Koestler).

(a)



(b)



Figures 3.3a, b Details of areas in Figure 3.2 are shown at a magnification of 5000 \times (photos by Charola and Koestler).

hyphae seemed to be the only substance providing sufficient structure to hold the material together.

An example of a quantitative assessment study of deterioration is provided by Koestler and Santoro (1988). In this study, a series of 16 conservation products, including water-proofing agents and consolidants, was assessed quantitatively for their susceptibility to deterioration by a mixture of six fungal species. This series of experiments statistically assessed for change by weight loss, sporulation, percent coverage, and FTIR. Loss of material ranged from negligible to nearly 40% during the course of the 5-week testing period (see p. 21 of Koestler and Santoro [1988]; those

that lost the most weight were a vinyl polymer [AYAC], a silicate ethyl ester compound [CONSERVARE OH], and a natural resin [dammar]).

The above examples show a range of responses from rapid (six weeks) to slow (six months) for biodeterioration of different substrates. The material response ranged from minor to major impact, with estimates of material loss up to 40%. Only one of these studies was designed to provide quantitative data on biodeterioration (Koestler and Santoro 1988; Santoro and Koestler 1991). Even though this study was not a multidimensional assessment, as proposed in Koestler et al. (1994), it is considerably easier to carry out and the results are applicable to field conservation. The data derived in this study have proven useful in predicting the real-life behavior of stone consolidants and water-proofing agents, and, in the U.S., have had a positive impact in the selection process of conservation material for high-stress biological environments (T. Frey, pers. comm.; Tudor et al. 1990).

This raises the issue of whether we really need a multidimensional co-association-type of experiment to draw meaningful conclusions, or can we do this with simpler qualitative-quantitative rate deterioration studies?

SYSTEMATIC APPROACH TO ASSESS LEVELS OF BIODETERIORATION

With the above discussion in mind, is it appropriate to attempt to devise an environmental impact assessment procedure similar to those devised for freshwater stream ecosystems (Bode et al. 1990), where only a few parameters are measured to give an overview of the condition of the water?

We think an attempt should be made and propose therefore the development of a method to assess decay using parameters or indicators known to estimate changes in properties of a material resulting from its decay. This methodology is similar to that used in the field of environmental studies, which assesses, a priori or a posteriori, the environmental impact of a certain action on an ecosystem. This method uses parameters of indicators that allow the scientist to evaluate the impact of the action. Some of the parameters used in environmental studies include species diversity, index of biotic integrity, or the invertebrate community index (Bode et al. 1990). They quantify the impact by comparing the species composition of a certain ecosystem at the present time with that of the same ecosystem, but undisturbed. Each of the parameters takes a value within a certain range, from nonimpacted to severely impacted. Generally, they are used together to obtain a certain value of a certain level of impact.

To apply a similar methodology to the field of biodeterioration of building materials, it is necessary to select appropriate indicators. The values of the indicators should range from nondecayed to severely decayed. The number of possible indicators for a given object should vary depending on the type of substrate. All of the indicators would be part of a standard set of indicators. The values assigned by the scientist to each indicator would be arbitrarily determined, based on the background knowledge of the particular substrate. To illustrate this approach we suggest some indicators below:

1. Color: a change in the normal color may be an indication of decay.
2. Presence of microbial growth:
 - a) type: fungal, bacterial, etc.
 - b) extent: percent of the surface affected
3. Biofilm:
 - a) extent
 - b) composition
4. Fragmentation and pitting:
 - a) presence of loose pieces
 - b) measurement of weight loss
5. Change in strength: measured as modulus of rupture (MOR) or modulus of elasticity (MOE)
6. Changes in electrical properties
7. Changes in acoustic properties
8. Presence of organic acids
9. Pore sizes and distribution
10. Scaling and blistering
11. Instrumental measurements may include those for proteins, phospholipids, fatty acids, ATP, respiration by-products, classical light microscopical staining techniques, etc. (e.g., for methodology see Becker et al. [1994] or Palmer [1992]; for ATP, Nieto et al. [1996]).

Some of these indicators have been used in the literature to detect decay in wood and may be applicable for stone. Many more can be added; the key, however, is to keep the number of indicators to the minimum necessary to achieve a reliable, and reproducible, indicator of the risk. In order to weigh all of the parameters at the same time, we need to assign a value for each and then add these values to obtain a single value, which is then associated in a matrix with a certain amount of decay. Some or all of the factors may have to be evaluated together, rather than individually.

Many laboratory experiments and field observations have resulted in volumes of data without deducing relationships of wide general use. Nevertheless, the quantification and design of a conceptual framework of biodeterioration rates are needed with respect to the interpretation of historical data, prediction of future degradation processes, and the evaluation of suitable countermeasures and control techniques.

The proposed model requires collection and compilation of published data—qualitative and quantitative; an assessment of the data to hypothesize possible ranges for rates of deterioration of each damage factor; and validity testing of the rates.

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