



Predictive digitization, restoration and degradation assessment
of cultural heritage objects

Our reference: PRESIOUS



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1 Introduction

This state of the art report on the monument stone deterioration represents the deliverable D3.1 of work package 3 (WP3) of the PRESIOUS project. It aims at exploring the determining factors related to the simulation of physical and chemical (physicochemical) phenomena that affect the composition, structure and texture of stone monuments exposed to weathering conditions. We focus on stone degradation mechanisms along with simulation and visualization techniques that can be applied for forward and inverse erosion predictions.

1.1 General Overview

Stone monuments worldwide are suffering from weathering and erosion due to natural causes and causes created through human impact [1]. As stone monuments are an essential form of cultural heritage, there is a concern about their sustainability and how their sustainable conservation can be implemented. It is therefore crucial to develop methods to predict the stone monuments deterioration for preventive conservation and reconstruction of earlier appearance in case of already damaged structures. An interdisciplinary approach is necessary to achieve this as knowledge from different fields is needed to understand the processes involved in the deterioration of stone. Simulations and the visualization of these processes can be based on a physical and chemical understanding of the interaction of both intrinsic and extrinsic factors that have an impact to stone deterioration.

Based on this our main aim is the realistic simulation of stone erosion and weathering effects. That will allow us to create artificially aged stone-monuments and fragments that can subsequently be used to evaluate the reassembly and completion methods to be developed in work package 4. Another driving factor for developing an erosion simulator is the fact that such a tool can help to compare the deterioration of cultural heritage objects over a long time-span with different protection methods applied (e.g. protections against rain, wind or temperature change). This will help to make educated decisions about how to best preserve cultural heritage monuments for future generations. Note that the interest in the simulation and estimation of degrading processes is not limited to cultural heritage objects alone. Erosion simulations are also of high interest in civil engineering where the monitoring of degradation damages at structural buildings like bridges, railway foundations or concrete buildings can have a large economic and social impact. Due to the huge amount and complexity of processes involved in erosion the focus of our work will be on selected relevant degradation mechanisms of stone for which the general physical and chemical processes are known.

In the first part of this report are we concerned with the fundamental processes that lead to the deterioration of stone. Then we look at interesting and important approaches that represent the current state of the art in the broader context of deterioration simulation and their realistic visualization.

2 Geomorphological Processes

The geomorphological processes, in particular stone weathering and erosion, are fundamental in shaping the surface of the Earth and have led to the formation of different topographic features of the landscapes (for example a glacial scenery, deserts, ragged mountains or the flat terrain in river valleys). The main features are:

- the production of regolith (e.g. loose, heterogeneous material like dust, soil, or rock fragments) by **weathering and erosion**,
- the **transport** of that material,
- and its **deposition**.

The speed and extent of stone weathering depend on the climate of the particular region, the nature of stone, and the characteristics of the diverse weathering processes involved. Though earlier weathering studies did not focus mainly on the degradation of cultural and historical objects, over the past 50 years, many researches have been conducted in connection with monument stone conservation including those on weathering processes and rate studies [1]. When it comes to the study of recession rates, monuments and tombstones were found to be useful historic weathering indicators as it is possible to acquire crucial data on known exposure time and stone composition. It is difficult to estimate the recession rate of a natural landscape due to the need to find original surface. The large scale geomorphological weathering processes and mechanisms are in principle also relevant for the deterioration of stone that occurs on a much smaller scale and which we wish to approximate and visualize within workpackage 3 of the PRESIOUS project

2.1 Erosion and Weathering of Stones

In geology the terms erosion and weathering are both used to describe the deterioration of rock and stone but can be distinguished on the basis of the involved material movement. **Erosion** involves the exposure of stones to **external forces and transport processes** that originate from water- or wind-flow and gravity. Note that this also includes forces and transport processes due to ice, snow or waves. In contrast **weathering** denotes the processes that are **weakening or loosening stone particles internally**. Beside the disintegration of stone into smaller pieces, weathering also involves the dissolution of material into water due to the effects of atmosphere and hydrosphere. The nature of the stone is the determining factor when it comes to its resistance to deterioration with time. From a geologic point of view, stone weathering is a response to the difference between the conditions in which the constituent minerals are formed and the conditions when the stone is exposed to Earths' surface.

2.1.1 Weathering Processes (Physical, Chemical and Biological)

Monument stones are known to undergo slow and sporadic deteriorations that appear in different forms and types. These deteriorations are sometimes obvious, sometimes not. The causes are intrinsic factors like low durability and extrinsic factors like environmental and anthropogenic impact, as well as the interplay between them.

Although there is progress a better understanding of these processes is needed as many mechanisms and interactions are not yet well understood.

The three main weathering processes which often work simultaneously to decompose rocks are physical, chemical and biological in nature. Physical or mechanical degradation processes are determined by the action of heat, water and pressure with the stone while chemical weathering describes the effects and reactions of atmospheric chemicals with the stone material. Physical weathering by splitting a stone into smaller pieces favors chemical weathering due to the resulting higher surface area to volume ratio. Both might involve biological processes as well (like forces from growing roots or biologically produced chemicals that react with the stone), but the impact of those play only a minor role for the scenarios we intend to model and are beyond the scope of this project. However, biodegradation is one of the causes of stone discoloration and degradation due to the colonization by living organisms such as bacteria, fungi, algae and lichens. The interaction between the stone and the organism can both advance and retard the rate of deterioration. Besides forming biofilms on surfaces of stones the organisms can dwell in cracks, pores and bores. The natures of the stone and prevailing environmental conditions determine the type, processes and extent of biodeterioration [2]. The basic processes for some of the physical and chemical weathering are detailed in section 3 and 4, respectively. The varying contributions of physical and chemical weathering to stone decay depending on the climatic conditions are presented in section 2.2.

2.2 Weathering Types Related to Rain and Temperature

Climatic factors such as temperature, precipitation, wind speed and direction, radiation and relative humidity can have an influence on the deterioration of monument stones. The degree of their impact varies depending on the stones local environment and their intrinsic nature. For instance, stone surfaces exposed to intense sunlight are also exposed to high temperature variations which can lead to stress and shock on stones which are especially heterogeneous in their composition as different minerals expand and contract differently [3]. Frost weathering becomes serious when there is a slight change in temperature around zero degree Celsius. Temperature variation when coupled with other climatic factors like humidity results in other synergy effects that determine stone weathering. For instance, the stone deterioration through freeze thaw cycles would be exacerbated if there is high precipitation before freezing and coupled with salts in stone structure [4]. Like temperature, precipitation is a key climatic factor since dissolution of stone materials [5] and many weathering processes are associated with it.

In 1950 the physicist Louis C. Peltier [6] put *morphogenetic regions* – regions showing different weathering characteristics – into a relationship with the mean annual rainfall and the mean annual temperature as shown in figure 1. This generalized representation of the distribution of chemical and physical weathering/erosion processes indicates that different climatic characteristics lead to different weathering processes. He pointed out that in each of the morphogenetic regions (they relate to Glacial, Periglacial, Selva, Moderate, Savanna, Semi-Arid and Arid regions) different weathering processes act together in certain proportions. Maritime regions which typically show a different character due to strong wind and water action are not considered

separately in this simplified representation. However, Norwegian stone monuments,

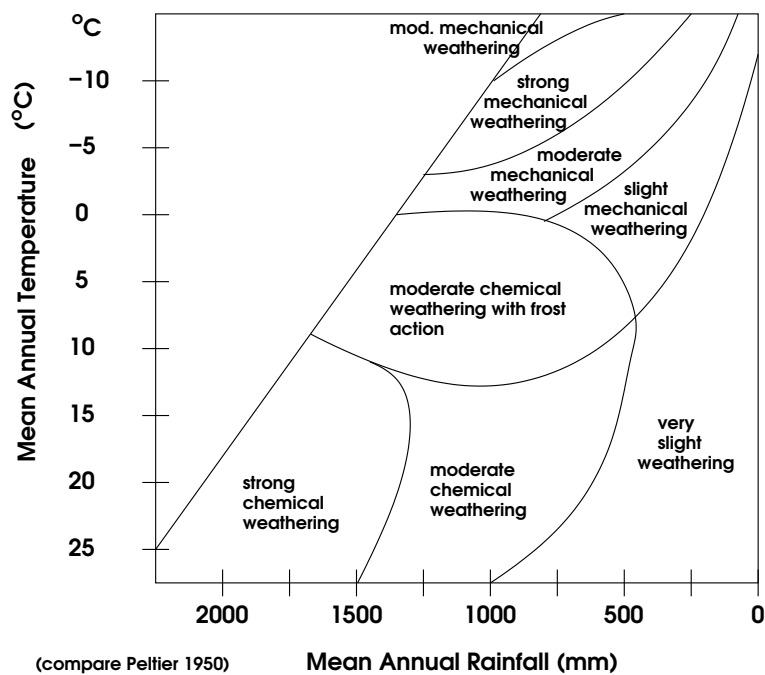


Figure 1: Graph indicating the present weathering processes in relationship to the mean annual rainfall and the mean annual temperature (Redrawn after Louis C. Peltier [6])

like the Nidaros cathedral, are often located along fjords or closely to the coast with cold to mild winters and cool to warm summers and about 900mm annually rainfall in Trondheim (compare [7]).

Coastal vs. Inland Weathering

Inkpen and Jackson [8] investigated data of marble gravestones from inland urban, inland rural, coastal urban and coastal rural sites in Britain that exhibit similar amounts and variations in rainfall and would therefore lie closely together in the Peltier diagram above. Their findings are inconclusive as they found that one particular investigated inland rural site had a significantly lower mean weathering rate but that the urban sites of Oxford, Lodge Hill and Portsmouth showed similar weathering rates, despite their diverse locations (coastal and inland) and histories. This indicates that beside rainfall and mean temperature other factors have an observable influence on the weathering as well.

In the following section we enumerate the principal physical weathering processes that affect stone mechanically and in section 4 we summarize some of the known fundamental chemical stone weathering mechanisms.

3 Physical/Mechanical Weathering

One can distinguish the following main physical weathering mechanisms that essentially do not change the chemical composition of the minerals within the stone.

- **Thermal expansion and contraction/differential thermal stress:** The daily and/or yearly temperature changes repeatedly warm up and cool down stone. The heating causes expansion and the cooling leads to a contraction of the stone material. As different minerals expand and contract at different rates this creates stresses along mineral boundaries (e.g. the contact surfaces of typically different colored minerals) where the stone finally cracks and breaks. Stones are relatively weak conductors of heat and in areas with very high daily temperature differences (about 50°C and more) this leads to an effect known as *onion skin* weathering or differential expansion affecting mostly the first few centimeters at the surface of the stones. For grained stones composed of differently sized and oriented crystals, like granites and marbles, cyclic heating and cooling results in deterioration even at small temperature changes. The thermal cycling can lead to granular decohesion of the stone. Stones that contain hydrated minerals like gypsum and clay are sensitive to thermal cycling due to the loss of the hydration water in these minerals. Treatments that causes the stone surface to react differently than the interior like salts, water films, or biofilms can lead to a shear stress, crack propagation, and, finally, flaking [9].
- **Wetting and drying:** Rocks or stones most affected by wetting and drying are the ones that contain various clays. Porous material like clay absorbs water vapor from the atmosphere and tends to expand. Such stone types are thus affected by the cyclic crystalline swelling and contraction even when the relative humidity fluctuates normally. For some stones in which phyllosilicates (sheet silicates like micas, chlorite, serpentine, talc, and the clay minerals) are found, sandstones for example, the hydric expansion can be two times that of the thermal expansion.
- **Frost wedging/frost shattering/ice wedging:** The freeze-thaw weathering (also known as frost shattering) denotes the process in which water gets trapped in cracks or joints of a stone and undergoes repeated cycles of freezing thereby putting pressure on the stone as the ice expands, followed by melting that releases the pressure. The repetition of this cycle weakens and eventually shatters the stone into fragments and chips. Due to its nature this process is predominant when the temperature fluctuates around zero degrees.
- **Salt crystallization:** In between physical and chemical weathering processes do we find the crystallization of salt. Salt formation is one of the most critical, often the major factor, within the deterioration mechanisms of building stones. Salt solutions (which might result from a chemical decomposition of the stone or the deposition of particulates on the surface or might be drawn from ground in the presence of water) seep into cracks and joints within the rocks and when the moisture evaporates, the salt is left behind and the growth of salt crystals creates stresses that can break down the stone. The salts of sodium chlorite

NaCl and calcium chloride CaCl_2 that are used as deicing agents in winter seasons are also considered to be a source for salt crystallization after they are transported to the stone by different mechanisms.

George W. Scherer examined in [10] several important weathering processes like the thermal expansion of calcite, freeze/thaw cycles, salt crystallization along with the swelling of clay inclusions and reviewed what is understood of these mechanisms and which aspects remain to be solved. He concluded that salt damage is one of the most serious, but least understood, causes of stone deterioration and that the essential mechanisms that cause stresses in stone are known, but that details are not clear.

4 Chemical Weathering

Chemical weathering is the disintegration of stone by chemical mechanisms such as carbonation, hydration, hydrolysis, oxidation, complexation and ion exchange in solution. Mineral dissolution of stones is closely linked to climatic conditions, air pollution and acidic particulate deposition on stones.

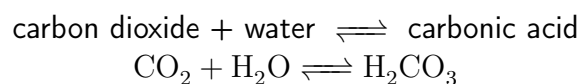
In [11] the author David G. Price noted that chemical weathering usually includes the solution of stone material the degree of which depends on the amount of water passing over the surface, the solubility of the material, and the pH value of the water. Considering all possible reactions of stone materials with all possibly present chemicals becomes quickly very complex. However, for some stones the chemical degradation or weathering mechanisms of particular material components are relatively well known.

4.1 Chemical Weathering Mechanisms for Particular Stones

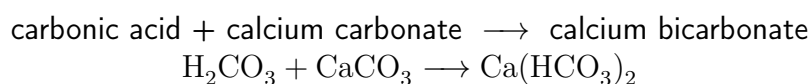
Some chemical weathering mechanisms that lead to familiar erosion and degradation patterns – like carbonation or the crust building on rain protected marble objects – are known in relatively detail. Below we provide a few examples of weathering mechanisms that are chemically well understood.

4.1.1 Limestone (Carbonation)

The chemical weathering of limestone is also known as carbonation. Limestone consists of different crystal structures (mainly calcite and aragonite) of calcium carbonate (CaCO_3) with its origin often from the remains of marine organisms. The carbon dioxide (CO_2) in the air is dissolved in rainwater resulting in weak carbonic acid (H_2CO_3 or equivalently $\text{OC}(\text{OH})_2$):



In contact with limestone – as it seeps into cracks – the weak acid reacts with the stone and forms calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$):



Since calcium bicarbonate is soluble, it is carried away in solution, eventually eroding the limestone. The acidity of the rain is often enhanced by reactions with atmospheric pollutants like sulphur and nitrogen oxides, resulting in increased rates for the limestone dissolution. Biocolonization of the cracks created might further exacerbate the deterioration.

For example, on a larger scale this process deepens and widens the joints of well-jointed limestone resembling an artificial pavement as shown in figure 2.



Figure 2: Limestone pavement above Malham Cove in the Yorkshire Dales, United Kingdom (© User:Lupin/ Wikimedia Commons)

4.1.2 Marble (Crust Creation)

Marble consists mainly of calcite (the most stable polymorph of calcium carbonate CaCO_3). Srinivas S. Yerrapragada et al. [12] investigated the weathering of marble, observing two processes.

- 1) **Crust building:** Sheltered from rain, dry deposition is creating a black crust composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and soiling materials deposited on the surface. Later the crust exfoliates meaning it peels off in flakes, splinters or scales. They list several crust formation reactions and mention that the overall mechanism may be more complex. For example they refer to a *galvanic cell model* to explain that the crust continues to grow although one would expect that the crust protects the underlying stone (marble) from future direct deposition of air pollutants.
- 2) **Surface recession:** On unsheltered surfaces, dry deposition happens too, but it is washed away by rain as CO_2 in rainwater plus H^+ ions corrode the marble.

Mentioning that the mechanisms of surface recession are too complex, the authors made outdoor experiments measuring the amount of material (calcium) that run off

during rain showers and related this to the exposed sample surface allowing them to estimate the recession through rainfall. They found that the surface recession is about 7 times larger than the crust formation rate. ($14.5\mu\text{m}/\text{yr}$ vs. $1.9\mu\text{m}/\text{yr}$). The sum of all these effects is then approximately described by a simple equation (see eq. 1) for the total surface recession rate of marble per meter of rainfall.

$$\delta_m \left[\frac{\mu\text{m}}{\text{m}} \right] = 6.56 + 27.38H^+ + \frac{1.131 \cdot 10^{13} C_{SO_2}^{0.7} C_{NO_2}^{0.3}}{V} t \quad (1)$$

In this equation H^+ is concentration of Hydrogen ions measured in mmol/L and the concentrations of sulfur dioxide (C_{SO_2}) and nitrogen dioxide (C_{NO_2}) in air are measured in mol/cm^3 . The time t is in years [yr], and the rainfall V is measured in meters [m]. Roberto Bugini et al. [13] investigated the rate of crust formation on marble surfaces by analyzing samples of black crusts in an urban area providing some growth numbers for the crusts.

4.1.3 Quartz

Quartz appears in many varieties (Amethyst, Rose quartz, Tiger's Eye, ...) with different colors depending on present trace elements. However, pure quartz is translucent and colorless. The crystal is made up of silicon-oxygen tetrahedrons (SiO_4) and the whole compound consists of one part silicon and two parts of oxygen (silicon dioxide, SiO_2). It is practically insoluble in water and in general not attacked by acids as it is an anhydrite of an acid itself (orthosilicic acid H_4SiO_4). It remains relatively unaffected by chemical reactions and its harder nature makes it also durable against physical processes.

4.1.4 Soapstone

Soapstone is a metamorphic rock that arises from the transformation of originally existing rocks due to several possible processes within the Earth's surface (e.g., tectonic processes) causing pressure, friction and distortion. Soapstone is rich of talc, which is a magnesium-rich (Mg) mineral that gives the rock a soapy, greasy feel. In [7] Per Storemyr discussed the geology, petrography (describing the mineral content and the textural relationships) and salt content of soapstone deposits which we list in a summarized form here:

- Soapstone originates from various magnesium-rich rocks, such as peridotites and dolomitic carbonates.
- The softness of soapstone comes from flaky minerals, mostly talc.
- Other common minerals in soapstone deposits are: chlorite and carbonates (calcite, dolomite and magnesite-breunnerite)
- Minerals in some deposits include: amphiboles, such as tremolite-actinolite, small amounts of mica
- Opaque minerals include: magnetite, pyrite and pyrrhotite

- Relics of original olivine-, pyroxene- and serpentine-rock may be present when the transition to soapstone is incomplete.

The so-called "Grytdal" soapstone (named after its origin) that was commonly used during the restoration period between 1869 and 1892 has led to massive stonework damage at the Nidaros cathedral (See figure 3).



Figure 3: Photo: Archive of the Restoration Workshop of the Nidaros Cathedral (ARW) 1992, taken from [14]. It shows the rapid weathering effects of a part of the Nidaros Cathedral (the frieze from the choir) made of Grytdal soapstone in the 1880s.

"Grytdal" contains up to 10% pyrrhotite which is an unstable iron sulfide mineral. Pyrrhotite oxidizes and forms iron hydroxides, jarosite, gypsum and some magnesium sulfates leading to the observed damage. According to Storemyr [14] the "Grytdal" stone seems also to contribute to the formation of black gypsum crusts as the observed crusts can not be blamed to air pollutants (SO_2 and particulate matter) alone. Storemyr noted that in Norway another stone, that was used in medieval monuments, is also called soapstone. This is a soft chlorite schist usually derived from tectonic metamorphism of basalt but with a low talc content and slightly different properties.

4.1.5 Sandstone/ Metamorphic Sandstone

Sandstone or grit consists of more or less rounded, water-worn sand grains and if it contains dull, weathered particles of feldspar, shining scales of mica or small crystals of calcite these are easily to spot too.

The formation of salt crusts on Baumberger sandstone (a historic building stone) exposed to gaseous SO under dry and wet surface conditions was investigated by Y. Bai et al. [15]. The surface change and decay of sandstone samples exposed to a polluted urban atmosphere over a six-year period in Belfast (Northern Ireland) is reported by A.V. Turkington et al. in [16].

4.1.6 Granite

Arlindo Begonha [17] studied the deterioration of granite stones of two Portuguese churches. There the crystallization of the minerals of soluble salts in the porous network of the granites is the major cause of stone decay. The deterioration factors act together in the course of deterioration of stone. Insight into these factors and modeling the effects of the deterioration factors to elaborate the observed deterioration feature is important. An example of such effort is the one used to describe the so-called granite decay sequence. Granite is considered to be durable in its lithology [18]. However, it shows the combined effects of salt weathering, chemical alterations and dissolution which converts the structurally stable stone into broken-down pieces leading to a continually retreating stone surface as shown in figure 4. The displayed four stages of the granite decay sequence are (taken from [18]):

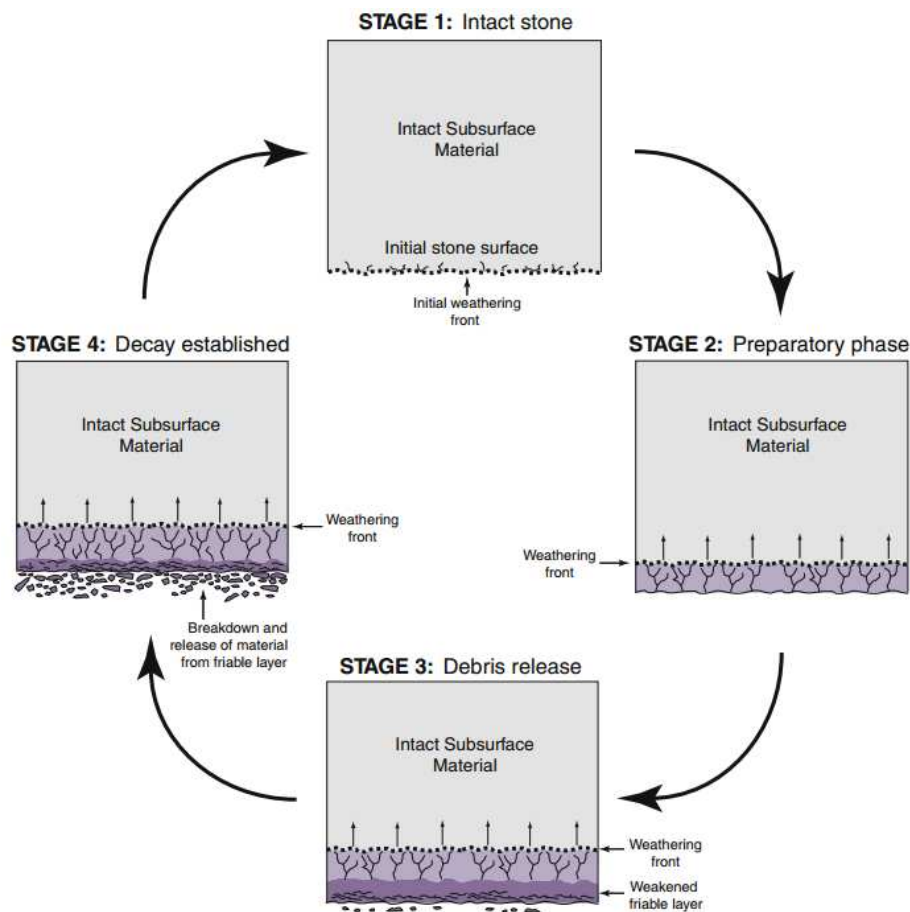


Figure 4: Conceptual model from [18] showing the different stages of the granite decay sequence at Eeragh and Eagle Island lighthouses.

Stage 1: surface flaws and discontinuities facilitate some salt penetration under conditions of limited condensation but with reduced ventilation and more frequent episodes of surface condensation, salts start to accumulate. **Stage 2:** micro-fracture networks initially developed at the stone surface begin to extend into subsurface material as a result of salt weathering and chemical alteration which break or weaken

intergranular bonds and degrade the lattice structure of individual mineral grains. **Stage 3:** positive feedback conditions prevail whereby release of weathered surface material facilitates further salt/moisture penetration which in turn maintains development and extension of microfracture networks with a gradual migration of the weathering front into intact subsurface material. **Stage 4:** loss of weathered material aided by the effect of gravity results in progressive surface retreat of granite blocks and facilitates inward movement of the weathering front-once established, the decay sequence is difficult to stop especially in the context of a salt and moisture-rich environment where reduced ventilation and condensation persist.

4.2 Pollutants Effect

Air pollution is one of the main causes of stone deterioration. The processes involved are complex in nature and are reviewed in a number of publications [19]. The studies have been undertaken on stone types such as limestone, marble, and lime mortars due to their vulnerability to acidic pollution. The deposition of atmospheric particulates appeared to be a common problem for all types of stones. Most of the research until recently were also emphasizing the direct effects of air pollutants like sulfur oxides, nitrogen oxides, and carbon dioxide on stone [9]. Other air pollutants of interest are ozone and aerosols. The direct effect of acidic pollutant can be gradual recession of the surface or black crust formation depending on the immediate local environment of the stone (sheltered or not for instance). Carbon dioxide, carbon monoxide, soot rich in elemental carbon, hydrocarbons and sulphur dioxide are produced in large quantities from combustion of fossil fuels. All these air pollutants, when deposited on stone monument surfaces, can contribute to its deterioration. They can play different roles and can have synergy effects when they act together. NO_2 and SO_2 turn into more acidic compounds like sulphuric acid and nitric acid upon contact with water; ozone is a powerful oxidant. The role of nitrogen oxides is not as clearly known as that of sulphur oxides. The nitric acid formed from the gas seems to exert its oxidizing acid effect. Aerosol containing black carbon further enhance the deterioration and blackening of the stone surface.

The survey on air pollution and deterioration of stonework in Venice from Vasco Fassina [20] addresses some of these pollutant effects along with a physicochemical characteristics of the deteriorations that are observed. The effects of ozone and NO_x on the deterioration of calcareous stone was investigated by S. W. Massey in [21]. He investigates the effects of these gases on the deterioration of different stones in chamber reactions and field works in urban and rural environments. The corrosive effects of gaseous SO_2 , NO_x , O_3 , HNO_3 , particulate matter, and acid rainfall are topic in [22], where Costas Varotsos et al. is concerned with the enhanced deterioration of the cultural heritage monuments.

4.3 Changing Environmental Conditions

In the future we will likely observe the tendency of increasing global carbon dioxide along with declining sulfur dioxide due to changes in fuel use in cities and fuel gas desulfurization in the case of combustion power-plants to comply with legislations regarding SO_2 levels. Climate factors like rising temperatures, changing precipitation

or extreme climatic events could result in the appearance of other weathering types and soiling patterns leading to a more rapid change of monument surface recession rates [4, 23]. The speed over time with which stones deteriorate or show decay effects depend not only on the current prevailing pollution and climatic pattern but also on the history of the environmental conditions and human interventions [24]. These effects have to be considered in attempts to explain observed deteriorations and should be considered too when predicting future deterioration features.

4.4 Inherent Stone Problems

Several degradation problems with building stones are related to the characteristic of the stone rather than the effect of the environment. Some stones are by their nature more susceptible for deterioration than others and should not be selected for monuments and sculptures. There are researches focusing on stones prone to deterioration [25]. Among the characteristics which renders a stone susceptible to weathering are the porosity and the pore size distribution, the permeability and the mineralogy of the stone itself.

4.5 Factors which make Chemical Modeling Difficult

For the weathering processes mentioned above, one can see that for a realistic visualization of the modeling it is necessary to incorporate measured erosion behavior as a constraint or as prior knowledge. Stone can have the same chemical composition but can show quite different weathering characteristics due to other factors like the porosity. For instance stones like Carrara marble, Istrian stone and others can have a similar chemical composition, but their contrasting deterioration behavior depend more on properties like porosity, pore shapes, pore size distribution, and grain size than on their chemical composition [9]. The heterogeneity in the component minerals of stones is quite immense in most cases and the synergy effects associated with diverse deterioration factors acting simultaneously needs to be studied to a larger extend. Another complication originates from the impacts of climate and air pollutants that have accumulated on stone surfaces often for long periods. Therefore, better prediction and understanding of monument stone deterioration requires the assessment of climate and air pollution over a long time span.

5 Phenomenological description

The fundamental weathering processes happen on a very small or even atomic scale, but today our knowledge of all involved processes in detail is limited and only particular relations are known, mostly in form of chemical and physical equations as discussed above. Many of the interconnections are still the subject of future research. But even if one gained the entire necessary knowledge at the atomic scale, modeling, simulating and solving the microscopic model in exact detail would be practically impossible.

Therefore, we must resort to the idea of extracting useful information from microscopic models and available measurements in order to simulate erosion processes at

Lit.	Monument location	Building century	Lithology (Stone)	Recession rate [mm/century]
[27]	French Churches West and South Brittany French Massif Central	11-17th 11-15th	Granite Biotite Soft limestones Sandstone Basalt, Marble, etc.	1.6 – 6.5 3 – 5 6 – 7 0.3 – 16 < 1
[27]	Khmer Temples Angkor temples	10-13th	Sandstone	0.2 – 5.0
[7]	Nidaros, heavily restored 1869-1969	11-14th	Soapstone	5.0

Table 1: Collected approximate stone recession rates measured in millimeters within 100 years (the first column refers to the sources). Note that 1 mm/century corresponds to 10 $\mu\text{m}/\text{year}$.

larger scales with a realistic appearance or required accuracy. The scale of interest is typically a few millimeters for longer periods and larger model-simulations and in the sub-millimeter range for shorter time-periods and higher detail investigations. Some prior knowledge for creating macro-scale models of erosion can be obtained from measurements of different degradation processes like the surface recession, crust building or color change over time. These measurements will help obtain a realistic behavior of the erosion simulation as they can be used to adapt the parameters of the model to real measured erosion effects. Below, we summarize some phenomenological erosion measurements performed on different stone materials that help us assess the magnitude of the erosion processes we intend to simulate.

5.1 Surface Recession Rates

One of the first and pioneering investigation of stone decay was performed in Edinburgh churchyards and published 1880 by F.R.S. Geikie [26]. Over time the surface recession has been measured in several different contexts for different monument types like Romanesque and Gothic churches. According to [27] some monument types, like marble tombstones (younger than 200 years old), are overrepresented in studies while others, like medieval sandstone monuments, are in need of more data and should be given more attention. Measurements with basic tools such as steel tapes, calipers and profile gauges on such monuments from several sources were collected by M.F. André and B. Phalip [27] into a provisional overview of stone recession rates for medieval French churches and Khmer temples. This indicates that real erosion processes lead to recession rates for different stone types in the range from sub-millimeter to 16 millimeters within 100 years. An overview for some observed weathering rates is shown in table 1. Beside the French churches and Khmer temples, it contains also the weathering rates found from other sources. A number of damage functions or dose-response functions like the one described in section 4.1.2 have been formulated for predicting the effects of air pollution and climatic factors on deterioration stone

surfaces [28]. Most of them are for limestone, particularly Portland Limestone [29]. In this connection, the most widely cited example is the Lipfert function [5], which determines the annual surface recession dx/dt using the equation (carbonate stone):

$$\frac{dx}{dt} = L_v R_n + 0.016 [H^+] R_n + 0.18 (V_{dS} SO_{2(g)} + V_{dN} HNO_{3(g)}) \quad (2)$$

where dx/dt is the recession rate measured in $\mu\text{m year}^{-1}$ (micrometer per year); R_n is the rainfall in m year^{-1} ; V_{dS} and V_{dN} are deposition velocities. $SO_{2(g)}$ and $HNO_{3(g)}$ are concentrations of SO_2 and HNO_3 in $\mu\text{g m}^{-3}$ and $[H^+]$ is the hydrogen concentration in $\mu\text{mol l}^{-1}$. The term L_v is known as Lipfert value, which is typically set to $18.8 \mu\text{m m}^{-1}$ (recession in micrometer per meter precipitation). The Lipfert function is derived for generic calcite, but is considered to be relevant also for carbonate stones with a porosity lower than 25%. Grossi et al. [30] note that the Lipfert function is valid for precipitation pH-values in the 3-5 range, as the effect of acid rain becomes small above pH 5.5. Also in [30] they made predictions for the annual rates of recessions for different cities (see figure 5) based on three different damage functions. Beside the Lipfert function (2) models for recession functions from the International Cooperative Program on Effects on Materials including Historic and Cultural Monuments (ICP) [31] and the MULTI-ASSESS project [32] were used.

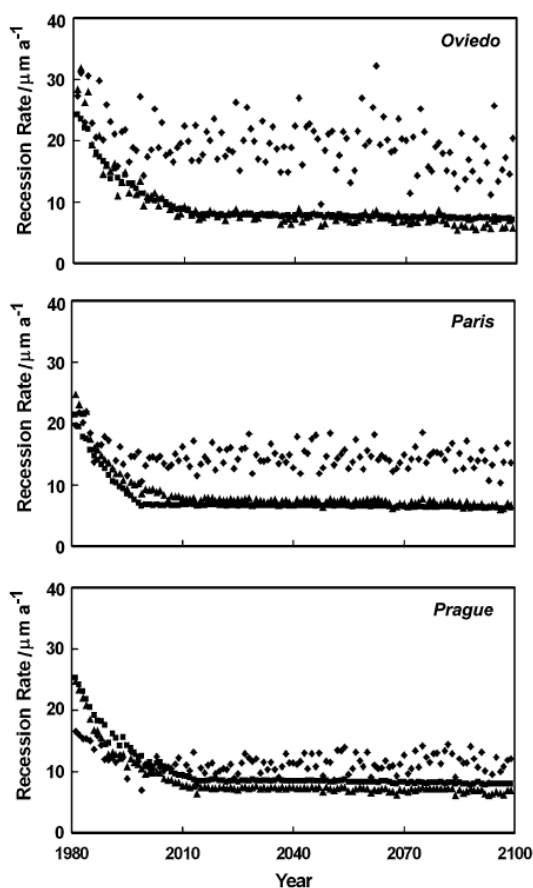


Figure 5: The annual rates of recession (micrometer per year) predicted from the three damage functions Lipfert (diamond), ICP (triangle) and Multi-assess (square), over the period 1981-2099 for Oviedo, Paris and Prague (Source: [30])

There is a need to derive similar damage functions for modeling varying stone materials in real settings incorporating the particular situation of the exposed stone surface. Some preliminary results from the laboratory modeled weathering processes on carbonate building stones were also presented in [33]. The assumptions made have simplified the parameters but it can be carried out with modest laboratory setup. In the case study [34] concerned with tuffeau (a French porous limestone) a characterization of stone and weathering effects in urban environment through the use of a combination of analytical techniques is given. The determination of the alteration types as well as the structural and mineralogical changes are illustrated. Thomas C. Meierding [35] studied serpentine stone considering stone composition, building geometry and chemical reactions between stone component materials.

As erosion clearly includes discontinuous processes – such as the sudden appearance of cracks or flakes falling off convincingly show – the question arises how adequate a linear continuous approximation of surface recession is.

5.1.1 Linear vs. Non-linear Modeling

Linear Model: Philip A. Baedeker and Michael M. Reddy [36] described experimental measurements (suitable for undergraduate experiments) on stone-slabs (Marble and Limestone) to obtain quantitative data for the stone damage processes. The slabs were first sprayed with distilled water with a pH of 5.6 and acidified solutions and the run-off was collected and investigated. He observed that the calcium concentration in the run-off solutions varies linearly with initial hydrogen ion concentration of the spray solution and depends therefore on the pH value of the spray solution and on the amount of the liquid. (Note that the pH value is defined as the decimal logarithm of the reciprocal of the hydrogen ion activity, which means that it is a non-linear relation to the pH value, but linear to the number of hydrogen ions and the amount of spray solution [=rain])

Non-linear Model: The authors of [37] mention that non-linearity prevails in stone decay/rock weathering systems, meaning that stones do not decay gradually (linearly), but instead experience seemingly unpredictable, episodic breakdown. They speculate that factors like the black, gypsum crust formation and the production of small-scale blisterings play a more dominant role before a catastrophic retreat of limestone blocks is observable. The basic simple conceptual model they use to explain the decay process assumes that surfaces are stabilized by the development of indurated crusts with occasional breaching of crusts followed by rapid breakdown as weakened sub-surface layers are exploited. The process of decay can be seen as accumulation of stresses with an accompanying decrease of strength. The process is conceived to involve thresholds (associated with intrinsic or extrinsic variables), with rapid decay following the overstepping of a stress or strength threshold. A review focusing on stone decay systems has shown that nonlinearities are common and chaotic responses of stone to environmental changes should be considered to interpret, model, and manage stone deterioration [38].

5.2 Visual features appearing in relation with stone decay

Stone decay features appears in a large number of variety: blistering, alveolization, curst formation (black, salt, iron-rich), scaling/flaking, sanding, exfoliation (delamination), cracking, splintering, crumbling/granular disintegration/sugering, roughening, rounding, pitting, relief, discoloration, soiling, case hardening, efflorescence, sub-efflorescence, detachment of stone elements, fissures, leaching, etc. They can be classified as additive or subtractive based on their effect. Some of the stones can appear intact superficially while losing cohesion underneath.

Bernard J. Smith et al. [37] listed features observed at buildings in several different locations (Oxford, Budapest, Cairo, Belfast and many more) that are associated with the decay of sandstones and limestones. Some examples of degradation forms are given below along with a short description of their visual appearance.

- **Black crusts:** As noted in section 4.1.2 atmospheric pollution, in particular sulphur dioxide SO_2 , reacts with water and calcite (CaCO_3) and forms a black crust composed of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). However, the specific composition of the black crust varies according to the environment and is typically rich in metals and carbonaceous particles in urban areas and is often characterized by the presence of microorganisms in less urban environments. This degradation process affects the stone and its appearance. If the crust is regularly washed away the surface of the stone will gradually recede. The crust remains in areas that are sheltered from rainwater. An example of a black crust on a stone sample of a monument is shown in figure 6 (Image from [39]).



Figure 6: Stone from the Tiburtina Town Gate (Rome) showing the black crust due to atmospheric deposition. (Image from [39].)

- **Salt crusts:** At the Nidaros Cathedral the introduction of Portland cement for reconstruction works resulted in stone damages that are visible as calcite crusts. According to [7] other salts (e.g., apthitalite, a sodium-potassium sulfate) are produced as well and leave visible traces at places where they cannot be washed away. Figure 7 shows a section of a wall at the Nidaros Cathedral with a calcite crust.



Figure 7: Calcite crust at the Nidaros Cathedral. (Photo: 2013 by C. Schellewald)

- Case hardening: Some chemical weathering mechanisms alter the mechanical firmness of the weathered stone surface. For example, it can be observed at sandstones where the accumulation of cementing agents (like wind-deposited calcite) cause the sandstone grains to held tighter together on the exposed surface.
- Granular disintegration: This kind of stone deterioration occurs mainly in granular sedimentary (sandstone) or granular crystalline (granite) stones. The grains become loosened and fall off.
- Alveoli (caving): Alveolar weathering appears typically as ellipsoidal eroded holes in rock and has its origin in salt weathering common in coastal and semi-arid areas. It is observable at granites, sandstones and limestones. Other names for this weathering type include: honeycomb weathering, fretting and cavernous weathering. An example for a rock showing alveolar weathering is displayed in figure 8.



Figure 8: A rock showing alveolar weathering. This weathering form also known as caving. (Photo: 2013 by C. Schellewald)

- Exfoliation and Flaking: This is the phenomenological description of stone decay processes where sheets or flakes break off from the stone surface along exfoliation joints (cracks) in parallel to the surface of the stone. This can be observed in large scale on mountains or in small scale on single rocks or stones and the causes for this could be the result of one of the above mentioned mechanism. A flake on a wall at the Nidaros Cathedral is shown in figure 9.



Figure 9: Flake at the Nidaros Cathedral. (Photo: 2012 by C. Schellewald)

- **Coloring:** Color alteration results from chemical weathering of minerals such as oxidation of iron and manganese compounds, or due to accumulation of coloring matter like carbonaceous air particles from emissions on gypsum crust or due to staining by biogenic pigments in case of biodeterioration [38].

Future research may gear towards developing model for some of the visual appearances of deterioration forms separately.

5.3 Texture as Clue for Stone Composition

The classification of metamorphic rocks is typically based on the mineral components, texture, protolith (this refers to the original rock prior to the transformation/metamorphism), and the general chemical composition of the rock. In optical mineralogy it is common to observe the stone under the microscope with plane polarized light and to characterize and identify the mineral components based on grains, refractive index, colour, colour variation. Therefore in principle a meaningful segmentation of the observed structure and their uniform regions could help to map the observed texture to the appropriate stone-material.

5.3.1 Tools for Quantifying and Monitoring Stone Surface Deterioration

Diverse methods have been applied to assess and quantify the amount of stone deterioration. They include direct measurements of surface recession with references made to carved or polished surfaces, tooling marks and ranking the visibility of inscription [1, 40]. Other techniques used for recording and monitoring stone surface conditions are 3D laser scanning, profilometry, photogrammetry, and microerosion meters [41]. At micro and nano level, scanning electron microscopy (SEM), atomic force microscope (AFM) and vertical scanning interferometry (VSI) can be used in studying surface roughness and morphology as well as mechanism and kinetics of mineral dissolution since they allow to investigate mineral-water and other interactions with stone materials [1, 42]. The microerosion meter has been used to monitor the rate of stone decay of a church from 1980-2000, during which atmospheric sulphur dioxide levels in the region have fallen by 50 percent. Erosion rates on horizontal sites were found to have decreased from 0.045 mm/year in the first 10 years to 0.025 mm/year in the next decade. Quite recently, atomic force microscopy (AFM) and vertical scanning interferometry (VSI) have been used to monitor mineral reactions and the effects of biodeterioration [9].

Microscale features as predictors of larger features

There are attempts made to link microscopic features of stone deterioration to larger scales. This is based on the assumption that microscopic features are diagnostic of specific processes that dictate the development of larger features [43]. In figure 10 erosion effects at different scales are shown.

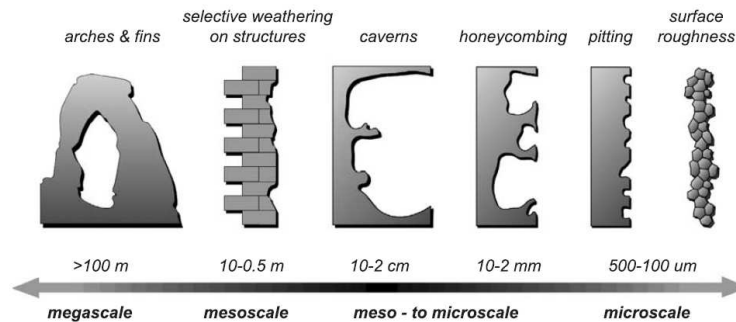


Figure 10: Scale-dependent weathering morphology from [44].

The authors argued that even though it is possible, morphometric similarity across scales does not necessarily mean that the same process-form relationships exist across scales [44]. They highlighted that the quantification of features at micro scale, along with the development of accurate definitions and descriptions, may lead to a better understanding of features on different scales.

6 Visualization/Simulation of Decay Processes

In this section we summarize the main ideas presented over time in different papers that are concerned with the simulation and/or visualization of erosion and degradation processes. Several ideas seem relevant and might be suitable (after some adaptations) for our efforts to simulate stone degradation processes.

6.1 Realistic Landscape Visualization

6.1.1 Terrain Simulation Using a Model of Stream Erosion

In an early computer graphics approach (1988) Alex D. Kelley et al. [45] aimed to create realistic-looking natural landscapes (also called stream networks, channel networks or drainage networks) that are formed by water erosion. They started with a three-dimensional skeleton of (uneroded) terrain where the main-trunk is specified by the user and a stream tree is constructed by recursively adding sub-branches randomly shifting the junction location and incorporating other parameters determining the stream network like the mean branch lengths or the typical junction angles. Then solving a minimization problem (*surface under tension* [46]) the final (eroded looking) terrain is approximated.

6.1.2 Synthesis and Rendering of Eroded Fractal Terrains

Beside creating fractal terrains F.K. Musgrave et al. describes in [47] the simulation of the erosion on such terrains with the aim to create more naturally looking mountain slopes and stream/valley networks. In their simulation approach the erosion process is split into two parts. **Hydraulic erosion** caused by running water and **thermal weathering** causing rock to fall off at steep inclines building the characteristic talus slopes at the mountain base. For the hydraulic erosion they basically drop water on the height field representing the terrain and let it run down the landscape, thereby eroding and depositing material at the traversed lower locations according to a function representing the sediment load of the water. This is modeled iteratively by applying a set of simple equations involving three parameters which determine the maximum amount of sediment which may be suspended in a unit of water (capacity constant), the rate at which material from the water is added to the current altitude (deposition constant) and the rate at which soil is taken away by the water (soil softness constant). The thermal weathering aims to create (global) constant talus angle. It is computed iteratively slope is greater than the talus angle, we then move some fixed percentage, of the difference onto the neighbor. This *ad hoc* model showed reasonable resemblance to natural erosion patterns.

6.2 Simulation of Liquids Interacting with Material

6.2.1 Hydraulic Erosion

In [48] Bedřich Beneš et al. presented a method for the visual simulation of hydraulic erosion on scenes that are modeled on a regular voxel grid. Their system exploits a practical approach from Nick Foster and Dimitri Metaxas [49] and Nick Foster and Ronald Fedkiw [50] to approximate the Navier Stokes equation (3):

$$\frac{\partial \mathbf{v}}{\partial t} = - \underbrace{\mathbf{v} \cdot \nabla \mathbf{v}}_{\text{Convective acceleration}} - \frac{1}{\rho} \underbrace{\nabla p}_{\text{Pressure gradient}} + \underbrace{\nu \nabla^2 \mathbf{v}}_{\text{Viscosity}} + \underbrace{\mathbf{f}}_{\text{External forces}} \quad (3)$$

Equation (3) determines the behavior of fluids by incorporating the viscosity (ν), convection, density (ρ), pressure (p), and an external force which often is just the gravity ($\mathbf{f} = g$). Modeling the liquid volume using a combination of particles and implicit surfaces and employing a so called semi-Lagrangian method along with enforcing incompressibility ($\nabla \cdot \mathbf{v} = 0$) a method is obtained which is considered suitable for applications in computer graphics to model and animate liquids. Beside the fluid approximation and a material transport the authors of [48] employ a erosion-deposition model acting on boundary voxels between water and material. The resulting animations of sand in water show a realistic looking behavior even on the small voxel-grids with sizes of about 120x120x32.

6.2.2 Erosion, Sedimentation, Strong chemical processes

In [51] the authors simulated liquid highly corrosive agents that cause erosion and sedimentation at the contact interface, therefore allowing to simulate corrosion of surfaces due to acid. Material eroded from the object surface is carried away by the

fluid and deposited onto the surface again. They basically employed physically based approximations to the complex erosion procedure studied in the geology community Chris Wojtan et al. [51] animated erosion, sedimentation, and acidic corrosion effects on scenes modeled as voxel-grids where the fluid and objects are represented as *level sets* (positive distance outside, negative inside). The motion of the fluid is computed by finite difference discretization, solving the incompressible Navier-Stokes equations for the velocity field. In order to represent the free surfaces of liquids, they employed particle level sets [52]. The fluid is modeled on a coarser grid (e.g. different coordinate system) as the objects but dominates – according to the authors – the computational effort. Shear stress resulting from fluid flow in parallel to the surface is used to compute an **erosion** rate (recession velocity) that is used to modify the level set interface of the object (assumingly in normal direction). Using *marching cubes* on the level set representations reveal the current surface of the objects at each simulation step. **Sedimentation** is modeled by a vertical settling velocity such that suspended particles that are assumed to be denser than water slowly sink and settle on the ground. They simulate chemical corrosion of metal-objects due to strong acid which is basically described by a **chemical reaction** of a solid piece of metal into a gas. In the given example hydrochloric acid (HCl) as strong acid, and magnesium (Mg) as metal-object. The driving equation of this process finally describes how the acid concentration changes, how much heat is released, and how the density at the surface of the metal changes at a single time step. Generally the solid-fluid coupling and other computed properties of the rigid objects are relatively rough approximations of the real physical properties of the objects. It should be noted that the simulation does not model the entering of the fluid into the object volume.

6.3 Visualization of Decay Processes

Recently a few people realized that for some applications – like in gaming – it might be sufficient to use prerecorded texture changes over time to create realistic looking decay processes. An approach that extends the bidirectional reflectance distribution function (BRDF) by the time-dimension and separates the spatial and temporal changes of a surface is given in the next section.

6.3.1 Appearance Based Surface Changes

Jinwei Gu et al. [53] measured the visual appearance of several different materials on flat surfaces over time. A bidirectional reflectance distribution functions (BRDF) that can be measured and usually describes how a particular material surface appears depending on how light is reflected within different camera-lightsource configurations. They extend the concept of BRDFs by adding a time dimension, resulting in a 7-dimensional description-function. The construction of a quite large measurement device allowed the authors to record image-sets (with 400x400 pixels for each recording, with a single parameter set) of temporal phenomena like drying, burning, corrosion and other decay processes (e.g., the ripening of fruits). Applying an iterative optimization within their *Space-Time Appearance Factorization (STAF)* model they were able to separate temporally varying effects from space varying effects (texture). This allows to modify both of them independently.

6.4 Physical/Chemical Based Erosion Simulation

There are only a few works about the simulation of erosion which try to simulate the physical and/or chemical processes that drive the decay. Two relevant approaches we found are summarized below. The first one removes particles from a flat surface with an engraving using a stochastic model while the authors of the second simulate physical and chemical mechanisms that contribute to the stone erosion.

6.4.1 Eroding Flat Marble Surfaces (Stochastic Simulation)

Paolo E. Bagnoli [54] used the simulation of erosion processes on a flat marble limestone with the aim to demonstrate that the engravings are still visible after a long time exposure to natural erosion. He used a monte-carlo technique to simulate stochastic events (making some assumptions about the used probability laws) like the removal of small marble particles at microscopic scale. The simulation takes two parameters into account: the average annual rain fall and the average erosion speed. The simulation was performed on a 3D voxel-block that essentially represents a small surface block ($n_x = 1000, n_y = 5$) with periodic boundary conditions in y-direction and a u-shaped engraving in the x-z-plane. The depth (n_z) has only to be considered close to the surface as inner object voxels have no likelihood to erode in the used model. The paper contains some interesting probability functions for erosion that depend on the number of not occupied neighbors (considering the 26 nearest neighbors).

6.4.2 Modeling and Rendering of Weathered Stone

Julie Dorsey et al. [55] developed an interesting approach to model and render changes in the shape and appearance of stone. Recognizing that the complex erosion processes change the stone mainly at the surface they introduced a *slap* structure that covers the narrow region around the stone surface. This volumetric boundary band represents the domain for the simulation of weathering processes. The authors confined themselves to *chemical weathering* in particular to the erosion or dissolution of a stone surface by water and pollutants. The basic weathering processes they modeled are

- 1) **Travel of moisture:** Alternating wet and dry cycles shift a waterfront ($p = 0$) below the stone surface according to Darcy's law

$$\mathbf{v} = -\frac{K}{\nu}(\nabla p(\mathbf{r}, t) - \rho \mathbf{g})$$

involving the density ρ , the permeability K , the viscosity ν and the gravity-acceleration \mathbf{g} . The water pressure p evolves in time according to the diffusion equation

$$\frac{\partial p(\mathbf{r}, t)}{\partial t} = -\nabla \cdot (\phi(\mathbf{r}) \nabla p(\mathbf{r}, t)),$$

where $\phi(\mathbf{r})$ models the spatially varying stone porosity. In dry cycles the boundary condition at the surface of the stone is set to $p(\mathbf{r}) = 0$ and $p(\mathbf{r}) \geq 0$ in wet cycles while the *boundary* condition for the inner water front is always $p(\mathbf{r}) = 0$. The two steps within their computational iteration consists of solving the diffusion equation and updating the inner waterfront ($p = 0$) accordingly.

- 2) **Dissolution, transport and recrystallization:** The authors model the dissolution of minerals or salt at the (moving) inner water front by computing the concentration C_i of the considered minerals i by

$$\frac{dC_i}{dt} = -k_i(m_i - C_i).$$

Here m_i refers to the maximum solubility (saturation level) and k_i is the solubility of the considered mineral (therefore determining the speed of the solution process). The convective-diffusion equation

$$\frac{\partial}{\partial t}(\phi C_i) + v \cdot \nabla(\phi C_i) = \nabla \cdot (\phi D_i \nabla C_i)$$

models the diffusion and transport of the mineral. The velocity v is computed from the pressure gradient and D_i refers to the diffusivity of the mineral i . The divergence ∇C_i through the surface determines how much material accumulates as crust on the surface.

- 3) **Erosion of the material:** For each voxel a decay probability d and a stone density s is stored. A zero density indicates the absence of stone. The decay rate is increased depending on the present mean amount of water and minerals. Its purpose is to determine the probability for an erosion event. A large number of erosion events are simulated on the surface of the object and within a zone of influence the stone density is reduced.

The differential equations were implemented using a finite difference scheme with additional care to obtain isotropic diffusion behavior (second order derivative) with the typical trapezoidal lattice. For the gradient (first order derivative) no corrections were applied.

7 Conclusion

Current studies of deterioration factors, mechanisms and processes of stone deterioration and its characterization at macro and micro level mainly lead to functions describing the recession rates of stone surfaces. Typically some relevant environmental factors (like the amount of rain, the temperature and pollutant concentrations) are integrated into the surface-recession function that involves empirically found parameters for a particular considered stone material. The mineralogical and petrographical complexity of stone materials makes the development of predictive erosion models based on physicochemical parameters a challenging task. A better understanding of the deterioration factors and their interaction over an extended time period would be helpful for a realistic modeling of stone decay. Today it seems that there is a lack of such an understanding which makes it difficult to explain why, for example, different stones of essentially similar composition and texture can show very different weathering features. For the physicochemical parameter estimation of selected stone-samples, a combination of in situ investigation, laboratory analyses and weathering simulation tests will be conducted. However, even as many aspects are not

yet fully understood, such processes might be successfully simulated and visualized exploiting Monte Carlo methods and/or other statistical approaches. A combination and extension of the reviewed methods for the visualization and simulation of decay processes represents a good starting point for designing new algorithms that finally will be integrated into the stone erosion simulator which we intend to develop. Another interesting research question is also if there is a link between erosion features at micro and macro levels that could be exploited for the simulation and visualization of stone deterioration processes. Statistical estimation methods that allow to incorporate certain prior knowledge of an undisturbed shape might also allow us to compute an inverse erosion leading to a reasonable estimation of the original stone-shape backward in time. We consider it worthwhile to combine accurate geometrical scanning of observed stone deteriorations with their simulated physicochemical phenomena. The high resolution differential scans will contribute to an understanding of the spatial and temporal variability of stone degradation.

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