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Anomalies in wall renders: Overview of the main causes of degradation

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Abstract

The assessment of historical buildings is usually focused on: i) structural features related to brick or stone walls, wooden floors and other structural elements, or; ii) highly valued decorative features such as frescoes, stuccos and façade details. During the last quarter of the 20th century some "secondary" elements also started to receive their share of attention from researchers and practitioners. Wall renders are one of the most important of such elements because of their role as a sacrificial protective layer and the numerous problems that were encountered in the past as a result of incompatibility issues in rehabilitation works. This paper discusses the main causes of the deterioration of wall renders, with emphasis on lime based ones, are thoroughly reviewed and their relative weight in the overall degradation is commented upon.

Keywords:

Mortar, wall renders, deterioration, water, climate, biodeterioration, human influence

1. INTRODUCTION

Mortar results from the intimate mixture of an aggregate (e.g. sand), a binder (e.g. lime, cement) and water and is widely used in constructions. RILEM (International Union of Laboratories and Experts in Construction Materials, Systems and Structures) established a classification of mortar based on its technical applications and another based on the nature of the binder. Other classifications systems and terminologies can be found in the literature (Palomo et al., 2002). Some authors (e.g. Heckroodt, 2002) refer to mortar as the bedding material binding masonry units and to plaster as a coating material. The latter can be divided, in general, into render, when it is applied to external surfaces, and plaster, when applied to internal surfaces. One uses the term 'render' to describe both external and internal wall coating mortar.

Coating mortars are subjected to several degradation agents and their performance will be crucial to the durability of the whole system. This paper presents a brief résumé of the parameters that govern the susceptibility of lime-based mortars to deterioration and overviews some of the main causes of degradation of wall renders, focusing on the most common mechanisms acting in traditional lime based mortars.

2. MORTAR PROPERTIES

The durability of a mortar is highly dependent on the properties of its components, in particular the binder, and on the physical properties of the mortar structure (e.g. porosity). Like many other construction materials, mortar has an open porous structure which is prone to the entry and movement of various potentially harmful substances and elements.

The main parameters (and their effect) on the mechanical performance of lime-based mortars

are: i) the binder/water ratio (within certain limits, lower binder/water ratios induce better mechanical performance); ii) the length of the curing period and curing conditions (crucial for mechanical strength, as higher strength is achieved for longer curing periods and better curing conditions); iii) the binder content (higher binder content improves strength up to certain limits); iv) the particle size distribution (adequate type and shape of aggregates yield higher mortar strengths). The curing duration and conditions are especially important because they control the carbonation phenomena that are responsible for the development of mortar's mechanical properties (Lanas & Alvarez, 2003; de Schutter & Poppe, 2004; Stefanidou & Papayianni, 2005; Hoffman & Niesel, 2008). This process depends on many factors, including: i) mortar porosity; ii) relative humidity; iii) temperature; iv) carbon dioxide (CO₂) concentration; v) lime particle size; vi) sand grain size; and vii) presence of hydraulic components (Dheilly et al., 2002; Martinez-Ramirez et al., 2003; El-Turki et al., 2007; El-Turki et al., 2009; van Balen, 2005). It has been suggested that the total carbonation of mortar could take centuries, which may be one of the reasons for the decline in lime-based mortar use (Cultrone et al., 2005; Ferreti & Bazant, 2006). Several other factors can also affect the performance of lime mortars. For instance, Hansen et al. (1999) observed the importance of the slaking time when using lime putty.

Some of the most relevant properties and characteristics of lime mortars are: i) low mechanical strength due to the low affinity of the calcite and quartz crystal, and to the weak bonding of the calcite particles; ii) high porosity, which induces high permeability to water and water vapour and low resistance to the freeze-thaw cycles (associated with low mechanical strength); iii) high capacity of deformation because of the low module of elasticity; iv) good workability, due to the slow setting process (though this depends on environmental conditions); and v) absence of soluble salts and low solubility of components in normal conditions (Martinez-Ramirez, 1995; Ariño & Saiz-Jimenez, 2004). The first two

properties are considered to be responsible for the vulnerability of lime mortars to deterioration (Martinez-Ramirez et al., 1998). In terms of porosity, the total volume of pores pore size is both relevant to the durability of mortars, as observed by <u>Sarkar et al. (1994)</u>. <u>Lawrence et al. (2007)</u> observed that lime-based mortar tends to exhibit two pore size ranges: i) one around 0.1-0.2 µm, regardless of the water content; ii) the other from 0.5-1.0 µm, depending on the water content. These ranges can be modified, however, by the different processes of production/execution of the mortar, the type of aggregate or binder used, the aggregate/binder and water/binder ratios, the curing conditions, and incorporated admixtures. For instance, the use of putty with a long slaking time instead of dry hydrated lime has been shown to lead to better performance of mortars, in particular in terms of workability and salt resistance (Faria et al., 2008). Von Konow (2003) observed that the use of filler can improve lime mortar properties, especially frost resistance. Traditional admixtures used down the centuries include milk, sugar, eggs, oil, blood, beer and urine, but these have now been replaced by modern products with similar effects (Michoinová, 1999).

In short, it can be stated that mortar, particularly lime-based mortar, is physically and chemically similar to natural carbonate stones (more specifically, sandstone with calcite as binder), despite some differences in terms of mechanical properties. This assumption is used as a basis to analyze the main causes of deterioration, which are described next.

3. MAIN CAUSES OF WALL RENDERING DETERIORATION

The deterioration of mortar in wall rendering is caused by isolated or simultaneous physical, chemical and/or mechanical phenomena. Regarding the classification of the phenomena underlying the deterioration of mortar it is noted that deterioration processes are traditionally grouped in physical, chemical and biological terms (e.g. <u>Hicks</u>, 1982; Martinez-Ramirez,

1995; <u>Mishra et al., 1995</u>; Martinez-Ramirez et al., 1998). 'Biological' can be considered to combine the other two and the authors suggest that a classification such as that proposed by Gaylarde et al. (2003) can be more useful.

Natural disasters (e.g. fire, floods, hurricanes, earthquakes) especially if resulting in interaction with the structural performance of the support under extreme solicitations are the most destructive forces to affect wall renderings. Fortunately natural disasters are rare events and it is water that is, either directly or indirectly, the main cause of deterioration of construction materials in general, and mortar in particular (Aguiar et al., 1997). Furthermore, water reigns over several other causes such as biological or chemical agents (Richardson, 1980; Mariconi et al., 1994; Martinez-Ramirez et al., 1998). Other causes are climate (e.g. humidity, temperature, wind), structural interaction (e.g. support deformation and vibration) and human interference (e.g. execution, use, maintenance, pollution, vandalism) (Addleson 1992; Aguiar et al., 1997; Feilden, 1982; Richardson, 1991).

3.1 Water

The mechanisms behind the ingress of water in liquid form are capillarity and/or infiltration and entry in vapour form is caused by condensation (surface condensation and capillarity condensation) and hygroscopicity (Feilden, 1982; <u>Charola, 2000</u>; Henriques, 1994). In walls, the mechanism involved and the amount of moisture content, will depend on the location and position of the wall (e.g. internal or external wall; in contact with the ground or with the roof), wall properties (e.g. thickness; porosity) and environmental characteristics (e.g. wind direction and velocity; precipitation; temperature; relative humidity) (Fassina et al., 2002).

By itself, excessive humidity can lead to aesthetical anomalies and its presence within the pores of the mortar may result in deterioration due to wetting-drying (physical phenomena)

and freeze-thaw cycles (mechanic phenomena). The first has been proven to increase the rate of cracking of rocks submitted to stress, which is explained by the reduction of surface tension between minerals (Rodriguez-Navarro & Doehne, 1999). In cold climates, the second can be a source of significant deterioration, depending on the mechanical resistance of the mortar, the porosity and pore size, and the degree of saturation (Waldum & Anda, 1999; Palomo et al., 2002).

Meanwhile, in most situations, the destructive potential of water is derived from its role in chemical phenomena as (Collepardi, 1990): i) an element actively involved in all the chemical reactions, in both liquid form or as vapour; ii) a means of transportation and of providing physical contact between components in the liquid form. Deterioration can happen either by direct chemical attack on the mortar components, weakening their structure or causing expansive reactions, or through the growth of soluble salt crystals capable of generating stresses that are sufficient to overcome its splitting tensile strength (Price, 1996). Even though most of the research on this topic has been focused on stone, masonry units and concrete, conclusions for these phenomena and deterioration are also valid for mortar (Lewin, 1982).

Traditional lime mortar is not usually notably affected by water alone. Nevertheless, assuming that sound aggregates are used, pure water will dissolve the calcium carbonate (CaCO₃) until balance is reached (solution with a pH of 9.93). The movement of the solution inside the porous structure of the mortar can eventually weaken the mortar matrix and lower its mechanical strength after a long time. Increased porosity may also enhance the susceptibility and vulnerability to other aggressive agents and further problems may rise from the precipitation of the leachate (Feilden, 1982; Richardson, 1991; Palomo et al., 2002). Clay or other harmful substances, e.g. reactive aggregates, may react with water and cause the mortar to deteriorate (e.g. via expansive reactions).

Soluble salts in the water path can have several sources: air pollution, de-icing salts, soil, sea

spray, building materials (e.g. masonry, concrete). This implies that salts are present in virtually all situations, as Cardell et al. (2003) concluded while observing marine salt damage in rock monuments up to 30 km from the coast in western France. In general, for lime based mortars, except for the transformation of CaCO₃ into gypsum in the presence of sulfur (Charola et al., 2007), most salt damage is due to the pressure generated by the precipitation of salts in the porous structure of the mortar. Salt crystallization pressure is controlled by the pore structure, the supersaturation degree of the salt and the magnitude of the repulsive force between the salt and the confining pore surfaces (La Iglesia et al., 1997; Scherer, 1999, 2004; Flatt, 2002; Benavente et al., 2004; Genkinger and Putnis, 2007). The resulting degradation depends on the location of the reactions, which can be (Honeyborne, 1990; Groot et al., 2009): i) at the surface (efflorescence); ii) within the mortar layer (cryptofflorescence or subefflorescence). Efflorescence usually only leads to aesthetic problems, but it can also indicate that subsurface crystallization is occurring elsewhere (Lewin, 1982; Palomo et al., 2002). Some authors (e.g. Groot et al., 2005; Groot et al., 2009) report that these superficial crystallization-dissolution cycles may lead to damage, often developing gradually from the peeling of paint and surface powdering to sanding, scaling, and crumbling. Salt accumulation inside a mortar layer causes more serious and faster damage, such as spalling of parts of the mortar, and can take place due to (Petkóvic, 2005; Groot et al., 2009): i) the occurrence of a drying front within the render; ii) changes in porosity of successive layers; iii) the application of water repellents; iv) voids (poor contact) at the interface between substrate and mortar. According to Fassina et al. (2002) the structure of the porous material is particularly important as regards the position in which salts are deposited. Physically, where salt crystallization takes place is controlled by the dynamic balance between the rate of loss of surface water and the rate of access of the solution. The dynamic balance is determined by environmental conditions, e.g. temperature, humidity and wind, while the solution rate of access depends on the materials properties (e.g. surface tension, pore radii, viscosity) and on the distance between the solution source and the evaporation surface. If the access rate of the liquid to the surface of the material is slightly faster than the rate of evaporation, the solute is deposited on the external surface. Conversely, if the surface of evaporation is located inside the material the solid crystals will precipitate inside the porous structure (Lewin, 1982; Palomo et al., 2002). However, the drying rate is also relevant, since this dictates the outcome of the competition between advection and diffusion of ions. Consequently, high drying rates can lead to crystallization just because ions cannot move into the remaining solution within the porous structure fast enough; (Pel et al., 2003; Pel et al., 2004). López-Acevedo et al. (1997) found that the location of salt crystallisation also appears to depend on the supersaturation rate and chemical composition of the solution (type of salt). In addition to the damage caused by salt crystallization from solution, some salts have different stable phases, depending on temperature and relative humidity of the air, and this causes changes in volume through hydration (Price, 1996; Flatt, 2002). A third way in which salts can cause damage is through thermal and/or hygric expansion and contraction, but this mechanism has received little attention (Price, 1996; Charola, 2000; Poupeleer, 2007). A recent theory on mortar degradation is based on observations and reports a phenomenon of dilatation that takes place for sodium chloride (NaCl) and other salts after each crystallization cycle (Lubelli, 2006; van Hees et al., 2009). Similar salt-induced damage can also take place in cracks. Poupeleer (2007) concluded from experiments that solution transport through cracks is considerably greater than transport through intact porous areas.

The extent of salt-induced damage surfaces also depends on the type of salt (Fassina et al., 2002) and the mortar's properties, especially its mechanical strength and porous structure (Theoulakis & Moropoulou, 1997; Yu and Oguchi 2009). Sodium sulfate (Na₂SO₄) appears to be the most damaging salt because (La Iglesia et al., 1997; Tsui et al., 2003; Poupeleer, 2007;

<u>Genkinger & Putnis, 2007; Yu & Oguchi 2009</u>): i) it has two stable phases at room temperature and another metastable one, resulting in volume changes with relative humidity variation; ii) the solubility of the salt is more temperature dependent, though not linearly, than relative humidity dependent; iii) a large amount of sulfates is available in solution due to Na₂SO₄'s high solubility; iv) solution absorption capacities are generally higher; v) the evaporation rate influences the crystallizing phase; vi) hydration of the salt may result in an increase of up to 240 times the molar volume; vii) crystals are needle shaped.

Finally, one must consider that salts-induced damage can happen through chemical transformations that result in the formation of expansive compounds (Charola, 2000). In this case there is additional deterioration associated with the direct chemical attack of the mortar components (e.g. gypsum formation as a result of CaCO₃ sulfation).

3.2 Climate and structure

Materials undergo dilatations and contractions with temperature variations. In extreme cases, like fires, the rate of change and the amplitude of the temperature can generate a thermal shock capable of disrupting the material. Even though theoretically possible, the surface temperature required to produce damage by thermal gradient is unlikely to occur through the sun's action (Honeyborne, 1990). In most cases, temperature-induced decay is caused by stresses at the interface between distinct materials produced by different thermal and hygric expansion coefficients (Palomo et al., 2002). Mechanical differences, especially of strength, deformability and elasticity modulus, can also be an underlying cause of decay, as seen by Sanchez-Moral et al. (2005) in Roman catacombs.

Besides extreme events like tornados, wind can participate in the deterioration of wall renders by dragging rain, solid particles or other deleterious substances (e.g. salts) across them. Except for earth constructions, wind-driven rain has been proven to be essentially responsible for enhancing the impact of other agents of degradation, i.e. water, biodeterioration and pollution (Selvarajah & Johnston, 1995; Tang et al., 2004; Abuku et al., 2009). Wind driven solid particles can erode material surfaces and the degradation potential depends on local wind intensity and availability and size of solid particles to be carried. Camuffo (1995) relates the size of wind driven solid particles to their erosion potential (also called "corrasion") in four classes: i). particles of diameter d<100 µm, which are airborne and induce soiling as a main effect; ii) particles of diameter 100<d<600 µm are dragged in successive leaps and can produce erosion when impacting the surfaces; iii) particles of d>600 µm move by creeping and rolling, accumulating in the base of the obstacles; iv) above 6 mm diameter, particles cannot be moved by wind. Therefore, only grains in the leaping range have a "corrasion" effect, but, on average, this only affects the first meter above a building's ground level. This weathering is important only in sandy, windy regions and it is so rare as to be practically unknown in urban areas (Camuffo, 1995). In Western Europe, wind erosion is limited, but wind alone can help to dry surfaces, thereby promoting salt crystallization, for example (Honeyborne, 1990).

Wall renders are also extremely sensitive to the structural behaviour of their support. Vibration, deformation, stress concentration, creep, shrinkage and other processes taking place within the structure of the building or embedded elements can produce stresses in the wall renders that may lead to damage (Feilden, 1982).

3.3 Biological agents

As a substratum, mortar allows the development of the same organisms found in natural stones and other materials (Tiano, 2002; Gaylarde & Morton, 1999). Ariño et al. (1997)

showed through testing that mortar favours the growth of a high number of calcicolous species, similar to those that commonly occur on natural carbonate substrata. Furthermore, considering bioreceptivity as the ability of any material to support biological growth, laboratory tests indicated that mortar is even more bioreceptive than stone (Guillitte, 1995), probably because its higher porosity promotes wetter environments (Crispim et al., 2003). Shirakawa et al. (2003) observed that, for fungal colonisations, the bioreceptivity of mortars is dependent on parameters such as the type of substratum for casting mortars, degree of mortar carbonation, and relative humidity to which mortar samples are exposed. Tiano (2002) notes that higher or lower biodeterioration of mortar can occur depending on whether it undergoes outdoor or indoor exposure, respectively. The commonest microorganisms on the external surfaces of buildings are fungi, algae and cyanobacteria, which can resist repeated cycles of drying and rehydration (Gaylarde & Morton, 1999; Crispim et al., 2003). Cyanobacteria and algae tend to colonize areas protected by shade, while lichens are dominant in dry sunny areas (Ariño & Saiz-Jimenez, 1996). Fungi, particularly moulds, grow readily on internal surfaces, since they only require nutrients and a suitable combination of temperature and moisture (Sedlbauer, 2001; Abuku et al., 2009). Some biodeteriogen develop on the surface (epilithic) while others grow within the porous structure (endolithic) (Ortega-Calvo et al., 1995).

Water is considered to be the basic requirement for the development of biological organisms (Gaylarde et al., 2003). The abundance and distribution of the communities of organisms are controlled by microclimatic factors, i.e. light, temperature and humidity (Ariño & Saiz-Jimenez, 2004; Prieto and Silva, 2005). It has been suggested that the structure (e.g. surface conditions, porosity, permeability) and nature (e.g. composition, colour) of the substrata are important in determining the nature of the communities of organisms (Ortega-Calvo et al., 1995; Ariño & Saiz-Jimenez, 1996, 2004; Gaylarde et al., 2003) and that the degree of contamination in mortars depends on the pore size distribution and alkalinity (Warscheid &

Braams, 2000). <u>Barberousse et al. (2007)</u> found that porosity and surface roughness favour the establishment of algae and cyanobacteria and <u>Giannantonio et al. (2009)</u> observed that biofouling susceptibility increases linearly with the water/cement ratio in Portland cement mortars. Chemical composition, in particular high pH values, is known to delay micro-organism colonization (<u>Barberousse et al., 2007</u>). These parameters are not independent. For instance, biological infections and intensity of biodeterioration are strongly influenced by water availability, which in its turn depends on the location and exposure of surface (microclimatic parameters) and substrata parameters such as porosity, permeability and capillarity (<u>Warscheid & Braams, 2000</u>). Furthermore, these properties can change with time as a consequence of several natural (e.g. biological colonisation; weathering) and artificial (e.g. maintenance; rehabilitation) processes.

Biodeterioration can result from a number of phenomena, the most important of which are chemical or mechanical. Chemical decay can be due either to the use of the substrata material as nutrient (assimilative process) or to the action of the metabolites produced (non-assimilative process) by the biological agents (Gaylarde et al., 2003). The latter is the most typical process of chemical degradation (Kumar & Kumar, 1999), leading mainly to the dissolution of the mortar binder. The growth of biological agents within the pore structure, or in cracks and other defects, induces mechanical stresses that can disrupt the material. Roots of large plants are often the most relevant cause of mechanical decay (Mishra et al., 1995). Physically-induced decay is rare and less well documented, but the retention of moisture within the mortar structure by biological agents may speed up degradation by strength reduction. Warscheid & Braams (2000) refer to changes in the vapour diffusion inside the substrata caused by extracellular polymeric substances and surface tension reducing components, discoloration by biogenic pigments, and thermal-hygric alterations. Aesthetic deterioration may be manifested in colour change and the development of biological patinas,

and it is also usually associated with the forms of deterioration mentioned above (Kumar & Kumar, 1999). Biodeteriogen can indirectly promote water-induced decay by retaining water and changing water flow patterns, and pollution-induced decay, through the absorption of gaseous and particulate air pollutants (Schiavon, 2002).

Microorganisms typically involved in the biodeterioration of building materials are bacteria, cyanobacteria, lichen, fungi and algae (Gaylarde et al., 2003). Gaylarde & Gaylarde (2005) found that cyanobacteria were the most common micro-organisms in biofilm samples from Latin American and European sites, followed by algae. Fungi and actinomycetes were the least common and lichens were not sampled in the survey. In mortar, the first stage of microbial contamination usually extends to a depth of 5 cm and is mainly dominated by bacteria. Ariño & Saiz-Jimenez (1996) found that the depth to which algae and cyanobacteria develop depends on the nature of the substrata and solar exposure. Biodeterioration processes are mainly biofilm formation, narrowing pores - possibly leading to an increase in capillary water uptake - and biocorrosion due to the microbial excretion of inorganic and organic acids. Later on, with the alteration of the physical-chemical properties of the mineral substrate, other types of biological agents may develop (Warscheid & Braams, 2000; Ariño & Saiz-Jimenez, 2004). This process is complicated by the dependence relations that are established between different microorganisms, which may be symbiotic or supportive, with the first colonizers acting as nutrient and forming the basis for the growth of other organisms (Moller, 2003).

BACTERIA

Bacteria are amongst the simplest organisms found in nature. Their huge diversity and adaptability enable them to live in different types of environment, especially surfaces with high water content. They cause material decay by chemical processes. Autotrophic bacteria include those capable of oxidizing sulfur and nitrogen compounds to produce sulfuric and nitric acid, respectively. These bacteria are commoner in anaerobic environments, such as sewer systems where they cause significant damage in concrete pipes (e.g. EPA, 1974), whereas in buildings they have mostly been identified in polluted environments (Mansch & Bock, 2004). Most bacteria found in buildings only produce weaker chelating agents and organic acids (Kumar & Kumar, 1999).

One particular type of bacteria, cyanobacteria (commonly known as blue-green algae), is protected by gelatinous pigmented sheaths that enable it to survive in adverse environmental conditions (Kumar & Kumar, 1999; Crispim & Gaylarde, 2005). This feature makes it similar to algae and several authors have studied them together (e.g. Ariño & Saiz-Jimenez, 1996; Crispim et al., 2003) since their effects on mortars are also similar (Crispim & Gaylarde, 2005).

FUNGI

Fungi are a group of chemoheterotrophic organisms with a typical vegetative growth in predominant filamentous hyphae. They can grow in building materials, even in the absence of light, as long as the humidity, temperature and nutrients are right. Since nutrients can be provided by algae and bacteria, decaying leaves and bird droppings and so forth, temperature and moisture are the parameters that most limit fungi development (Kumar & Kumar, 1999; Moller, 2003). Fungi growth can occur for relative humidity (RH) ranging from 62% to 100%, with most fungi requiring RH above 85%, but saturation is inhibitory, and for temperatures between 0 °C and 52 °C, with most fungi requiring temperatures between 5°C and 35 °C (Adan, 1994). Fungal decay may take place by mechanical processes, due to the growth of the hyphae, but it mostly occurs by chemical processes, associated in particular

with the secretion of organic acids, such as oxalic and citric, and the oxidation of mineralforming cations (Kumar & Kumar, 1999; Warscheid & Braams, 2000; Grbić & Vukojecić, 2009).

ALGAE

Along with cyanobacteria, algae can be considered the pioneering inhabitants of a stone surface (Tiano, 2002). Their development requires dampness, warmth, light, and inorganic nutrients, particularly calcium and magnesium (Kumar & Kumar, 1999). Algae are capable of producing hygroscopic, extracellular polymeric substances to store water during dry weather (Moller, 2003). This has been linked with the following processes of decay (Ortega-Calvo et al., 1995): i) loosening of grains due to volume fluctuation during drying and rewetting or freezing/thawing cycles; ii) sealing action caused by water retention that may affect the water flow through the stone, thus contributing to water-driven processes such as salt dissolution and recrystallization. Decay may also be caused by chemical processes since algae release acidic or chelating metabolic products (Flores et al., 1997). But their main role in deterioration is to support the growth of other organisms such as fungi or bacteria, with higher destructive potential (Gómez-Alarcón et al., 1995).

LICHENS

Lichens are a symbiotic association of a fungus and a photosynthetic partner, generally green algae or cyanobacteria. Their resistance to desiccation and extreme temperatures associated with efficient means of accumulating nutrients allow them to colonize a wide range of habitats (Kumar & Kumar, 1999; Chen et al., 2000). Four main processes are responsible for biodeterioration due to lichen growth (Kumar & Kumar, 1999; Chen et al., 2000; Moller,

2003): i) hyphae penetration of the substrate through intergranular voids, cleavage and fissures, inducing mechanical stresses; ii) moisture-induced volume change of the medulla from wetting and drying cycles, which can induce stresses in the substrate since the medulla can contain up to 300% of the dry weight in moisture; iii) release of the so-called lichen acids (although not all of them are acids), which promote chemical processes that enable lichens to decompose lithic constituents; iv) incorporation of mineral fragments that are loosened by different processes into the thallus. In colder climates, freezing and thawing of the lichen thallus also causes deterioration (Chen et al., 2000). According to Price (1996) chemical damage is more important, and may arise in three ways: i) secretion of oxalic acid; ii) generation of carbonic acid; iii) generation of other acids capable of chelating metal ions such as calcium. Since calcareous rocks are believed to suffer much more severe weathering by lichens (Chen et al., 2000), largely due to the reaction with oxalic acid, it may be assumed that their effect on lime based mortar will also be significant.

Lichen growth has also been reported to provide bioprotection to surfaces by: i) protecting against thermal stress; ii) protecting against abrasion, in particular by windborne particles; iii) forming metal oxalate through chemical reactions with the substrate, which is insoluble in water and may help to prevent further deterioration of the surface (Ariño et al., 1995; Carter & Viles, 2003; Moller, 2003).

BRYOPHYTES

Bryophytes develop in inorganic building surfaces where enough nutrients have accumulated and conditions are in place for their fixation. Mosses, one of the most common bryophytes found in buildings, are small green plants with stems and leaves but no roots. Mosses absorb water and nutrient solutions throughout their surface (leaves, stems and rhizine), and most mosses need very damp conditions for survival, even though some can endure drought for a long time and revive when moisture is supplied again (Moller, 2003). Most references regard bryophyte decay as mostly aesthetic (e.g. Kumar & Kumar, 1999; Tiano, 2002), but biochemical and biomechanical mechanisms may occur (Altieri & Ricci, 1997; Kumar & Kumar, 1999).

LARGER PLANTS AND ANIMALS

Larger plants usually establish themselves when the substrate is already under serious attack by other biodeteriogens that provide them with the required nutrients. They also need light and suitable climatic conditions (Mishra et al., 1995). They are mainly distinguished from bryophytes by their roots, which can induce both mechanical damage, when growing into cracks and fissures (exerting pressure up to 19 atm. axially and one-third to one-fourth of that in the radial direction), and chemical damage, through the production of acidity and exudates from their rootlets (Winkler, 1994; Mishra et al., 1995; Tiano, 2002). The presence of plants also influences the microclimate of the surface by increasing relative humidity and water retention. These favour the growth of other microorganisms and attack from acidic gases in polluted atmospheres. However, a change in the microclimate of a stone surface is not necessarily harmful and may actually help to protect it against other factors of decay (Kumar & Kumar, 1999).

Animals, in particular birds (e.g. pigeons), can directly or indirectly damage mortar substrate. The direct destructive action of birds is mechanical, caused by trampling and grazing, and chemical, caused by acid excrement (guano). This is high in nitrate and phosphate compounds. Along with other organic substances accumulated by the fauna, it can be used as nutrients by heterotrophic micro flora (Tiano, 2002). Guano contains phosphoric acid that can also cause considerable damage (Hicks, 1982).

Biological agents do not tend to develop at the same time since their requirements are different. Phototrophic organisms are considered to start the colonization, building up a visible biofilm of enriched biomass that supports the development of heterotrophic organisms (Crispim et al., 2003). According to Mishra et al. (1995) the sequence of biological growths is: i) algae/lichens; ii) fungi/bacteria; iii) mosses; iv) higher plants. This sequence is based fundamentally on nutrient demand, with the first biological agents feeding the next, and on anchorage ability. They produce extrapolymeric substances, too, and develop into biological communities that enhance their destructive potential (Sand, 1997; Papida et al., 2000).

3.4 Humans

Human influence on the deterioration of buildings is often forgotten, but it also contributes directly and indirectly to wall render degradation. Direct influences include the execution of renders itself, where selection of unsuitable materials, preparation of the support, application of the mortar or curing cause many cases of premature deterioration. For ground level external surfaces, generally up to 2 m high, accidental actions (e.g. being struck by vehicles) and vandalism are other direct human actions that explain several anomalies. Ultimately, political, social and economic constraints also dictate direct human action related to historical buildings in general, with war being one of the most destructive agents of historical buildings (ICOMOS, 2001, 2002). Among the human activities that may pose the most significant indirect threat to wall renders on historical building are tourism, in the case of internal surfaces, and pollution, for external surfaces.

A wide range of standards have been designed to ensure that the properties of the material are adequate (e.g. EN 459-1:2001 for lime; EN 13139:2002 for aggregates). However, in

historical buildings, ensuring compatibility between new and old materials, whose properties are usually unknown, is an additional problem. Past experience has proved that mortar used in rehabilitation works can be a source of decay due to incompatibility, which may be: physical (e.g. low permeability - Veiga & Carvalho, 1998), chemical (e.g. source of soluble salts -Corinaldesi et al., 2003) and mechanical (e.g. excessive retraction - Veiga, 1998) (Michoinová, 1999; Veiga & Carvalho, 2002; Sandrolini et al., 2007). Extensive research has been conducted to develop methodologies to identify existing mortar types. The method proposed in the EDAMM Project (van Balen et al., 1999) has international scope. In Portugal, a methodology aiming at the full characterization of lime-based mortars has been developed at LNEC (Veiga et al., 2004). These and similar approaches (e.g. Arioglu & Acun, 2006) have been used as a starting point for the design of replacement/repair mortars (e.g. Binda et al., 2003; Moropoulou et al., 2005; Maravelaki-Kalaitzaki et al., 2005; Maravelaki-Kalaitzaki, 2007). The heterogeneity of historical building walls requires special care before the application of mortar. The three main issues related to the substrate that generally come up are (Sousa, 2003): i) presence of loose particles/dust and dirt in the surface; ii) uneven surface; iii) high water absorption potential. The last two factors are frequently forgotten and lead to: i) cracking as a result of the shrinkage of excessively thick layers of mortar (Vadstrup, 2008); ii) lack of adherence as a result of water being absorbed from the mortar by the support (Pavía & Caro, 2006). The execution of render as a sequence of thin layers prevents shrinkage cracks and enhances carbonation (Moropoulou et al., 2000). Lime-based mortar performance is extremely sensitive to curing conditions. Lanas et al. (2005) observed the importance of maintaining a high degree of humidity during the application of lime-based mortars in order to carbonate calcium hydroxide (optimum at 60% RH), as long as it is not excessively high (above 80%) (Moropoulou et al., 2000). This factor has been found to have a strong influence on the mechanical properties (Lanas et al., 2006). Furthermore, since full carbonation of limebased mortars can take many years, serious deterioration can occur during the first period of exposure. Lanas et al. (2005) observed, through weathering tests in a climatic chamber, the total deterioration of aerial lime-based mortars within 7 days, while natural hydraulic lime-based mortars withstood them.

The release of pollutants into the atmosphere alone is not sufficient to explain the degradation as the transfer process must also be considered. Thus two main forms of surface deposition of air pollutants are identified (Hicks, 1982): i) dry deposition; ii) wet deposition. Dry deposition is the transfer of pollutant gases and/or particles, including aerosols, from the atmosphere to a surface in the absence of rain. This is thought to be far more important than wet deposition in highly polluted areas, particularly for vertical sheltered elements, and pollutants are generally generated in nearby sources - short range deposition (Charola, 1998). For dry deposition, the mechanism and rate of transfer is dependent on the state of the pollutant (Hicks, 1982): i) gaseous pollutant transfer is largely determined by the chemical affinity with the surface materials; ii) large particles are deposited by gravitational settling and by inertial impaction, and deposition efficiency depends on particle shape and on the structure of the surface at the impact point; iii) small particles are captured by van de Waals forces but their access to the surface is controlled by the adjacent boundary layer. The deposition rate is enhanced by: i) higher pollutant concentration; ii) greater air turbulence; iii) increased surface moisture (Charola, 2000). When pollutants are incorporated in water, in cloud droplets or rain drops, before being transferred to the surfaces, wet deposition takes place. The pollutants incorporated in wet deposition are usually produced by distant sources - long range deposition - and only affect exposed surfaces (Charola, 1998). This acid rain has two antagonistic effects: i) it transports pollutants to surfaces in a low pH solution; ii) it can wash the surfaces and remove, for instance, pollutants from dry deposition. The interaction between water and pollutants and consequent damage is extremely complex. Some parameters that are

involved in this mechanism are (Hicks, 1982; Charola, 1998): i) pollutant concentration; ii) rain characteristics (e.g. intensity, duration, total amount); iii) surface exposure. Evidence suggests that deterioration by action of chemicals in precipitation may be less aggressive than the hydration and mobilization of pollutants already deposited on the surface (Hicks, 1982). Surface properties also influence the action of pollutants. Surface roughness and high porosity facilitate the deposition of pollutants by reducing the removal of particles and damage products by resuspension and washout (Brimblecombe, 2003).

According to Hoffman et al. (1976) (op cit Brimblecombe, 2003) the effects of air pollution on fully carbonated lime/sand mortar are similar to those on loosely bound sandstone. Sabbioni et al. (1998) observed that black crusts in ancient lime mortars have a similar composition and structure to the damaged layers found on sandstones. However, there are great differences since the alternating dissolution and reprecipitation over geological periods leads to the densification or consolidation of calcite in sandstone (Hoffman and Nielsen, 2008). Three main classes of deterioration mechanisms are involved the in air-pollution damage of lime-based mortars (Lanas et al. 2005; Brimblecombe, 2003; Bravo et al. 2006): i) aqueous dissolution reactions of CaCO₃, as a result of increased water acidity; ii) chemical attack by CaCO₃, i.e. sulfation into gypsum; iii) staining associated with particle deposition, which may catalyze deterioration processes. Dissolution of CaCO₃ in polluted environments is a consequence of higher acidity. The presence of carbonic, sulfur or/and nitrogen acids, formed when water combines with CO_2 , sulfur dioxide (SO₂) and nitrogen oxides (NO_x), respectively, considerably increase the solubility of CaCO₃ (Feilden, 1982; Richardson, 1991; Palomo et al., 2002). Sulfur and nitrogen acids can even cause slow deterioration of silica (Richardson, 1991). The dissolved CaCO₃ is then free to move with the water throughout the porous structure and precipitate elsewhere. Related to weakening of the calcareous matrix, crystallization can produce efflorescence and subefflorecence, in a similar way to that described previously for soluble salts. In exposure chamber testing, Martinez-Ramirez (1995) found that SO_2 with water (H₂O) and ozone (O₃) was far more reactive than NO or NO₂ in mortars. Furthermore, SO₂ alone has a destructive effect on lime-based mortars similar to NO+O₃+H₂O or NO₂+O₃+H₂O (Martinez-Ramirez et al., 1997). Some pollutants, e.g. SO₂, can react with mortar components to produce chemical changes with destructive consequences. Lanas et al (2006) observed that lime-based mortar exposed to SO₂ in an outdoor environment resulted in gypsum formation and in increase of porosity, causing strength decrease and higher levels of alteration degrees. The problems generated by gypsum formation depend on several circumstances (van Balen et al., 1999): i) after forming at the surface gypsum is easily washed away from elements exposed to rainfall due to its greater solubility; and ii) gypsum formation either leads to growth of black surface crusts on low porous materials (marble and limestone) or takes place inside materials with high porosity (sandstone and mortars). The colour of the crusts is given by carbonaceous particles, particularly fly ashes, which are trapped within the crust. More important, however, is that the particles are not passive prisoners in the crust. They contain metal oxides that catalyze the oxidation of sulfur dioxide and hence promote formation of the crust in the first place (Price, 1996). Laboratory tests have shown that particulate matter plays a role in the fixation of atmospheric sulfates on calcareous materials (Rodriguez-Navarro & Sebastian, 1996) and in the formation of damaging products (Sabbioni et al., 1993). But in situ phenomena are far more complex due to the interaction between different pollutants and salts. The presence of other salts in the solution influences the solubility of calcium sulfate and the relative humidity at which it may crystallize (Price, 1996). Kucera & Fitz (1995) report the synergistic corrosive effect of SO_2 and NO_2 that results in the formation of nitric acid (HNO₃). International project MULTI-ASSESS (2005) reviewed the dose-response functions developed by ICP Materials for SO₂ dominating situations to account for these synergies. For limestone, the surface recession (R in μ m) can be estimated by the following equation:

 $R = 3.1 + \{0.85 + 0.054 Rain[H^+] + 0.0059[SO_2]Rh_{60} + 0.078[HNO_3]Rh_{60} + 0.0258PM_{10}\}t$ With

$$Rh_{60} = \frac{Rh - 60 \text{ when } Rh > 60}{0 \text{ otherwise}}$$

Where Rain is the amount of precipitation (mm/year); H^+ is the degree of acidity (mg/l); SO_2 and HNO₃ are concentrations (µg/m³); Rh is the relative humidity (%); PM₁₀ is the particulate matter concentration (µg/m³) and t is the length of exposure (years). The equation shows that SO_2 alone is the least important pollutant and HNO₃ is the most relevant. Also interesting is the role played by Rh. In principle this equation is conservative for mortars since exposure tests performed in a laboratory chamber show that the reactivity of mortar to SO_2 is higher than that of stone (Zappia et al., 1994).

Tourism can be a significant cause of degradation due to building use (e.g. abrasion, impacts) and the creation of microclimatic conditions favourable to other degradation agents. Sanchez-Moral et al. (2005) observed that microenvironmental conditions resulting from the presence of visitors in Roman catacombs created temperature, humidity and light conditions propitious for the development of biological agents.

4. FINAL REMARKS

A résumé of the main causes of degradation and the associated anomalies is presented in Table 1. For that purpose, the anomalies were grouped into four broad categories: i) aesthetic/visual, which comprise stains, dust, superficial growth and other non-structural defects; ii) superficial deterioration, including, along with erosion/abrasion, anomalies such as pitting and sanding; iii) internal deterioration designates anomalies that can produce a general destruction of the mortar over the entire depth resulting at the end in crumbling (it may also manifest itself in a similar way to interfacial deterioration); iv) interfacial deterioration, comprising anomalies such as flaking, delamination, blistering, spalling; and v) cracks/fissures, related to situations where a tension is created able to produce a visible crack or fissure without being a consequence of other phenomena (e.g. cryptofflorescence resulting in superficial fissures).

Most damage to mortar arises from various causes that can take place at the same time or sequentially. Furthermore, apparently secondary influences unexpectedly turn out to be apparently primary ones (Hoffman and Nielsen, 2008). Other than direct human actions, water is reported as the main cause of deterioration. From the literature and observation of buildings in Portugal, salt-induced decay was found to be the most relevant in wall renders in urban or maritime environments. Damage is usually more intense at a building's ground level (capillarity action) or near its roof (roof leakage). In rural environments, biodeterioration is more relevant, particularly in internal yards protected from wind and with shady areas that provide the most propitious conditions for the development of biological agents. The interrelation of different mortar/substrate combinations has not been fully explained, despite some research work on this subject (e.g. <u>Buzzi et al., 2007</u>). Consequently, not only the presence of both elements, but also their mutual influence, makes such a system very complex.

The multitude of variables influencing the degradation of real buildings in general makes it extremely complex to identify all the underlying causes, their relative importance and eventual interrelation. Degradation tends to have several causes, where synergistic relationships may be established (e.g. <u>Herrera & Videla (2004)</u> observed interaction between biological and atmospheric effects). Identifying these causes in historic buildings is even more complex because of the longer exposure to changeable and unknown environmental

conditions, uses, alterations and/or maintenance operations (Mariconi et al., 1994). Furthermore, interaction between the different materials (e.g. brick/stone and mortar) that compose building elements can lead to selective decay (Cultrone et al., 2007).

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Cause	Water effect			Potential source		Anomalies				
	Control	Enhancement	Indifferent	Acids	Salts	Aesthetic Visual	Superficial deterioration	Internal deterioration	Interfacial deterioration	Cracks Fissures
Water										
Pure	-	-	-	-	-					
With salts	-	-	-	-	-	(1)	(1)	(2)	(2)	
Climate ^(a)										
Temperature	(3)	(4)		-	-		(3)	(3)	(4)	(4)
Wind				-	-					
Structure				-	-					
Biological Agents										
Microorganisms ^(b)				Yes	No	(5)	(6)			
Bryophytes				Yes	No					
Higher plants				Yes	No					
Animals				Yes	Yes					
Humans										
Intervention				No	Yes					
Pollution				Yes	Yes					
Tourism				No	No					

Table 1 - Most common anomalies resulting from the main causes of deterioration of lime-based wall renders.

Primary effect/anomaly

Secondary effect/anomaly

(a) Except for freeze-thaw deterioration, it is only possible in extreme environments (e.g. deserts)

(b) Except in very favourable environments (e.g. tropical regions), the rate of decay is very low

(1) Efflorescence

(2) Cryptofflorescence

(3) Freeze-thaw

(4) Hygrothermal volume changes

(5) Bacteria, fungi, algae and lichens

(6) Bacteria, fungi and lichens