

# CHAPTER 1

## Environmental factors that influence the deterioration of materials

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### 1 Introduction

The process of deterioration of materials induced by outdoor environmental factors is a complex interplay of the effects of climate and local meteorological characteristics, of biological processes and frequently of complicated chemical processes resulting from the impact of pollutants and natural constituents from the surrounding environment. Except for the decay caused by cataclysmic events, the principal natural environmental factors affecting the deterioration of materials include, but are not limited to, moisture, temperature, solar radiation, air movement and pressure, precipitation, chemical and biochemical attack, and intrusion by micro- and macro-organisms. Natural factors, together with those expected to be a part of the pollution processes, continuously promote weathering and material decay, including metal corrosion.

The evaluation of the influence of each of the environmental factors in a given situation requires an understanding of which mechanisms are potentially of concern for the type of material or structure in question. In general, the main deterioration mechanisms include: (1) erosion, (2) volume change of the material and the volume changes of the material in pores, (3) dissolution of a material and the associated chemical changes, and (4) biological processes.

In material science, erosion is described as the recession of a surface because of repeated localized shock. In an outdoor environment, the erosion of a material is usually affected by suspended abrasive particles, especially by fine solid particles driven against the material surface by moving fluids. The surface area to particle size ratio controls deterioration because for a given volume of material, the smaller



particle size, the larger is the surface area exposed to erosion (the presence of joints also increases a material's surface area). The nature of the fluid flow is likewise important – a markedly smaller effect may be observed for laminar flow than for turbulent flow.

Changes in the volume of a material are a function of temperature, solar radiation and humidity; the volume changes of the material in pores are controlled by humidity and temperature. The thermal expansion and contraction of a material is influenced by temperature variation, which, in outdoor environment depends on the duration and intensity of exposure to the incoming solar radiation and the direction in which the material surface faces (although expansion caused by changes in temperature from day to night or from summer to winter has only a minor effect). Rainfall, fog and wind can cause volume variation due to uneven moisture content. The differential dimensional changes associated with the change in moisture content can be observed in different materials that are bonded together. Such dimensional changes can have a warping effect. A similar attack may be caused by differential moisture content through the layer of a homogeneous material, since the side with a lower moisture content will expand less than that with a higher moisture content (this effect can be observed when rainwater is absorbed on the outdoor surface of a material). Water in combination with freezing conditions can lead to a rapid destruction of certain materials. Water that penetrates into a material may freeze. Frozen water expands and strong pressure is exerted on the structure of the material. A climate with temperature fluctuations across the freezing point can cause the most damage, as repeated freezing cycles can effectively destroy the surface material. The degradation process thus depends upon the degree of saturation with water, the rate and number of freezing cycles, the elastic properties and the strength of the material, and the pore structure of the material.

Deposited contaminants and products of reaction between pollutants and materials can also induce expansion. Chemicals from the surrounding environment can affect the oxidation of a material into more voluminous forms; surface hygroscopic contaminants such as salts, metal oxides, and vegetal fibres in which moisture can be present also play an important role. They can absorb water in different ways including: binding using surface energy, sorption with the formation of a hydrate, diffusion of water molecules in the material structure, capillary condensation, and formation of solution. The moisture content of these substances depends on the nature of the substance, the temperature, and the partial pressure of water vapour in the immediate environment.

Chemically induced damage involves dissolution, oxidation, and hydrolysis. The decay is a result of the interaction between material and natural constituents and pollutants and the amount of water present. The interactions will vary depending on the reactivity of a material, the character of the intercepting surface, the extent of exposure, and the nature of the contaminants. The chemical changes are enhanced by heat (most chemical reactions proceed more rapidly as the temperature increases); therefore, chemical damage to materials is most prevalent in warm, humid climates.

Dissolution of building materials, especially structures containing carbonates, is most frequently caused by the action of acidic solutions such as rain containing



carbonic acid or both carbonic acid and sulphuric acid. The overall effect of carbonic acid and sulphuric acid can be extensive weathering of a surface. The crystallization of dissolved compounds from solutions and the hydration of deposited contaminants and products formed during the reaction of a material with chemicals accompany crystallization and hydration pressures. The pressures may be surprisingly high and can lead to mechanical deterioration of a structure.

Oxidation of a material by atmospheric oxygen leads to chemical changes in the composition of the material (especially the material surface); for example, the reaction of metal ions with oxygen to form oxides or hydroxides.

Hydrolysis reaction between a material and water can affect the dissolution of the material and/or change of its chemical composition. Hydrolysis leads to a decrease in material cohesion and a change in porous structure.

The biological factors that cause deterioration include biochemical effects and intrusion by different organisms. A biochemical attack is usually a crucial factor in the biodeterioration of building structures, as the metabolites (such as enzymes, excrements, and faeces) of macro-organisms, plants, and animals living in the material can affect the material chemically. Hyphae of fungi and lichens and plants root systems, which spread through the structures, induce mechanical damage of the structures. In addition, boring insects may destroy structure cohesion, which can allow water to penetrate more quickly and deeply, speeding other deterioration processes.

## 2 Meteorological and climatic factors

Climatic conditions and meteorological characteristics can affect damaging processes such as mechanical stress, desiccation, surface scaling, attrition, and cracking and may accelerate certain forms of chemical attack on materials.

Climatic factors including air temperature, sunlight radiation, air humidity, different forms of precipitation (rain, snow, etc.), and wind velocity and direction are undoubtedly significant. The impact of these factors varies and depends on the seasons and the intraseasonal variability because they determine the duration of sunshine, the temperature fluctuation (e.g. rapid and large diurnal temperature changes), air movement/pressure, rain intensity and frequency, and local soil hydrology.

The meteorological conditions affect processes of transport, transformation, dispersion, and deposition of emissions from sources and thus may influence pollution-induced damage of materials. Conversely, the cycles of pollutants can affect physical processes in the atmosphere. Increasing atmospheric concentrations of carbon dioxide and other trace gases alter air chemistry and affect chemical reactions. Carbon dioxide emissions influence temperature variation by the greenhouse effect, which can accelerate reactions and stimulate chemical changes on the material surface in an outdoor environment. Sulphur dioxide emissions have a cooling effect as they backscatter sunlight and produce brighter clouds by allowing smaller water droplets to form.



## 2.1 Moisture

Moisture and temperature affect the chemical, biological, and mechanical processes of decay. The formation of a moisture layer on the material surface is dependent upon precipitation. It may also be generated as a result of the reaction of adsorbed water with the material surface, deposited particles with the material surface, and deposited particles with reactive gases.

On a surface with moisture, particles have a better possibility of adhering and water-soluble gases are more readily captured. Both gas and particle fluxes increase when condensation takes place on the material surface and decrease when evaporation occurs.

A moisture layer is a medium for the chemical and photochemical reactions of surface contaminants and is also a conductive path for the electrochemical reactions. Two variables are important from the viewpoint of the damage caused by moisture: dew point and relative humidity of air. Dew point is a characteristic of the water content of the large-scale air mass, whereas relative humidity depends on the local temperature and therefore on the local meteorological parameters. When the temperature of a material is below the ambient dew point, water condenses on the material, a moisture layer (condensation) can form, and the material damage may proceed. In most materials, an increase in relative humidity causes further deterioration due to more prolonged wetness time, higher deposition rates of pollutants and better conditions for biodeterioration.

Among climatic factors, humidity plays the most important role in outdoor metal corrosion. In the absence of atmospheric moisture, there will be very limited non-pollutant-induced and pollutant-induced corrosion. The rate and nature of the corrosion is a function of relative humidity, sunlight radiation, surface contaminants, the properties of the film of electrolytes formed on the metal surface, and the duration of the effect on the metallic surface. The rate of drying after wetting is dependent on conditions such as ambient temperature, relative humidity, and wind velocity. Corrosion induced by pollutants results from the interaction of a particular pollutant with the metal surface and the metal corrosion layer.

For metallic corrosion, the critical relative humidity value and the time-of-wetness (TOW) are defined. The critical relative humidity value is the minimum concentration of water vapour required for corrosion to proceed. The film of electrolytes is formed at a certain critical relative humidity level. The critical relative humidity value depends upon the material that is being corroded, the hygroscopic nature of the corrosion products and surface deposits, and the nature and level of atmospheric pollutants present. Hydrated products and hygroscopic salts can decrease the 'critical relative humidity value', resulting in large amounts of moisture on the metal surface.

TOW refers to the period of time during which the atmospheric conditions are favourable for the formation of a layer of moisture on the surface of a metal (or alloy). The TOW value may be indicated experimentally or estimated from the temperature-humidity complex. Instrumentally recorded TOW can be determined by various measuring systems and is strongly correlated to the number of days with



precipitation and average temperature above freezing. For the purpose of standards, TOW is defined as the time period during which the relative humidity is in excess of 80% and the temperature is above 0°C. Changes in seasonal and annual rainfall will change the period of time for which a surface is wet, affecting the surface leaching and the moisture balance that influence material decay processes.

Moisture is considered to cause significant damage to inorganic building materials. The moisture content and the permeability predominantly influence the impact of pollutants on the rate of weathering of the material. The main risk factor is the cyclic variation of moisture content (wetting and drying) in the presence of hygroscopic salts. The rate of drying after wetting is dependent on conditions such as ambient temperature, relative humidity, and wind velocity. Deterioration of stone proceeds usually at higher relative humidity, above 65%, and is frequently associated with freeze–thaw weathering. The deterioration of external walls made of porous building materials is caused by the excessive moisture content, particularly after driving rain and exposure to long durations of moist conditions.

## 2.2 Temperature

Temperature affects the processes of deterioration of a material gradually and in a variety of ways. Changes in temperature induce a thermal gradient between the surface layer and the inner layer of materials (particularly in materials with lower thermal conductivity), which may result in the degradation of the mechanical properties of the material and can lead to the formation of fine cracks. The formation of cracks is accompanied by a loss of strength and by an increase in material porosity, which may lower the chemical resistance of the material.

Temperature fluctuation of materials may influence bulk expansion, such as the expansion of stone grains, the dilatation of different materials in joints, and the expansion of water in material capillaries.

Increased ambient air temperature is one of the reasons why the rate of wet deposition is more important for deterioration processes in tropical and subtropical regions than in temperate regions. Higher ambient temperature reduces the effects of freeze–thaw cycles.

Large thermal stress may originate during a fire, when temperature rapidly increases within a short time and may induce serious damage to specific types of materials (e.g. explosive spalling in concrete – see Section 4.2 in Chapter 8).

In a polluted environment, a rise in ambient air temperature can speed up material damage due to the increased rate of chemical reactions on the material surface. However, lowered ambient temperature may enhance the chance of damage. During a temperature inversion, objects usually cool to a temperature below that of the surrounding air. If the object's surface temperature falls below the dew point, a condensation layer will form on the surface and, in the presence of pollutants (whose concentrations may increase under the influence of the temperature inversion), this will accelerate deterioration.



### 2.3 Solar radiation

Solar radiation causes temperature changes in materials and may induce volume changes of material in the pores due to expansion of water which is heated by solar radiation. Solar radiation plays an important role in photochemical reactions since it supplies the energy for the excitation or splitting of bonds in the reacting molecules. Adequate intensity of solar radiation at suitable wavelengths is an essential condition for photochemical reactions that influence the deterioration of different construction materials. Of the total energy impinging on the earth's surface, approximately 10% is ultraviolet radiation, 45% is visible light, and 45% is infrared radiation. The primary substances absorbing ultraviolet radiation include molecular oxygen, oxides of sulphur and nitrogen, and organic compounds such as aldehydes. A molecule of oxygen is split into reactive oxygen atoms after the absorption of ultraviolet radiation below 240 nm. Sulphur dioxide reaches the excited state only during the absorption of solar radiation at wavelengths of 340–400 nm. The oxidation of excited sulphur dioxide in air leads to the generation of sulphur trioxide. Sulphur trioxide subsequently reacts with ambient moisture to form sulphuric acid aerosol. In contrast to sulphur dioxide, nitrogen dioxide is photochemically very active. It absorbs solar radiation over the whole of the visible and ultraviolet range. In a spectral range of 380–600 nm, excited molecules are formed, and below 43 nm photodissociation occurs. Sunlight-induced atmospheric photochemical reactions between nitrogen oxides, organic gases, and vapour produce ozone as a reaction product. Ozone accelerates the deterioration of synthetic organic materials used as protective coatings against environmental effects on a variety of surfaces including metals, concrete, wood, etc. Ozone was also found to have an incentive effect on limestone and dolomitic sandstones. Visible and ultraviolet radiation result in the generation of free radicals in wood. The oxidation of these radicals leads to the formation of oxidation products or to the decomposition of radicals, which is accompanied by the production of low molecular weight products.

### 2.4 Wind effect

An increase in wind velocity may affect the deterioration of materials in various ways. Wind drives liquid and solid particles from the air to the material surface, where they cause local attrition and contribute to the weathering of the material. The kinetic energy of particles and the degree of inertial impaction of droplets on the material surface depend on the wind velocity. The high-speed end of the wind spectrum is of interest for abrasion and the low-speed end for diffusion. Wind flows around buildings can influence the deposition rates of both gaseous and particulate pollutants, as well as strengthen the effect of driving rain. During rainfall, windward walls are wetted considerably more than leeward walls. On the windward side, wind promotes the penetration of rainwater and aqueous solutions into porous materials or, during other weather conditions (solar radiation, temperature changes), supports desiccation of the aboveground part of a construction. Both processes, wetting and drying, may affect volume changes in the structure. A serious effect of wind may be



an increasing transport of sea salt inland which can substantially extend the areas that are affected by marine aerosols along seacoasts.

### 3 Harmful effects of air, water, and soil

#### 3.1 Effects of air pollutants and natural atmospheric constituents

In the atmosphere, materials undergo deterioration through a series of physical and chemical interactions and biological activity. In addition to environmental loading, exposure to atmospheric pollutants accelerates the damage and multiplies the effect of weathering.

The atmosphere is a mixture of gases and liquid and solid particles. Dry air contains 18 permanent gaseous constituents. Among these, nitrogen, molecular oxygen, argon, and carbon dioxide are the major constituents, whereas the rest are gases present in minor quantities. The minor constituents include the group of trace gases that are considered to be pollutants: nitrous oxide, carbon monoxide, ammonia, ozone, nitric oxide, nitrogen dioxide, sulphur dioxide, and hydrogen sulphide. Particulate matter of biological origin, dust, small crystals, and droplets represent solid and liquid atmospheric substances. Water can be found as water vapour as well as in liquid and solid phases.

The atmosphere is polluted both by the release of different chemicals into the air (primary pollutants) and by chemical processes occurring directly in the air (secondary pollutants). Primary pollutants enter the atmosphere from natural sources and due to human activity. In the atmosphere, they react with water vapour and water droplets, oxygen, and other reactive substances such as liquid and solid particles and form secondary pollutants. Among the pollutants that cause damage, sulphur and nitrogen compounds and particles deserve special mention. It has been demonstrated clearly that they enhance the natural weathering of various materials but in some cases it may be difficult to quantify their contribution to this process.

In the atmosphere, primary and secondary pollutants are transported, scattered, and deposited on the surface of a material. On the material's surface, pollutants induce the reactions either with the material or with the reactive products generated on the surface. The extent of exposure, the chemical composition, and the concentration of pollutants, coupled with the amount of moisture present on the surface, determine the changes in the material and the extent of deterioration. The structure and the type of material are likewise important. Along with these, the atmospheric corrosion of metals is also dependent upon other factors such as concentration of surface electrolytes and variability in electrochemical reactions, the orientation of the metal surface, and the influence of the protective corrosion layer.

##### 3.1.1 Wet and dry deposition of pollutants

Different substances that are released into the air or those that originate during the processes occurring in air may fall to the ground in either dry form (*dry deposition*) or wet form (*wet deposition*). The sum of both, the dry and wet depositions,



is *total deposition*. It is estimated that dry deposition ranges from 20% to 60% and wet deposition varies from 80% to 40% of the total deposition.

*Wet deposition* refers to substances that are scavenged from the air by hydrometeors such as rain, clouds, or fog drops. Dry deposition relates to particles and gases that fall on the material surface close to the sources of emissions. Wet deposition loads sudden but random doses of contaminants (most of which are usually in a dilute solution), whereas dry deposition is a slower but more continuous process. Wet deposition can influence areas that are many tens of kilometres away from the sources of pollution; however, under certain meteorological conditions, the dry deposition process is also capable of delivering pollutants to areas that are considerably distant from the pollution sources. It is assumed that within highly polluted industrial areas, dry deposition delivers as much material to exposed surfaces as does wet deposition and is relatively more important.

Factors influencing *dry deposition* are meteorological conditions, the nature of the material's surface, and the chemical and physical properties of the deposited species. During dry deposition substances are transported downwards by turbulent diffusion, eddy transport, or sedimentation through the atmospheric surface layer. The mechanisms that take place close to the surface in a region of calm are gravitational settling, inertial impaction and interception or Brownian motion for particles as well as diffusion processes for gases. The temperature and humidity gradient near the surface can also support or retard the deposition of both gases and particles. Thermophoresis (in the submicron size range) can interfere with Brownian deposition when the surface is warmer than the air. Electrophoresis is another deposition mechanism that is active in the presence of an electric field.

The deposition of gases on the surface of a material is to a large extent determined by the chemical affinity of the surface, the extent of exposure, and the chemical composition and reactivity of gases in the vicinity of the surface that control the reaction between the gases and the intercepting surface. Atmospheric turbulence plays an important role in particle deposition because it determines the rate at which particles are deposited on the surface. Particle deposition is strongly influenced by particle size. Inertial impaction and interception are usually highly efficient for particles larger than 10  $\mu\text{m}$  in size and can be enhanced by gravitational settling. Impaction is not effective for particles of size less than 0.3  $\mu\text{m}$  due to their low inertia. Brownian motion transports submicron particles, but Brownian diffusion can be so low that small particles have difficulty penetrating into the surface.

Wet deposition is more complex than dry deposition due to the great variety of processes and parameters influencing this action (equilibrium chemistry, more phases and phase transitions, different chemical reactions or transformations in the water phase, etc.). In addition to these, the process can take place either inside or outside a cloud, and pollutants might exist in several different phases, with each phase having its specific reactions and characteristics. Wet deposition processes comprise: (1) in-cloud scavenging (*wash out* – incorporation in cloud droplets, granules, and crystals); (2) below-cloud scavenging (*rain out* – removal by falling rain); and (3) removal by raining clouds (*precipitation scavenging*).





In-cloud scavenging includes nucleation scavenging and collection of a fraction of the remaining aerosol by cloud. Substances scavenged by cloud droplets can be eliminated by wet deposition without rain formation when the cloud comes in contact with the earth's surface. The concentrations of pollutants are up to 10 times higher in cloud drops due to the small size of cloud droplets compared with raindrops. Cloud deposition may be significant in mountainous regions. Fogs are created by the cooling of air close to the earth's surface and are often formed in polluted areas due to the presence of a high amount of small particles. In such a case, fog is usually enriched with pollutants. During below-cloud scavenging, rainfall may have different chemical compositions depending on the local ambient air pollution. More intensive rainfall washes more effectively and may also be chemically less reactive. Scavenging of air contaminants by raining clouds denotes removal by precipitation (atmospheric water in liquid and solid states). Precipitation depositing on the material surface may infiltrate into the porous structure. Material mass absorbs aqueous solution that is transported inside and causes mechanical stress both by freezing and by hydration and follow-up crystallization of salts. The content of the solute of reactive compounds (such as hydrogen ions from acid compounds) can react with the material and lead to chemical deterioration of the structure. The precipitation can also provide a partial cleansing, as rain removes previously deposited contaminants from exposed surfaces.

Acidic substances that react in air with water and oxidants form acid pollutants and return to the ground as *acid deposition* (in dry form as *dry acid deposition* and in wet form as *acid precipitation*). About half of the acidity in the atmosphere falls back to the ground as dry acid deposition. Damage to materials can result from the dry acid deposition of acid aerosols (such as  $\text{SO}_4^{2-}$  aerosol) and the dissolution of acid-forming gases on the material surface. The major acid pollutants are oxides of sulphur and nitrogen.

The effects of acid precipitation on materials depend on the type of material and the pH of precipitation. The pH value defines the degree of acidity or alkalinity of water and its solutions and is defined as the negative decadic logarithm of the activity of hydrogen ions  $\text{H}^+$ , although they are in fact hydroxonium ions  $\text{H}_3\text{O}^+$  because a proton  $\text{H}^+$  never exists in condensed phases and always occurs in the solvated form, i.e.  $\text{H}_3\text{O}^+$ .

Acid solutions formed by scavenging, diffusion, or other processes of involving acidic compounds in the atmosphere can lead to the lowering of the pH of precipitation. The severity of the impact on pH depends on the dissolved substances and the location of the precipitation. In industrialized areas, concentrations of sulphuric acid and nitric acid in cloud water and in precipitation may be up to 50–100 times greater than their concentrations in areas that are not influenced by emissions of anthropogenic pollutants. Precipitation is normally slightly acidic and has a pH between 5.0 and 5.6 because of natural atmospheric reactions and the dissolution of carbon dioxide – a natural constituent of air. Rain is considered to be acidic when its pH falls below 5.6 (the pH of pure distilled water is 7). For example, as of 2001, the pH of precipitation varied from approximately 4.6 to 4.9 at selected EMEP sites in Europe; in the US, the pH of the acidic rainfall ranged from about 4.3 to 5.3 in 2003.



All forms of acid deposition (especially synergistic effects of dry acid deposition and precipitation) cause serious deterioration if deposited on the surface of materials that are sensitive to acidic compounds. In fact, most materials are susceptible to some degree of acid damage. In exposed areas, the decay can take several forms including roughened surfaces, the removal of material, the loss of carved details from objects or buildings, and the build-up of crusts in sheltered areas. An object's surface may be lost all over or only in certain spots. Especially at high concentrations of contaminants or after prolonged exposures, acid compounds induce numerous undesirable reactions on material surfaces and speed up the weathering process of exposed structures. Those that are most vulnerable are: limestone, marble, carbon-steel, zinc, nickel, copper and copper alloys, and some polymer composites. It is estimated that 10% of chemical weathering of marble and limestone is caused by the wet deposition of hydrogen ion from all acid species. Acid deposition is less harmful for stones with low porosity and resistant compounds containing silicates. Aluminium and stainless steel are more resistant metals.

### 3.1.2 Effects of gaseous pollutants

The gaseous pollutants that cause the most damage to construction materials include sulphur dioxide, which is the main pollutant with respect to material deterioration, but other pollutants also contribute, especially carbon dioxide, nitrogen oxides ( $\text{NO}_x = \text{NO} + \text{NO}_2$ ), and salts from sea spray. Atmospheric oxidants such as ozone, atomic oxygen, and different free radicals generated during photochemical reactions are responsible for the formation of sulphuric and nitric acids. They are produced via a complex sequence of photochemical reactions and some acid-generating chemical reactions that occur among gaseous components in the air (such as reaction of pollutants with hydroxyl radical) or among dissolved gaseous constituents in atmospheric clouds.

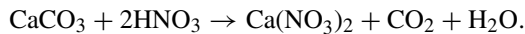
Emissions of sulphur dioxide from natural and anthropogenic sources are the primary sources of sulphuric acid and fine sulphate particles in the air. Atomic oxygen, nitrogen dioxide, hydroxyl radical, and hydrogen peroxide may oxidize sulphur dioxide in the atmosphere. Reactions that convert sulphur dioxide to sulphuric acid, including reactions with hydrogen peroxide in clouds and hydroxyl radical in air, are important. The dominant process is the heterogeneous oxidation of sulphur dioxide and the formation of sulphuric acid in the aqueous phase, which occurs both in the atmosphere and on the material surface. The reaction of sulphur dioxide with the hydroxyl radical can be of importance, in practice, in the formation of sulphuric acid aerosol. Sulphur dioxide deposited on the material surface is absorbed by the surface moisture. The migrating moisture primarily serves as a transport medium for sulphur dioxide that can be translocated internally while being oxidized to sulphates. Sulphur dioxide may react with the material itself in the presence of oxidants and catalysts. Fly ash promotes sulphur conversion since it contains  $\text{Fe}_2\text{O}_3$  and the oxides of other metals (such as V, Fe, Cu, Cr) that catalyse the oxidation of sulphur dioxide into sulphur trioxide, which thereafter directly reacts with moisture to form sulphuric acid.



Sorption of sulphur dioxide on porous building stones causes physical changes in stones, especially with regard to changes in porosity and water retention. Sulphuric acid aerosol has a corrosive effect on all surfaces, including ceilings and walls of buildings and monuments.

Nitrogen oxides contribute significantly to the total loading of air pollution. In the atmosphere, a major portion of nitric oxide is gradually oxidized to nitrogen dioxide. The removal of nitrogen dioxide from the air occurs via oxidation and hydration to form nitric acid. Oxidation of nitrogen dioxide is performed by hydroxyl radicals and by a heterogeneous reaction involving  $\text{NO}_3$  radicals and ozone that occurs at night. Nitric acid is among the main acid components of the atmosphere. The dry deposition of nitric acid is a relatively slow process and its mean time of residence in the atmosphere may reach thousands of hours, during which it is transported over large distances. During the course of wet deposition, nitric acid can be absorbed in cloud and precipitation droplets and fall on the material surface in the form of acid rain.

Nitrogen compounds tend to accelerate the atmospheric attack of materials. Nitric acid decomposes calcium carbonate in inorganic materials by a reaction in which calcium nitrate is formed:



The calcium nitrate that is generated is highly soluble and may be washed off from the surface by rainwater.

Nitrogen dioxide also induces the corrosion of certain metals. In such a case, the deterioration mechanism can be attributed to the oxidation of nitrogen dioxide to nitric acid and its subsequent effect on metals.

Atmospheric contaminants such as chlorine and chlorine compounds when present in the atmosphere can intensify atmospheric corrosion damage. They are released into the atmosphere from natural as well as anthropogenic sources. The corrosive effects of chlorine and hydrogen chloride in the presence of moisture tend to be stronger than those of 'chloride salt' anions due to the acidic character of the former. Apart from enhancing surface electrolyte formation by hygroscopic action, the direct participation of chloride ions in the electrochemical corrosion reactions is likely.

The deterioration of a material may promote synergic effects of different types of gaseous pollutants and particles and/or their combination. Sulphur dioxide is, for instance, more reactive under higher nitrogen dioxide concentrations when increased rates of corrosion occur. This is because nitrogen dioxide oxidizes sulphur dioxide to sulphur trioxide thereby promoting further absorption of sulphur dioxide, and generating sulphur trioxide reacts with moisture to form sulphuric acid.

### 3.1.3 Effect of atmospheric aerosols

Dry deposition of aerosols (defined as minute liquid and solid substances that are dispersed in air) affects most building structures to a certain extent. Aerosols of



anthropogenic origin are particularly important from the viewpoint of aggressiveness with which they attack a material. Anthropogenic aerosols may contain different inorganic and organic species that include inorganic acids and salts, such as sulphates and nitrates, a number of polar and non-polar organics, as well as metals, which are incorporated in the early stages of particle formation from combustion processes. Sulphate ions are most frequently contained in the atmosphere in the form of acid aerosols. They particularly attack carbonate stones such as limestone, dolomitic sandstone, and cement; however, the acid also affects the stone binders that contain calcium carbonate. Most ferrous metals such as mild steel and galvanized steel are susceptible to corrosion from exposure to acid aerosols. Zinc corrosion induced by sulphuric acid aerosol proceeds at relative humidity greater than 60%. In contrast to this, processed aluminium and aluminium alloys are corrosion resistant because after exposure to a low concentration of acid sulphate particles, a protective aluminium oxide layer is formed. The corrosion of copper and its alloys occurs in the presence of sulphate ions and involves the formation of a protective corrosion layer that is mostly composed of basic copper salts.

### 3.1.4 Effect of particles

Both primary and secondary atmospheric particles can be of principal importance in the damage caused to materials and building structures. The particles emitted directly (such as sea salt, wind-blown dust, volcanic emissions) are approximately equal to those originating from gas-phase conversions. Gases can become liquid or solid particles on cooling or by chemical reactions in the atmosphere.

The deterioration of materials depends on the chemical composition and properties of the particles. The most aggressive species are salts (chlorides from the seacoast) and several types of fly ash from municipal incinerators. Dust particles that are inert and insoluble in water have practically no impact on materials but may have detrimental mechanical effects through abrasion of the surface of objects or may reduce the aesthetic appeal of a material by soiling. However, such particles can behave as carriers of aggressive chemicals and/or serve as the concentration site for chemically active ions, such as sulphates, nitrates, or chlorides, and may create ideal conditions for oxidation processes on the material surface. All particles are susceptible to electrostatic forces that promote deposition if either the particles or the surface carries an electric charge. The deposition of solid particles from the atmosphere can have a significant effect on the corrosion of some metals because these deposits can stimulate corrosive attack by reducing the critical humidity levels, through hygroscopic action, and by providing anions that stimulate metal dissolution.

### 3.1.5 Formation of crusts and patinas

The reactions of materials with air contaminants deposited on their surface can lead to the generation of salts that form a layer on their surface. This layer on stones is seen as soiling and is called crust. The corrosion layer formed by the deposition of sulphates and chlorides on copper and copper alloys is called patina.



The properties of the salts that are deposited on the stones vary. Some of the salts dissolve in the superficial moisture layer and may be washed off from the surface by rainfall, whereas other less water-soluble salts, together with dust or soot and other deposited particles (e.g. of biological origin), form a relatively thin, hard, and adhesive layer on the stone surface, whose colour changes from grey to black. These crusts can be observed on the exposed stone surfaces of any structure. The composition, structure, and thickness of the crust differ from the primary material and are dependent on many factors, especially the type and shape of the stone, the shelter against rain and snow, and the type of climate. The composition of each crust, however, is governed by the composition of the particular airborne pollutants in the area. Crust development may be enhanced if the stone is porous or has an irregular surface area.

A significant component of the crust of stones containing carbonates (such as limestone and marble) is calcium sulphate dihydrate (gypsum –  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ). Gypsum crystals form at the pore opening–air interface, where evaporation is greatest. The gypsum crust readily traps dust, aerosols, and other particles of atmospheric origin; among these, the most abundant are black carbonaceous particles. These black particles, originating from oil and coal combustion, have a large specific area and contain metals, which may catalyse the formation of black crusts. The crust may also comprise calcium carbonate, transported by water in the form of hydrogen carbonate from the primary stone. It behaves as a binder that cements the crust but along with this it also leads to a reduction in the strength of the inner layers of the stone. This process is often aided by bacterial action. Secondary layers and crusts of gypsum may be formed by dissolution and may redeposit in the presence of sulphate.

A typical crust containing gypsum is formed on the surface of marble, which has a high content of limestone and low porosity. A surface that is directly exposed to rainfall is white in colour because the deterioration products that are formed on its surface are continuously washed off (as calcium sulphate dihydrate is approximately a hundredfold more soluble in water than calcium carbonate). On these sides, the surface is rough. An irregular hard crust composed predominantly of crystals of gypsum mixed with black particles covers the black areas found in zones protected from direct rainfall.

Porous sandstones may contain salts that infiltrate from the inside to the surface of the stone. In many types of sandstone, the surface hardening may develop a honeycomb pattern, with crumbling behind the crust and in the cavities. Honeycombs are frequently observed in buildings made of sandstones. Along with salts, the crusts of most sandstone can contain some organic compounds, largely of paraffin type. The presence of this organic matter influences the hydrophobic properties of the sandstone to a certain extent. It may result in the accumulation of salts under the crust and lead to crust splitting. Unlike sandstone, a relatively thin, hard, and cohesive crust originates on the surface of igneous rocks. It usually contains deposited solid particles, including soot. The decay of silicate minerals proceeds very slowly, except tremolite present in some dolomite marbles and black mica in specific marbles or granites.



On copper and copper alloys, basic sulphates and chlorides form a patina. This corrosion layer is not readily dissolved by acids and thus is a good protection for a metal surface. The formation of this layer is controlled by the ability of copper to react with the compounds present and varies with the humidity, the temperature, and the concentration of these pollutants.

### 3.2 Effects of water

Water damage is considered to be one of the essentially problematic elements in the decay of building materials. Water can deteriorate building structures with which it is in continuous contact and can influence the damage to the material surface by acid deposition reactions. To a certain extent, water may also directly affect the quality of building materials such as concrete during its production. Deterioration is induced by the simultaneous effects of different ions and molecules present in water (including pollutants), by aquatic environmental factors (such as the physical characteristics of water, aquatic macro- and micro-organisms), climatic conditions, resistance of a material to attack, mode of contact between the material and water, and water mass motion.

Water is a good solvent for a number of solid substances, liquids, and gases. Due to its dipolar nature, water is a good solvent for ionic compounds and is particularly suitable for the formation of addition compounds with ionic substances and with substances having a dipolar character. There are very few compounds known that do not dissolve at least to some extent in water.

Water is a medium for the transport of salts in pores, it accelerates chemical reactions that proceed in the material and on its surface, and it may support the growth of micro-organisms (such as algae, lichens). In the areas where the temperature fluctuates around 0°C, water gives rise to freeze–thaw weathering that especially deteriorates porous building structures. It is estimated that more than three-quarters of all registered building damages have resulted from these effects.

Among the essential inorganic constituents of natural waters, hydrogen carbonate, sulphate, chloride, and nitrate are the main anions and the important cations are calcium, magnesium, sodium, and potassium. In the majority of natural waters, the concentration of these ions decreases in the above-given order. However, in mineralized waters, sodium prevails over calcium, and sulphates and chlorides over hydrogen carbonates. Ammonia and ammonium ions are generally present in low concentrations in these waters. Biological processes significantly influence ground-water composition. Depending on the level of dissolved oxygen, these processes can involve either reduction or oxidation reactions. At greater depths, in the absence of oxygen, anaerobic reactions are observed (particularly reduction of nitrates and sulphates), whereas in the layers with sufficient access to oxygen, aerobic degradation of organic substances takes place. In this manner, aggressive components such as hydrogen sulphide, carbon dioxide, and some inorganic compounds of nitrogen are introduced into water. Seawater is slightly alkaline (the pH varies between 8.0 and 8.3), but in shallow coastal areas carbon dioxide can be accumulated and thus the pH can drop below this value. Seawater contains, on average, 35 g/l of dissolved



solids, but this amount is not the same everywhere (the Dead Sea has 280 g/l of dissolved solids).

From the viewpoint of environmental deterioration of materials, the term water usually comprises not only natural waters, but also service (like cooling water, feed water, etc.), industrial waters, and wastewater. There is a huge variation in the composition and content of substances in these waters, depending on the purpose for which the water is used or in which processes originates; thus, various factors determine these parameters. In wastewaters with a predominance of inorganic pollutants, components can be either in dissolved or in suspended forms. Among the dissolved salts, sodium, potassium, calcium, and chloride and sulphate ions can occur most frequently. The composition of sewage water depends on the pollution sources of the contaminants, including kitchens, laundries, bathrooms, and sanitary facilities. The most important components in sewage waters are chlorides, sodium, potassium, phosphates, and inorganic forms of nitrogen – ammonia, nitrides, and nitrates.

Water can enter and cause deterioration of structures in a variety of ways. Rain leakage, condensation, and rising damp are the basic sources of damage caused by water. The moisture and the origin and the course of travel of water determine the extent of damage it can cause through the above-mentioned processes.

Rain leakage influences the dissolution of salts, which may decrease a material's resistance. Rainwater that moves through the pores dissolves the salts that are present inside the material and then deposits them on the surface as the water evaporates. The crystallization of these salts on the surface manifests as efflorescence and that beneath the surface as subflorescence. Efflorescence is the most obvious effect and often only disfigures the face of a building. The effect of the crystallization of the salts beneath the surface is destructive and can accelerate the scaling of the structure and the subsequent deterioration. The conversion of calcium carbonate to calcium sulphate results in a type of efflorescence called 'crystallization spalling'. Rainwater leakage in porous sandstone is an example of the impact of dissolution of the grain cement on stone resistance. After rainwater exposure, the calcareous grain cement in sandstone may dissolve and moves outwards. Along with the dissolution of the grain cement, it may cause loss of coherence of the grain bond.

Rising damp occurs when a building is in direct contact with damp soil or ground water. Moisture from the ground is drawn upwards by capillary action up to a height at which there is a balance between the rate of evaporation and the rate at which it can be drawn upwards by capillary forces. A 'wet line' often associated with efflorescence develops. Groundwater may damage a material that is submerged in water and fluctuations in the level influence the quality of building materials. Rotting of wood is another destructive phenomenon that requires the presence of water to proceed.

### 3.2.1 Aggressiveness of water

Most frequently, aggressiveness of water against materials is evaluated in connection with the undesirable effect it has on different buildings and metallic pipes. Depending on the content and type of components, aggressive waters may be

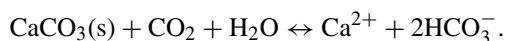


divided into *waters containing aggressive carbon dioxide*, *water with a low content of salts*, and *acid and sulphate waters*.

Significant damage to building materials (such as limestone, concrete, mortar, or some metals) results from the exposure to natural constituents of non-polluted rain-water such as carbon dioxide and oxygen. Oxygen has a significant impact on metal corrosion (by the control of the oxygen reduction rate and by the support of protective layers on the surface of the metal). Oxygen enters water via diffusion from the atmosphere and/or is released by photosynthesizing organisms that simultaneously bind carbon dioxide and reduce it to organic compounds. Carbon dioxide is usually not considered a harmful gas but carbonic acid which is formed by the reaction of carbon dioxide with water reacts with inorganic materials containing calcium and magnesium and deteriorates their structures. Aqueous solutions of carbon dioxide can also stimulate serious metal corrosion.

Carbon dioxide is considerably soluble in water; about 2360 mg/l dissolves at 10°C. It is dissolved in water in the molecular form as *free hydrated carbon dioxide* that is denoted by the symbol  $\text{CO}_2$  (aq.). Slightly less than 1% reacts with water to form non-dissociated molecules of carbonic acid. Carbon dioxide dissolved in water is called *free carbon dioxide*; the term is used for the sum of the concentrations of free hydrated carbon dioxide and carbonic acid. Dissolved free carbon dioxide can be found in almost all natural waters with  $\text{pH} < 8.3$ ; in running surface waters, carbon dioxide is present only in units of milligrams per litre and does not exceed 30 mg/l of free carbon dioxide; fresh groundwater usually contains several tens of milligrams per litre and mineral water frequently contains more than 1000 mg/l.

The calcium carbonate equilibrium in water is of considerable technical importance in terms of the aggressive effects of water. Calcium carbonate can dissolve only when dissolved carbon dioxide is present, according to the reaction:



Equilibrium is established between  $\text{Ca}^{2+}$ ,  $\text{HCO}_3^-$ , and carbon dioxide. Carbon dioxide which is in equilibrium according to this reaction is called *equilibrium carbon dioxide*. If a higher amount of free carbon dioxide is present in water than that corresponding to the carbonate equilibrium, then water dissolves calcium carbonate. When free carbon dioxide is exhausted (e.g. by ventilation) from water, the carbonate equilibrium shifts to the left and calcium carbonate has a tendency to separate from water. The difference between free and equilibrium carbon dioxide is called *excess carbon dioxide*. A part of the total excess carbon dioxide has aggressive effects on some materials. To ensure the non-aggressivity of water and to avoid the corrosive effects of residual carbon dioxide, water must contain a certain minimum amount of hydrogen carbonate.

Aggressive water, which has a low content of salts, influences the process of extraction of soluble constituents of a material. Attack by this type of water depends on the mode of contact between water and the material, the material's resistance to attack, and the water temperature.





Acid aggressive waters contain mineral and organic acids, which dissolve components of building structures, destroy water installations, and may also dissolve the heavy metals contained in them.

Some buildings may deteriorate considerably when exposed to aggressive waters containing dissolved sulphates. The destructive effect of these waters on concrete is more intense due to the formation of strongly hydrated compounds – ettringite, which crystallizes with 30–33 molecules of water, thus considerably increasing its volume and influencing the material via crystallization pressure. Sulphates occur in water predominantly in the form of simple  $\text{SO}_4^{2-}$  anions. The essential part of sulphates may come from sulphates leached from the soil or from groundwater. In groundwater, the content of sulphates ranges from tens to hundreds of milligrams per litre. They may also be generated by the reaction of carbonates present in building materials with sulphur dioxide. The deterioration effect can be enhanced by the interaction with other dissolved substances that are present in water.

### 3.2.2 Effect of soluble salts

Salt weathering is probably the most important deterioration process of inorganic building materials (such as stone) in cities, but it may be important in coastal areas as well. There are several sources of soluble salts: they can be present in primary materials, or form during weathering processes, or may also penetrate from the outside, e.g. from groundwater or sea spray in coastal areas. In inland areas, salts of chlorides such as  $\text{NaCl}$ ,  $\text{CaCl}_2$ , and  $\text{MgCl}_2$  are nearly always from road salts, where they are used as winter de-icing agents. Two types of soluble salts may be found in the building materials: salts whose crystals contain crystalline water and salts that can crystallize without water. Salts with crystalline water are less soluble in water and in such cases the formation of crystals from solution is easier. When there is a decrease in the ambient air humidity, they lose crystalline water and form anhydrous salts. The converse effect occurs when humidity increases: salts again bind water. Salts that crystallize without water are very soluble in water. Solutions of these salts diffuse into the pores and infiltrate relatively deep into the material. The concentration of salts increases in the surface layers, e.g. in the sides, where water evaporation is maximum.

The effect of soluble salts depends on various factors, such as the type of material and its porous structure, the nature and quantity of soluble salts, the quantity of penetrating water, and the mode of contamination. In addition, these salts dissolve in water and increase conductivity. The effect is largely attributable to three basic mechanisms: (1) the dissolution of salts and its crystallization in a material's capillaries, channels, and crevices during repeated wetting and drying of the material, resulting in contraction and expansion; (2) the hydration of salts that can exist in more than one hydration state; and (3) the expansion of salts in the pores when salts have higher coefficients of thermal expansion than the material (this factor is less important).

The crystallization of dissolved salts and the associated damage can occur every time a salt-contaminated porous material is wetted and dries out. If the migration of the salt to the surface of the material is faster than the rate of drying, the crystals



deposit on top of the external surface and form visible efflorescence, which does not damage the structure. When the migration is slower than the drying rate, the solute crystallizes within the pores at varying depth. The crystals grow and press against the immediate material which can lead to the crumbling and powdering of the structure. The rate of drying after wetting is dependent on conditions such as ambient temperature, relative humidity, and wind velocity. The frequency of contraction and expansion due to salt crystallization may determine the speed at which a material undergoes weathering.

The hydration and dehydration of salts takes place under specific conditions of variation in temperature and humidity when some salts can absorb and release molecules of water. These processes cause the salt to expand and contract and thereby exert pressure on the building material which may cause damage. Cyclic changes of moisture in the presence of hygroscopic salts are particularly dangerous.

If the pores of a material are filled with salts that have higher coefficients of thermal expansion than the material, heating causes the salts to expand more rapidly and exert pressure on the material. This differential thermal expansion may in some cases contribute to defects in the structure.

### 3.3 Detrimental effects of soil

The deterioration of constructions and equipment buried in the soil can be influenced by the physical characteristics of the soil, its chemical properties, and the micro-organisms living in the soil.

Soil is characterized as a heterogeneous polydisperse system, consisting of solid, liquid, and gaseous phases. The solid phase contains a mineral fraction and an organic fraction. The solid mineral fraction is the dominant part of the soil and it constitutes 95%–99% of the solid phase. Organisms and the debris of organisms form the organic part of the soil. The soil water is the total content of water present in the soil pores in the liquid, solid, and gaseous states. Only that part of the soil water that is able to dissolve electrolytes and gases and to disperse colloids is considered to be the liquid soil component – the soil solution. The composition of the soil solution varies and is dependent on the changes in soil humidity and on the reactions of soil water with the inorganic and organic compounds present in the soil. Among the inorganic substances, the soil solution predominantly contains soluble salts, such as chlorides, nitrates, carbonates, sulphates, and phosphates; as regards organic compounds, different low-molecular weight substances are present. The gaseous phase is the soil air, representing a mixture of gases and vapours filling the vacant spaces in the soil. It is characterized by higher carbon dioxide and water vapour content and lower oxygen content. In the topsoil, carbon dioxide is present in the range of 0.1%–1.0%; in lower layers it may be as high as 5%. Water vapour saturates the soil air and the relative humidity is frequently above 98%. The soil air is also enriched with hydrogen sulphide, hydrogen, sulphur dioxide, methane, and other trace gases, which can have a negative effect on soil air quality. These can stimulate damage in materials.



The deterioration of materials embedded in the soil depends on the composition, the moisture content of the soil, the pH value, the buffering capacity, and the oxidation–reduction potential of the soil solution (the oxidation–reduction potential governs the course of oxidation and reduction reactions). The physical and mechanical characteristics of the soil, such as the porosity and the sorption capacity of the soil, the adhesion and cohesion, the resistance to deformation at a certain soil moisture, and the swelling and carrying capacity should also be taken into account.

With respect to considerably stimulating negative effects, the chemical attack of soil is especially important for buried constructions. The soil's chemical properties may cause the corrosion of embedded steelwork or the decay of embedded timber within walls. The corrosion damage caused by aggressive road salts to transportation infrastructures, including steel bridges, large span-supported structures, parking garages, and pavements, leads to shortening of the service life and the usefulness of structures and thus has serious economic implications.

Soil may contain different harmful substances that have the potential to cause damage to structures. They occur naturally, enter the soil during atmospheric deposition of pollutants, or leak into the soil during storage (such as leakage from underground pipes, tanks, and landfills) and transport of materials. Dry and wet acid deposition of airborne emissions adds hydrogen ions and lowers soil pH; however, acids can also be neutralized by the soil. The extent to which soils can neutralize acid depositions depends on factors such as the type of soil, thickness, weather, and water flow patterns. If the ground is frozen, the neutralization process of the soil cannot function and the acid is not neutralized.

$\text{HCO}_3^-$  and  $\text{NO}_3^-$  anions occur most frequently in soil, the remaining portion corresponds particularly to  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  anions (in non-saline soils); in the soil solution of saline soils, the amounts of sulphate and chloride anions are enhanced. Sulphur is present in the soil in the form of sulphates and sulphides. Predominantly, sulphur dioxide, sulphuric acid, and sulphates enter the soil during dry and wet depositions. The hydrogen ions in sulphuric acid exchange places with the metal ions present in the soil and the calcium, potassium, and magnesium ions are leached or washed out of the topsoil into the lower subsoil. The acid can be immobilized as the soil or vegetation retains the sulphate and nitrate ions (from sulphuric and nitric acids).

The major sources of chlorides in the soil are, in addition to sea spray on the seashore, the road salts used in winter for de-icing and anti-icing. Road salts include mainly potassium, calcium, and magnesium chlorides and magnesium acetate. Sodium chloride is one of the most commonly used de-icers and calcium chloride or magnesium chloride is frequently used in brine solution for anti-icing. The chloride ion often initiates and promotes the deterioration of various concrete components and the corrosion of steel reinforcements. Chlorides penetrate and migrate through the concrete and cause corrosion of steel bars in the concrete. Formation of corrosion products lead to increase in volume and build up stresses which can cause cracks in the concrete. Salts applied to the concrete surface of pavements and roads can increase the frequency of freezing and thawing cycles, thereby increasing the



potential for scaling. In addition to the impacts of the chloride anions, the associated cations of sodium, calcium, magnesium, and potassium also have environmental effects. Sodium cation, which is highly soluble in water, can bind to soil particles, break down soil structure, and decreases its permeability.

Porosity is considered the most important soil structural characteristic and it influences the sorption capacity of soil. Porosity is highly variable and depends on the mutual arrangement of soil particles and aggregates, affecting the total volume of pores and their size and shape.

The soil pH considerably affects soil characteristics and is important for most chemical reactions in the soil, for coagulation and peptization of the soil colloids, for ion sorption, and for solubility of many components. Soil acidity is the result of the effects of several factors, particularly the soil composition, the moisture content, and the soil biological processes. The pH of a soil solution usually ranges between 4.0 and 8.5. It is influenced particularly by the presence of dissolved acids and acidic or basic salts from the solid phase and from infiltrated surface or ground water. Intensive biological activity of micro-organisms can cause the soil to become alkaline, resulting in an increase in pH. The buffering capacity of the soil solution is defined as its ability to restrict changes in soil pH. This capacity depends on the presence of weak acids or bases and their salts. A mixture of carbonic acid and calcium bicarbonate or possibly a mixture of phosphoric acid and phosphates is frequently the most effective buffer system in the soil solution.

Cohesion, the ability of the soil to resist external pressure, reduces the disintegration of soil aggregates. It increases with the drying of the soil and is reduced in the presence of increased moisture. The adhesion is manifested by the soil sticking on the surface of the material and depends on the grain size and soil moisture.

Soil saturation by subsurface flow can lead to softening or wash out of the ground below footings. A common problem is the presence of clayey soil beneath the footings. Cracking of buildings originates wherever clayey soils of significant depth are found underlying buildings. Clayey soil shrinks and swells with changes in moisture content, which can cause the buildings to rise or sink.

## 4 Biodeterioration of materials

Many micro- and macro-organisms cause physical and chemical changes as well as mechanical damage to materials. Bacteria, cyanobacteria, algae, fungi, lichens, insects, animals, and plants have been found to be involved in the deterioration process. Relative humidity and temperature levels determine whether these organisms flourish or exist at all.

Micro-organisms are present in air, water, and soil and may grow and live on material of inorganic and organic origin. Many micro-organisms cause damage through a range of chelating and etching processes. Enzymes secreted by these organisms can be catalysers of chemical reactions that stimulate an attack. Micro-organisms may utilize products of these reactions (e.g. corrosion products) or use certain components from their habitat as nutrients, which are returned to the habitat in the form of excreted metabolites and may affect the habitat. Chemical damage is



more important and may arise by excretion and generation of different acids. These acids are capable of chelating metal ions such as calcium and magnesium.

Stone and wood may be damaged when they serve as the substrate for some higher animals (e.g. the larvae of *Plecoptera* or the macroscopic *Ephydatia luviatilis* adhere to a solid base) or are deteriorated by products of metabolic processes. Serious damage may also be induced by animals' excrement. They react with the material surface chemically or serve as nutrients for further attack by micro-organisms.

Occasionally, bushes and even trees are observed on buildings. They can cause mechanical and chemical deterioration of constructions; during growth, plant roots generate surprisingly high amounts of pressure which may damage buildings. The humic acids present in root systems attack the carbonate components of stone and decompose them.

#### 4.1 Effects of micro- and macro-organisms

Viruses, vegetative cells and spores of bacteria, small algal cysts, fungal spores, and spores of lichens are the most common types of airborne micro-organisms that are found near the ground level. The groups of all major categories of micro-organisms can be found in various types of water, whereas in the soil, the predominant groups are bacteria and fungi. Micro-organisms normally found in outdoor air are also present in indoor environment. High microbial concentration is often observed in farm buildings. Extensive growth of some fungi (*Sporotrichum heurmanni*) has been observed on fresh timber in mines, and the fungus was also isolated from the air in mines.

The bacterial chemical action constitutes the major risk for the deterioration of stones. Especially harmful are those bacteria that obtain carbon from carbon dioxide and energy from light or by chemical redox reactions; some are capable of oxidizing inorganic compounds of sulphur and nitrogen to produce sulphuric and nitric acids. Heterotrophic bacteria utilize organic compounds to obtain carbon and produce chelating agents and weak organic acids.

Both ammonia-oxidizing bacteria producing nitric acid and sulphur bacteria oxidizing hydrogen sulphide and elementary sulphur to sulphate influence the pH of the environment where they live and can cause damage to various stone structures. The concentration of sulphuric acid, for example, may increase by approximately 5% in such media.

The majority of bacterial species in the genus *Thiobacillus* use the oxidation of hydrogen sulphide and sulphur as an energy source and convert these forms of sulphur to sulphuric acid. The process takes place only when there is an adequate supply of atmospheric oxygen and hydrogen sulphide (>2.0 ppm) and high relative humidity. Because a species of bacteria can survive only under specific environmental conditions, the particular species inhabiting the colonies changes with time. For example, one species can grow only when the pH is between 9 and 9.5, but when sulphuric acid, which is an excreted waste product, decreases the pH of the surface below 6.5, they die and another species that can withstand the lower pH takes up residence. The process of successive colonization continues until a species that can



survive under extremely low pH conditions takes over. *Thiobacillus thiooxidans* (also known by its common name *Thiobacillus concretivorus*) has been known to grow well in the laboratory when exposed to a solution of sulphuric acid with pH of approximately 0.5. Growth of *T. thiooxidans* and *T. thioparus* has been observed on exposed monuments made of travertine, marble, or sandstone and concrete. The pH of the surface of freshly placed concrete is approximately 11–12.5. This pH does not allow the growth of any bacteria however, the pH of concrete surfaces is slowly lowered over time (by the effect of carbon dioxide and hydrogen sulphide present in the environment) and is reduced to a level that can support the growth of bacteria (pH 9 or 9.5).

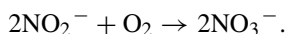
Sulphate-reducing bacteria, having the unique ability to convert sulphate and to produce sulphite as metabolite, are well known for the damage they can cause to metals. *Desulfovibrio vulgaris* and *Desulfotomaculum nigrificans* produce hydro-sulphide that induces corrosion of different systems, e.g. oil and gas pipelines, gas distribution system, and sewerage systems. In sewerage pipes, the first step in the bacterially mediated process is the generation of a thin layer below the water level. When this layer becomes thick enough to prevent dissolved oxygen from penetrating, an anoxic zone develops within it. In this biofilm, sulphate-reducing bacteria use sulphate ions from the surrounding microenvironment as an oxygen source for the oxidation of organic compounds. The catalysers are the enzymes of the bacteria. The product of oxidation–reduction reactions in these processes is sulphide, which is released.

Micro-organisms may support the corrosion of some metals by using corrosion products during their metabolism. The chemoautotrophic iron bacteria, for instance, oxidize iron (II) compounds. The oxidation takes place under aerobic conditions in which bacteria utilize the liberated energy and the oxidized compounds are precipitated. The genera *Ferrobacillus* and *Thiobacillus* play an important role in the oxidation of iron. *Thiobacillus* are able to oxidize ferrous ions to ferric ions and simultaneously sulphur compounds to sulphates.

Some autotrophic bacteria, which are members of the nitrifying genera *Nitrosomonas* and *Nitrobacter* that employ nitrification as their sole source of energy, facilitate the production of compounds that damage materials. *Nitrosomonas* mediate the oxidation of ammonia to nitrite and *Nitrobacter* converts nitrite to nitrate. Nitrification proceeds as follows:



and



The typical result of the action of nitrifying bacteria on stone is an increase in its porosity and progressive decay. This type of deterioration is observed predominantly in the ground floor of buildings, in parts where water leaks in and rises by capillary action.



Bacteria may lead to a change in the physical characteristics of wood, e.g. permeability and absorptivity, and cause a loss in strength. Some bacteria such as those belonging to the genus *Cytophaga* are highly specialized; the only substrate they can use as a carbon and energy source is cellulose. They can completely destroy the structure of the cellulose fibres. These bacteria are widely distributed in soil, continental waters, and seawaters. The genus *Clostridium* participates in the anaerobic decomposition of cellulose. Actinomycetes also play an important role in the decomposition of organic material. They constitute a group of bacteria that usually possess a unicellular mycelium with long branching hyphae. They attack resistant substances such as cellulose, hemicellulose, chitin, and keratin and decompose lignin. Actinomycetes occur in both fresh and salt water and in soil.

Although the bacterial processes do induce damaging effects on materials, they can also be useful for the conservation of fine stone artworks. Bacterially activated carbonate mineralization has been proposed as a strategy for the conservation of deteriorated ornamental stone. This conservation method copies natural processes during which many carbonate rocks have been cemented by bacterially induced calcium carbonate precipitation. The selected micro-organism, *Myxococcus xanthus*, is an aerobic soil bacterium. Calcium carbonate precipitation stimulated by *M. xanthus* cements calcite grains by depositing on the walls of the pores and enables effective reinforcement and protection of porous ornamental limestone.

Algae are another group of micro-organisms that grow in the water film on the stone surface and deteriorate it. They have been found on limestone and sandstone of historical objects and listed buildings. Algae may attack stones by exhaled carbon dioxide, which in the presence of water supports the dissolution of the carbonated component of the stone. Some algae living within the stone may contribute to the disaggregation of the stone. Also, mechanical deterioration of stones takes place if algae develop to such an extent that the generated multicellular colonies increase the pressure on the walls of the pores, thereby damaging the stones.

Most fungi are organisms with mycelium as their vegetative structure. The germinating fungal spores put out hyphae, which branch repeatedly to form a ramifying system of hyphae that constitutes the mycelium. Fungi are well adapted to life in the soil, their most common habitat. They are heterotrophs and predominantly aerobic, and therefore usually occur at or near the surface of any organic material. Fungi can destroy the structural integrity of a material mechanically and chemically. Mechanical damage to stone, concrete, and other building materials is caused by the intrusion of the hyphae into the structure and by the contraction and expansion of the mycelium with changes in humidity. Chemical deterioration is more important and may be caused by damaging excretions such as oxalic, tartaric, citric, succinic, and acetic acids. These acids are capable of chelating metal ions. One additional effect of fungal (and also algal) colonization is that it tends to form a film over the surface which blocks the pores. In particular, any moisture that does penetrate will dry out more slowly, the material will stay wetter for longer, and any dissolved salts could penetrate more deeply.

Wood-destroying fungi induce several different types of decay, ranging from the formation of felt mycelia on the wood surface to destruction of wood and rotting,



and each species of fungus may attack different parts within the wood. Conditions suitable for fungal growth are temperatures of 24–32°C, air volume of 20% in the wood, and moisture content of 25% or higher. The classes *Basidiomycetes*, *Deuteromycetes*, and *Ascomycetes* are important. The mycelia of *Basidiomycetes* spread on the surface of the wood and bore deep into it. Several groups of this class, such as *Merulius lacrimans*, *Coniphora puteana*, *Poria sinuosa*, *Lentinus lepideus*, and *Gleophyllum sepiarium*, decompose only cellulose and induce the so-called destructive decay of wood. In such cases, a significant loss in the weight and volume of wood may be observed; the wood becomes fragile, gradually changes colour, and turns brown due to the liberation of lignin. This fungal attack frequently causes wood splitting. Other members of the class *Basidiomycetes*, such as *Armillaria mellea*, *Phellinusignarius*, and *Canoderma applanatum*, induce the decomposition of cellulose as well as lignin; as a consequence of this action, the wood crumbles and becomes lighter. This type of wood decomposition is called white or honeycomb rot. Some genera of the class *Deuteromycetes* decompose only cellulose and cause soft rot that may lead to wood splitting. Some fungi belonging to the class *Ascomycetes*, such as *Ophistoma*, *Aureobasidium pullulans*, and *Cladosporium herbarum*, may cause wood blueing or blackening. These types of fungi usually do not cause the rotting of wood, they only induce colour changes. Aquatic fungi, such as *Monoblepharidales* and *Gonapodya*, are found on submerged twigs in fresh water ponds and springs, and some species of *Pyrenomycetes* (e.g. *Ceriosporopsis*) attack wood submerged in the sea.

Analogous to fungi, lichens also excrete organic acids that attack materials and produce compounds such as salts of salicylic acid and tartaric acid, which also degrade carbonates in an alkaline medium. Lichens have hyphae that can grow through the pores in stones. After absorbing water, they enlarge considerably in volume and affect the walls of pores by applying pressure on them. Lichens are extremely sensitive to gaseous sulphur compounds, which accounts for their rare occurrence in polluted areas.

Mosses often grow on the surface of stones that are covered by humus. They have the ability to absorb large quantities of water and they also produce organic acids.

Pests attack wood in the soil, water, and also in ambient air (outdoor as well as indoor environment). There are different types of insects such as ants, termites, certain species of beetles, and marine insects that frequently cause great damage. Insects cause a loss of wood strength and, in extreme cases, they result in the collapse of wood structures.

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