



# Mortars and plasters - How to characterize mortar and plaster degradation

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## Abstract

The degradation of mortars and plasters can represent a threat for their preservation. That is why a deep understanding of the degradation mechanisms and the identification of degradation patterns is strongly recommended for who is in charge of conservation of archaeological sites and of built heritage in general. Here, it has been described what are the main degrading agents that can be detected on mortars and plasters and how they act to produce degradation. Moreover, an overview of the analyses which can be carried out directly on site and in laboratory as well has been reported. The knowledge that can be achieved by using such methods represents an essential tool to set up a suitable conservation plan. In addition, a more detailed analysis can also have a research purpose, since they can be useful to clarify some mechanisms and interactions that still remain unclear.

**Keywords** Degradation of mortars · Salt decay · Black crusts · Biodeterioration

## Premise

This Topical Collection (TC) covers several topics in the field of study, in which ancient architecture, art history, archaeology and material analyses intersect. The chosen perspective is that of a multidisciplinary scenario, capable of combining, integrating and solving the research issues raised by the study of mortars, plasters and pigments (Gliozzo et al. 2021).

The first group of contributions explains how mortars have been made and used through the ages (Arizzi and Cultrone 2021; Ergenç et al. 2021; Lancaster 2021; Vitti 2021). An insight into their production, transport and on-site organization is further provided by DeLaine (2021). Furthermore, several issues concerning the degradation and conservation of mortars and plasters are addressed from

practical and technical standpoints (this paper, Caroselli et al. 2021).

The second group of contributions is focused on pigments, starting from a philological essay on terminology (Becker 2021). Three archaeological reviews on prehistoric (Domingo Sanz and Chieli 2021), Roman (Salvadori and Sbrolli 2021) and Mediaeval (Murat 2021) wall paintings clarify the archaeological framework. A series of archaeometric reviews illustrate the state of the art of the studies carried out on Fe-based red, yellow and brown ochres (Mastrotheodoros et al. 2021); Cu-based greens and blues (Švarcová et al. 2021); As-based yellows and reds (Gliozzo and Burgio 2021); lead-based whites, reds, yellows and oranges (Gliozzo and Ionescu 2021); Hg-based red and white (Gliozzo 2021); and organic pigments (Aceto 2021). An overview of the use of inks, pigments and dyes in manuscripts (Burgio 2021) and on glass-based pigments (Cavallo and Riccardi 2021) is also presented. Furthermore, two papers on cosmetic (Pérez-Arantegui 2021) and medicinal pigments (Knapp et al. 2021) provide insights into the variety and different uses of these materials.

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This article is part of the Topical Collection on *Mortars, plasters and pigments: Research questions and answers*

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## Introduction

Mortars and plasters are artificial stone materials, which can be considered having generally a high durability, especially if we compare them with other materials, such as organics, for example, wood, fabric and so on. However, even these building materials may suffer modifications that can compromise their function; mortars and plasters are not forever.

Observing an ancient mortar, we can look for the degradation forms; it is important to assess the conservation state of the material itself and then to plan an intervention to preserve the material and the whole structure to which the mortar belongs to. However, if we pay all our attention to how a mortar made 2000 years ago (Roman structures for example) is degraded, we can fall into the survivorship bias, which had been stated by Abraham Wald, during World War II. The damaged planes during battles had been mapped out; it had been observed that planes were receiving most bullet holes on the wings and tail, while the engine was spared. The early conclusion was simple: the wings and tail are more vulnerable to receiving bullets, so these areas must be needed to be reinforced. On the contrary, Wald said that engines of the aircrafts have to be armoured, because planes with bullet holes on wings and tail were able to come back, while those with bullets on the engine were shoot down. Survivorship bias describes the error of looking only at subjects who have reached a certain point without considering the subjects who have not. This bias can fit our case: if we only look to those materials that have reached the present time, there is the chance we only pay attention to their bad conservation state, but sometimes the right question could be how did this material arrive to present days? This is the question that some researchers asked themselves when they came across some mortars made by Romans and perfectly conserved in an underwater environment (Jackson et al. 2017; Brandon et al. 2014). The study of mortars and plasters in terms of their degradation most of the times has not have a relevant archaeometric implication, because the degradation itself is something that proceeds inexorable along time, although with different rates, depending on the nature of the material, and on the environment as well. Considering two mortar samples having different ages, the older one would not be necessarily more degraded than the younger one; this can also be due to the above-mentioned bias. The main aim of the characterization of the degradation is essentially the understanding of what should be done to preserve the artefact and to improve its durability. Beside the biases that can be experienced, in order to know, restore and conserve mortars and plasters belonging to a structure, it is important to understand the state of conservation. The characterization of mortar and plaster degradation represents a prerequisite for planning a proper intervention (Caroselli et al. 2021; Comite and Fermo 2018).

Before performing such characterization, it is essential to know how to name each degradation form; this is useful to let the other stakeholders (i.e. researchers, restorers, archaeologists) to understand to what we are referring to. One of the main glossaries used is that issued by ICOMOS (Vergès-Belmin 2008). It worth to report two terms of such glossary: alteration which indicates a modification of the material that does not necessary imply a worsening of its characteristics from the point of view of conservation, while degradation indicates the decline in condition, quality or functionality of the material.

Beside the above-mentioned terms, there are terms for each degradation form which can be generally identified by visual inspection.

The analysis of the degradation has a dual purpose; on one hand, there is the need to understand what is going on in the materials and how is the state of health of the materials and of the whole structure of which the material is made of. On the other hand, there is the need to understand what are the causes of degradation; we can refer to the weathering agents, which means something that comes from the environment. However, within the causes, intrinsic factors can be included, related to how the material or the structure is made.

## How and why degradation occurs

The alteration of mortars and plasters can be caused by chemical, physical and biological agents; however it is common that an alteration/degradation pattern is due to a combination of the above-mentioned agents. Undoubtedly, water represents the main degrading agent for mortar and plaster. Without water, a mortar would never exist, since water plays a crucial role into the lime cycle, in which CaO (or MgO) reacts with H<sub>2</sub>O giving slaked lime Ca(OH)<sub>2</sub> (or Mg(OH)<sub>2</sub>), which is the starting material for the making of mortar. In addition, water is needed for the setting of hydraulic or gypsum binders as well. However, water can be also the big enemy of the mortar itself, especially for aerial and gypsum binders, since calcium carbonate and gypsum have a certain solubility in water, so they can be corroded by water; moreover, water can transport salts in the porous structure of the material.

The most important factors affecting degradation processes are related to environment, materials, design, construction procedures and maintenance (Hees et al. 2004) (Table 1). The environmental factors, strongly connected with material factors, exert influence on the development of degradation processes. Orientation and architectural details finally determine the extent to which moisture supply and drying may play a role (Maurenbrecher 1998).

**Table 1** Summary of factors involved in the degradation of mortars and plasters

	Degrading factor	Description
Environment	Water	Rain, ground water, surface water, floods
	Salts	Soil or surface water, air, flood, de-icing salts
	Pollution	Gases and aerosols
	Temperature	High excursions, fires
	Dynamic loads	Earthquakes, wind, traffic, vibrations
	Biological	Epilithic and endolytic colonization, biodeterioration
Materials	Mortar composition	Binder type and composition, aggregate grain size distribution, binder/aggregate ratio, presence of salts into the materials
Design, construction procedure and maintenance	Design	Choice of combination of materials, detailing of the building, choice of repair methods and materials
	Quality of execution	Mixing phase, curing conditions, protection of fresh mortars
	Maintenance	Lack or inappropriate maintenance program

All building materials are prone to degradation processes. These are up to a certain point natural processes, which can be more or less influenced by human activities. Degradation processes exert a stress on the building materials (physical, chemical, physicochemical, mechanical), which, under certain conditions or after a certain time, leads to damage.

## Salts

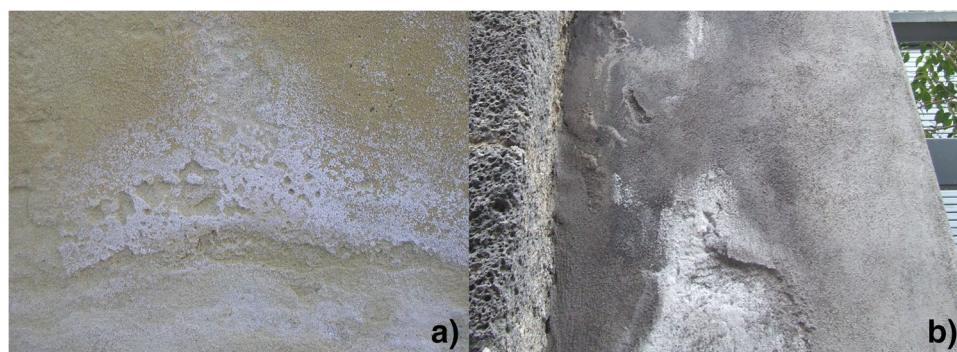
The presence of soluble salts in mortars and plaster reveals that we are facing a degrading factor. Then the question is why do salts represent a threat for the integrity of the mortars and plasters? Soluble salts can easily dissolve and precipitate with temperature and humidity fluctuations that can occur during daily and seasonal cycles. This transformation is the real danger for the mortars, since the crystallization process usually creates a pressure in the pores where the process itself takes place. It is quite intuitive that such pressure is proportional to its salt content: more salt generally means more decay. It is also intuitive that if crystallization process occurs more times, there is a greater chance to have a greater decay: more crystallization cycles, more decay. Salts may have many origins; they can come from

the environment, from human activities, and they could even originate from the materials themselves. Such salts are able to get into the material following different dynamics, such as capillary absorption and diffusion (Binda and Baronio 1987). In all these cases, water is always the transporting agent, and then the moisture content plays a key role in such degradation (Angeli et al. 2007). It has to be pointed out that the water transformation itself can create similar damage to salt crystallization; the freezing of water into the pores creates pressure, since ice is less dense than liquid water, and then freeze–thaw cycles within the material can produce degradation.

Turning back to salts, they can crystallize in several ways originating many forms and habits (Arnold 1984); their damage to the materials is related to the resistance of the materials itself but also on the structure of the pores (i.e. pore size distribution, connections) (Fitzner et al. 1996). The mechanisms responsible for the damage features of salts are the crystallization/hydration pressures and the thermal expansion; these processes exert a pressure on the pore walls.

The areas that are wet the longest are those where the salts are concentrated, so there are areas where the damage from salts can be more pronounced (Charola 2008).

**Fig. 1** Examples of salt degradation: **a** efflorescence, **b** subflorescence



A high rate of water evaporation leads to a crystallization of the salts on the surface of the material, leading to the formation of efflorescence (Fig. 1a), which generally only has an aesthetic consequence. If the evaporation proceeds slowly, there is a high probability to have subflorescences (Fig. 1b), that is, the crystallization of the salts in depth; this is considered one of the most damaging mechanisms for mortars and plasters, where the volumetric salt expansion causes stresses (Theoulakis and Moropoulou 1997; Mosquera et al. 2002).

The main pathological form in mortars/plasters due to salts is the breaking and disintegration of the surface. In masonry structures, mortars and plasters are generally lime-based and play a fundamental role in the circulation of saline solutions throughout the wall. The porosity in these materials is generally high, up to about 25% (Papayianni and Stefanidou 2001) and with many interconnections, and therefore, there is a large fraction of open porosity; this means that there is a high evaporation rate and a low retention of water (Stefanidou and Papayianni 2006). These characteristics lead mortars and plasters to be considered as carriers of water inside the walls and, therefore, also salts, not only between the different wall materials, but also at different heights of the structure causing problems mainly aesthetic and often functional to structures. According to different theories, if the growing crystals exceed the pore size, significant pressures build up on the pore walls resulting in the structure breaking (Scherer 2004).

## Sulphation

It is quite usual to observe a blackened architectonic surface, especially in urban environment. Taking into account just those materials having a carbonate nature, such as limestone or mortar/plaster, this can be due to two mechanisms. The first one is just soiling, which means a bare accumulation of dust on the surface, whose black colour is due to the high carbon content. The second mechanism implies a chemical alteration of the surface: the formation of black crusts. This phenomenon consists in a chemical reaction between sulphur oxides, present in the air as pollutants, and calcium carbonate of the substrate. This reaction leads to the formation of gypsum, which can embed particulate matter becoming black.

The other atmospheric components, such as metals and metal oxides, act as catalysts in the sulphating reaction (Barca et al. 2014). The formation of black crusts leads to a detachment of the degraded layer, because these newly formed materials have different properties with respect to the substrate in terms of texture and porosity, and then the adhesion between them is compromised, that is why black crusts are often observed together with detachments (Fig. 2).



**Fig. 2** Black crust on a plastered wall. Detachment phenomena are also visible

## Biodegradation

Biodeterioration is the degradation process that follows the initial deterioration effects of inorganic agents; biodeterioration effects can be clearly detected in the early stages of exposure to stone (Gaylarde and Morton 1999). These processes include the aesthetically aspect of colour changing of the surfaces by biogenic pigments, which is generally considered unacceptable from a conservation point of view (Urzi et al. 1993). The second effect is the development of extracellular polymeric substances (EPS), which can cause mechanical stresses in the porous structure due to the shrinking and expansion cycles of such EPS (Dornieden et al. 2000). Lastly, biofilms can accelerate the accumulation of air pollutants (Steiger et al. 1993). Also in this case, water plays a key role, since its presence in the material strongly influences the biodeterioration processes. The latter is also influenced by several features of the material, such as porosity and permeability, by the environmental parameters where the object is located and lastly by its specific exposure (Berthelin 1988).

The biomass accumulated by photosynthetic microorganisms (Palmer et al. 1991) and anthropogenic pollutants (i.e. nitrogen compounds, hydrocarbons) from agricultural and industrial sources can satisfy the nutrient needs of the microorganisms that colonize the stone (Zanardini et al. 2000). The bioreceptivity (Guillitte 1995) of mortars and plasters depends on environmental factors, which are the most important (Gaylarde 2020) such as availability of water, pH, climatic exposure and sources of nutrients, and on intrinsic factors: chemical composition, physical and petrological features (Ariño et al. 1997; Sanmartín et al. 2021).

Values of high porosity (from about 14% with an average pore radius between 1 and 10  $\mu\text{m}$ ) lead to a deep penetration of moisture (Warscheid 1996). When solar radiation and high temperatures occur, stone flakes and crusts provide adequate protection for the microflora colonization from harmful UV light and drying (Warscheid and Krumbein 1996).

Susceptibility to microbial attack depends on pore size distribution and on alkalinity (Gu et al. 1998); the higher the alkalinity, the lower will be the bioreceptivity. Mortars containing organic additives have a greater susceptibility to microbial attack (Palmer et al. 1991).

The formation of biofilm initially manifests itself as a colour changing of the surface due to organic pigments. Depending on the type of stone, the upper layers are subsequently preconditioned by the enrichment of adhesive epilithic biofilms deriving from fungal and bacterial growth. Here, the precipitating salts encrust together with the airborne particles and chemical compounds that serve as an additional source of nutrients for the microflora (Viles and Moses 1996). Subsequent physical stresses induced by freeze–thaw changes and salt recrystallization processes continue the weakening and leaching of the mineral material under the surface crust (Arnold 1984).

The microflora colonizing mortars/plasters is a complex ecosystem, whose dynamics are regulated by the environmental conditions and the features of the material itself. Microorganisms can be divided into the following groups:

- *Photolithoautotrophic* organisms, such as algae, cyanobacteria, mosses and higher plants. They use sunlight and release oxygen during photosynthesis and fix CO<sub>2</sub> from the atmosphere producing organic carbon.
- *Chemolithoautotrophic* bacteria use inorganic compounds (i.e. ammonia, nitrites, sulphur) to obtain energy and fix CO<sub>2</sub> from the atmosphere; they produce compounds such as nitrous acids, nitric acid or sulphuric acid.
- *Chemoorganotrophic* bacteria and fungi use organic substrates. They release complexing biocorrosive organic acids or weaken the mineral lattice through the oxidation of metal cations such as Fe<sup>2+</sup> or Mn<sup>2+</sup>.

Studies have emphasized the importance of chemoorganotrophic bacteria and fungi, along with photoautotrophs, as primary microbial colonizers of building stones (Krumbein et al. 1996).

Microbial colonization of stones commonly begins with phototrophic organisms building a visible biofilm enriched with inorganic and organic biomass on the nutrient-depleted surface (Darlington 1981). The photosynthetic biomass acts as nutrient for the heterotrophic microflora and their biodeterioration activity (Caneva and Salvadori 1989), although the growth of heterotrophic microorganisms is also possible without the photosynthetic biomass. In this case, the microorganisms use organic substrates derived from rock material or from deposits introduced by dust and rain, also enriched with organic atmospheric pollutants (Steiger et al. 1993).

Chemoorganotrophic fungi are often present on stone surface, and they can penetrate into the rock material (Krumbein



**Fig. 3** Plastered wall of an archaeological site affected by biological colonization

et al. 1996) and induce discoloration of surfaces, due to melanin (Urzi et al. 1993), and mechanical stress (Dornieden et al. 2000).

Furthermore, their ability to attack a wide range of polymeric substances, including those added to the stone for protective reasons, means that their presence must be considered during conservation treatments (Salvadori and Nugari 1988; Tiano et al. 2000) (Fig. 3).

Biodeterioration processes are rarely caused by a single distinct group of microorganisms. Many groups of microorganisms coexist simultaneously in the same place. Any degradation that occurs is likely the result of complex microbial interactions. This complexity must be taken into account when assessing the conditions and controlling the biodeterioration phase for each historical stone (Warscheid and Krumbein 1996). Microbes are directly and/or indirectly involved in the erosion of constituent stones and minerals (Koestler et al. 1997). The processes of biodeterioration can be grouped in biogeochemical and biogeophysical mechanisms. While the effects and extent of biogeochemical (i.e. biocorrosion) are controlled and determined by the chemistry of the minerals and the binding cement of each rock, biogeophysical influences are mostly regulated by the porosity or shape of the inner surface.

Biocorrosion is caused by the microbial secretion of inorganic and organic acids. These agents can dissolve the minerals of the stone (Kurakov et al. 1999). Depending on the texture and on the physicochemical feature of the stone, biocorrosion results in local little holes called “pitting” and, on a larger scale, in sanding and flaking of the surface (Resende et al. 1996).

Microbial discoloration represents a biogeophysical impact on mineral surfaces and can lead to the loss of aesthetic value (Urzi et al. 1993; Agrawal et al. 1987). Such colour alteration can be due, for example, to melanin, iron and manganese minerals which provide a black colour; photosynthetic pigments which provide a green

colour; and carotenoids which provides a yellow–brown colour.

Another biogeophysical effect is due to the fact that biofilms are often “sticky”; this made the surface prone to collect particles suspended in the air such as soot and dust as well as absorbing corrosive atmospheric pollutants, thus contributing to an increase in the reaction speed of corrosion processes. Penetration of hyphae of fungi and lichens induces stresses into the mortar/plaster and reinforces any mechanical processes caused by freeze–thaw cycles or by salt crystallization.

### Example of how many factors act together

An interesting example of how salts and biological growth can act together and produce an interesting degradation form is the pattern called *Flos tectorii* (Brancato 1986).

It is a unique form of deterioration present on aerial and hydraulic plasters on external walls. It is characterized by the development of concentric or sub-concentric grooves (Fig. 4). Currently it is not fully clear what are the factors that trigger on this degradation, although salts and biological growth seem to be involved. However, recently Actinobacteria has been isolated from plasters affected by this degradation, suggesting its active role in the process, together with hygroscopic soluble salts, leading to selective intergranular decohesion (Randazzo et al. 2015). On the contrary, mineralogical, petrographic and physical–chemical features seem to not have any effect on such deterioration development.

It would appear also that the kinetics of the phenomenon might be related to the microclimate conditions, which favour recurrent high relative humidity. The proximity to the sea seems to be the major risk factor for the advance of this type of degradation, with faster kinetics under more aggressive environmental conditions.



Fig. 4 A plaster affected by *Flos Tectorii*

## Techniques and procedures to characterize the degradation forms

The characterization of the alteration and degradation forms can be divided on two levels. The first one is the characterization on a macroscopic scale. Who makes such evaluation has to have sufficient skills to recognize each degradation form and has to know how to name each one, according to the chosen glossary. Considering a plastered façade, for example, what is usually done is to draw the façade and report the areas affected by different degradation forms, this represents a map of degradation patterns. This procedure is quite simple, and it is a powerful tool if there is a need to plan a conservation action; it can help to understand which is the effort that has to be spent to carry out conservation. It has to be stated that most of the times this is the only characterization that is made; this fact is mostly due to the shortage of funds, so deeper investigations are not possible. But if we are lucky and have the chance to make other analysis, we can go further and perform on-site instrumental analysis or collect some samples and perform laboratory analysis. When we deal with analytical methods, we have to know the distinction between invasive/non-invasive methods and destructive/non-destructive methods. The invasiveness is related to the collection of a sample from the object, while the destructiveness is referred to a method that involves or not the destruction of the sample. A non-invasive non-destructive technique that can be used for assessing some degradation forms is infrared thermography; it is a useful tool for the diagnosis of plaster detachment and may facilitate early detection (De Freitas et al. 2014). An infrared sensitive camera is able to collect infrared radiation emitted by an object and/or surfaces and convert it into an electrical signal and finally into a visible image, in which each level of energy is represented on a colour scale. A detached plaster can have a different temperature from the sound one, and then, it can be detected by this imaging technique. Moving on laboratory analyses, which have an invasive nature, we should ask ourselves why should I perform more accurate analyses in addition to a degradation map? Sometimes instrumental analysis is useless; this is because the conservation team is not able to ask for the right questions, and therefore, useless answers are provided. Generally, such analysis is aimed to have deeper information about the degradation, and then these insights can be used to plan a more focused intervention, which can be more effective than a more general one. In the next paragraphs, it is reported how to make an instrumental analysis of materials affected by the main degrading agents.

### Salt analysis

The presence of salt in mortars and plasters can be macroscopically visible, since they can generate degradation

pattern including efflorescence, sub-efflorescence, flaking and disgregations. However, sometimes, the presence of soluble salts is not quite visible; for example, if a plastered wall is wet, soluble salts can be inside the material but not crystallized. This represents a threat because if some variables change (i.e. temperature or humidity), the salts can crystallize and then create pressure within the material. Each salt has a characteristic temperature and humidity at which it precipitates, so it is important to understand with which salts we are dealing with. Moreover, the determination of the nature of the salt, or of the ions, is also important to understand their sources; for example, nitrates could originate from agriculture and farming activity. Some salts can originate from the mortar itself; thaumasite is a compound that can be formed by the reaction of mortar components with calcium sulphate and water. Thaumasite itself has no binding capacities, but it is able to induce the swelling of the mortar (Collepari 1999). Another example is represented by magnesium sulphates, which can originate when a dolomitic raw material was used, and the mortar suffered a sulphation process (Cultrone et al. 2008). Quantitative salt analysis is required, for example, to assess the effect of treatments aimed to lower the salt content or to make comparisons among different treatments. Moreover, it can be useful to measure the salt content in those materials that have to be used in conservation. Qualitative and quantitative analysis can be made, depending on the aim. An efflorescence can be characterized by qualitative analysis, if there is just salt with monomineralic composition. By collecting a mortar sample, it would be useful to have a quantitative analysis, in order to assess how much salt is present into the material. There are techniques that identify the salts and those which identify just the ions. The first case implies that it is necessary to have salts with no dilution and at the conditions as similar as possible to those where and when the sample has been collected. Methods for salt identification are microscopy, Fourier transform infrared spectroscopy (FT-IR) and X-ray diffractometry (XRD) (Arnold 1984; Bruni et al. 1997, 1998). FT-IR spectroscopy deals with the interaction between infrared radiation and matter. More precisely, infrared radiation interacts with the vibrations of chemical bonds, such bonds can absorb radiation and the technique can measure such absorption. The output of such technique is a spectrum; each matter has a characteristic spectrum. To perform such analysis, the collection of very small samples (few milligrams) is required, although currently there are now available portable FT-IR devices that made it possible to perform non-invasive analysis. The XRD technique is based on the scattering of X-ray radiation due to crystal lattice, each crystal structure has a characteristic scattering pattern, and then

it can be identified. These methods can be hardly applied for quantitative analysis. The instrumental analysis of ions can assure a reliable quantitative assessment; for this, purpose ion-exchange chromatography can be used, which separates ions based on their respective charged groups. The method allows retaining the molecules on the column based on ionic interactions. The ion-exchange chromatography matrix consists of positively and negatively charged ions. For all the above-mentioned analysis, the collection of at least 50–100 mg is required.

### Identification and characterization of black crusts

The issues related to the formation of black crusts on building materials have attracted a strong interest among the conservation scientists since the 1980s of the last century (Gobbi et al. 1998). Mortars and plasters having a high aerial character are very sensitive to black crust formation, since those materials have high amount of calcium carbonate. In order to identify black crusts and have the confirmation that actually what we are observing is gypsum, a simple analysis with FT-IR can be performed. There are many researches that dealt with further and deeper investigations on black crusts (Ruffolo et al. 2015; La Russa et al. 2018; Comite and Fermo 2018). Samples of black crust have been characterized by microscopic techniques (optical and electron microscopy (SEM)) and inductively coupled plasma mass spectrometry (ICP-MS). Microscopic techniques were aimed to understand the microstructure of crusts and how the degradation affected the substrate (Pozo-Antonio et al. 2017). ICP-MS is an analytical technique, which allows to measure the concentration of elements within a sample. By the use of laser ablation, it is possible to understand the spatial distribution of metals in a sample (Barca et al. 2014). ICP-MS allowed the assessment of the amount of heavy metals within the crust and the substrate as well. These analyses have shown the presence of heavy metals coming from air pollution in the material substrate. This situation should be avoided, because those elements could be able to catalyse further sulphation in the presence of sulphur dioxide, so this has an important conservation implication. On the other hand, such researches revealed that black crusts themselves can act as passive samplers of air pollution, and then the analysis of such degradation products can provide information of current and past pollution of the surrounding areas.

### Characterization of biodeterioration

Most of the times, the characterization of the biological growth on mortars and plaster, or more in general on a stone substrate, is limited just to a visual identification, for example, lichens, moss or fungi, although the latter, also because of its general dark colour, can be confused with

non-biological degradation, such as soling or black crust. In order to make deeper analyses, and identify those microorganisms which are not identifiable with macroscopic observations, biological techniques must be used. Such techniques can be divided in culture-based analysis, microscopy and molecular analysis (Negi and Sarethy 2019).

Culture-based techniques consist in letting the microorganisms grow in a solid or liquid media in which nutrients are provided. Once growth, the colonies are identified by morphological observations. Such techniques are well codified by protocols, but unfortunately, only about 1% of the microorganisms are cultivable (Frank et al. 2003). Moreover, culture-based techniques do not provide an accurate estimate of the total microbial population, since such techniques are biased in favour of spore-forming bacteria (Laiz et al. 2003). The sampling of the biodegraded surfaces can consist in collecting small samples with Lancet or swabbing the surface with a cotton swab; all these tools have to be sterile.

One of the commonly used approaches for the characterization of microorganisms involved in biodeterioration is microscopy, which can be performed in situ, by portable microscopes where microorganisms are detected directly in their original position. Microscopy can also be performed in laboratory, in this case a sampling is required, and for this purpose, a small piece of material is removed. A less invasive procedure involves the use of adhesive tape; in this case, a thin layer of the surface containing the microorganisms is peeled off (Urzi and De Leo 2001) and examined by employing optical microscopy and SEM.

Molecular analysis represents the most expensive, but also the more sensitive approach for the identification of biodeteriogens (Gonzalez and Saiz-Jimenez 2004). The most representative analysis is the DNA fingerprinting, in which DNA is extracted from the sample, and then some genes are amplified by the PCR method, which means that many copies of a certain DNA fragment are made. Once sequenced, this fragment is compared with a database such as GenBank or Ribosomal Database Project (RDP) to identify the microorganism; hence, cultivation is not involved.

One of the drawbacks in this technique is the nonstandardization of protocols related to DNA extraction method, primers, sequencing protocol and analytical methods to be used for investigating microbial composition and diversity over monuments.

However, in order to have a more complete analysis of the biological communities on the mortar/plaster surface, an integrated approach, which involves more than one cited techniques, is required.

## The degradation due to the underwater environment: a new challenge

Underwater archaeological sites are fascinating places, which are attracting a growing attention by tourism since the last decades. Focusing our attention on the conservation of the building materials, it can be guessed that the mechanisms of stone decay are different from those observed in aerial environment. When it has been discussed about mortar and plaster degradation, it has been stated that water is the main degrading agent. In this case, building materials are surrounded by water, so we would say that mortar could experience very dramatic stress. Actually, this is not necessarily true, because sometimes such materials establish an “equilibrium” with the environment. It has to be taken into account that if the materials are constantly submerged, there are not great salt crystallization processes, freeze–thaw cycle and other decay process related to water, although the dissolution of the carbonatic binder can take place. Water can also act in a physical way by eroding the surfaces, thanks also to the solid suspension. However, observing an underwater archaeological site, we realize that the main degradation is due to biological growth. Biodeterioration is the main degradation process which occurs in the underwater environment, because mortars/plasters, stone materials and solid surfaces, in general, are substrates for the growth of diversified biotic communities, which are generally benthic forms (communities living close to the seabed) associated with plants and animals (Ricca and La Russa 2020). Communities of benthic organisms lead to the formation of biofouling, just surface encrustations having variable thickness. It can be classified as macrofouling, microfouling and biofilm; its composition varies temporally according to the different biological, physical–chemical and environmental factors (Antonelli et al. 2015). Most of the organisms belonging to the biofouling communities are epiphytic; they just live on the surface, without going deep inside the material. However, some of these organisms cause bioerosion phenomena leading to extensive and irreversible losses (Ricci et al. 2016); these organisms, called endolithic, include both micro-perforating (i.e. algae, bacteria and fungi) and macro-perforating organisms (i.e. bivalves and sponges). Mortars particularly suffer this phenomenon that can occur superficially or inside the substrate, producing internal holes.

Such colonization may cause structural, functional and aesthetic damage, although those can occur simultaneously despite the prevalence of one over the other, depending on the environmental parameters (i.e. light, temperature, depth, salinity).



An ecological study of the marine habitat (Taylor and Wilson 2003) represents the most appropriate methodological approach to make a correlation between degradation and biological growth. As stated for aerial deterioration, the first investigation tool is the macroscopic mapping of the degradation. After that, the collection of samples is generally required, and then laboratory analyses can be carried out to identify as many organisms as possible which are involved into the decay and to understand how and how much the mortar/plaster itself is degraded; this analysis is usually made by means of optical and electron microscopy (Taylor 1990).

## Concluding summary of key concepts

The degradation of mortars and plasters is due to several factors. Beside those related to the bad design, construction and maintenance, the main factors can be ascribable to the environment and the materials, in particular to their interactions. Here, our attention focuses on the main environmental factors: salts, pollution and biological growth. All these agents are linked by water, which is considered the most powerful one. It can dissolve and transport saline solutions and increase the bioreceptivity of the surface and promote the absorption of air pollutants. Salts are dangerous because they can crystallize within pore structure leading to variable entities of degradation. Air pollution represents a threat for mortar/plaster conservation, since sulphur dioxide can react with calcium carbonate, generating gypsum and therefore black crusts. Biodeterioration is a complex interaction among the biological community present on the mortar/plaster surface and the mortar/plaster itself. The degradation induced by such colonies can vary from aesthetical alteration to more serious corrosion of the substrates. It has to be taken into account that all these factors rarely act alone; indeed, degradation is a combination of more than one factor. An overview of what should be done to assess the degradation of mortars and plasters and to understand the degrading factors is provided. The analysis of the salt content can be qualitative and/or quantitative; but in all cases, a sampling is needed. Regarding the identification of black crusts, its identification can be quickly carried out. The analysis of biodeterioration can be carried out by visual inspections, although more precise information is provided by microscopic observations, culture-based analysis and molecular analysis. Before performing any analysis, it is important to understand what are the questions that are worth to be answered; this is the best way to set up the right diagnostic plan.

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**Conflict of interest** The authors declare no competing interests.

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