Review of the Literature on the Topic

of Acidic Deposition on Stone

Report for

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Executive Summary

It is extremely difficult to determine how much of the deterioration observed on stones is due to "acid rain" since its action is not limited to one mechanism. Rather, it results from the interaction of various mechanisms, many of which also occur in natural weathering. The aim of this survey is to present a summary of the most relevant publications in the field of acid precipitation on stone to help identify the relative importance of the various factors that contribute to the deterioration of this material. It should also contribute in pointing out those areas in which further study and research will prove more fruitful.

The review has been organized on a relatively chronological order so that the readers can understand how trends in the research within this field have developed. It has been divided broadly into four areas discussing thy deposition, wet deposition, deterioration mechanisms and site studies. The articles reviewed have shown that dry deposition, which is mainly influenced by short range transport of pollutants from local sources, is the main source of damage. Wet deposition, responsible for long range transport of pollutants is secondary. However, in areas where buildings and monuments remain wet for a long time, and in rural areas, wet deposition can be the major source of damage. If pollution is very low, this phenomena becomes indistinguishable form the "normal" weathering due to "clean rain".

Of the most common pollutants, sulfur dioxide from combustion of fossil fuels, or nitrogen oxides from combustion engines, and its oxidation product nitric acid, the former is the most important factor in the deterioration of stone. In part this is due to its capability of reacting with any calcareous component in the stone or atmosphere and producing gypsum. The contribution of sulfates from aerosols, however, are not as important as the contribution of the gaseous sulfur dioxide.

One of the important issues in the susceptibility of stone to attack by sulfur dioxide is its receptivity, i.e., the capability of retaining this compound and reacting with it. This depends on the nature of the stone and the presence of moisture. Since the stone is a porous material, the condensation of moisture on it and within its pores is critical to its reactivity. This is an area, which although it has been studied in many of the laboratory simulation tests, still requires further study. Particularly with regards to defining "time of wetness".

The deterioration that affects stone, either by crust formation or by dissolution has been studied all over the world. However, much needs to be done in processing the data obtained as a function of the mineralogical composition of the stone, its porosity and pore size distribution, and the finish to which it has been subjected when introduced in the monument.

The present survey should also serve to give a general view of the field to professionals who are interested in the acid rain problem as well as background information for scientists who are planning to continue research in the field.

Acknowledgements

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ACIDIC DEPOSITION ON STONE LITERATURE REVIEW

Foreword

It is extremely difficult to determine how much of the deterioration observed on stones is due to "acid rain" since its action is not limited to one mechanism. Rather, it is the result of the interaction of various deterioration mechanisms, many of which also occur in natural weathering.

The present survey aims to give a historic overview of the most relevant publications in the field of acid precipitation on stone to help identify the relative importance of the various mechanisms contributing to the deterioration of this material. Its objective is to give a state of the art picture of the various branches within the field to allow a better understanding of the present knowledge of the field. It was not intended to be an exhaustive report on all published literature but should serve to give a general view of the field to professionals who are interested in the acid rain problem as well as background information for scientists who are planning to continue research in the field.

The report, which essentially summarizes the key points of the reviewed papers, is broadly divided into four chapters: dry deposition; wet deposition; deterioration mechanisms and site studies, including "case studies" of actual monuments. A fifth chapter highlights those areas where further research would appear to be most rewarding.

Dry deposition refers to the deposition of pollutants gases and particles in the absence of rain. ft can result from pollutant gases or from particulates falling and attaching themselves on the surface of the stone. The most important contribution to dry deposition is that of the gases and in general it is due to nearby polluting sources.

Wet deposition refers to the deposition of pollutants dissolved in moisture droplets and rain falling on to stone surfaces. Of these, rain is more efficient than moisture droplets in scavenging pollutants from the air. ft is the main contributor to wet deposition and long range transport of pollutants. Only in specific environmental conditions can the latter have a significant effect.

The deterioration mechanisms consider first how the nature of the stone itself affects acid deposition. Then the type of surface deterioration is discussed as well as that of the black crust formation. Finally, damage functions are discussed.

A good starting point for this review is the summary presented by Price (1996) in the section dealing with the effect of air pollution on stone. He emphasizes the fact that this problem has only recently received attention although it has long been with humanity. He also stresses that the highest effect on calcareous stones results from pollutants in their near environment. The complex influence that the resulting black crusts have on the enhancement of the acidic attack is mentioned and their growth mechanism succintly described. Finally the so-called *memory effect* of the stone, i.e., the influence of its past history on its present deterioration rate, is addressed.

Price's report groups the research conducted into three study areas: epidemiology, i.e., those based on monitoring and individual buildings; field studies, i.e., those that address exposure of new samples to current environment; and, laboratory simulation. He also discusses the derivation of damage functions which should serve to quantifying damages and benefits of pollution-control policies. In spite of differing details, they show that overall decay rate depends on the pollution levels, rainfall amount and its acidity. But there still is no consensus regarding a safe level for pollutants.

As Price indicated in his report "there has been very little effort to pull it all together and to produce a clear statement of findings to date". It is the aim of the present review to attempt this daunting task.

I. Dry Deposition

I.1 Introduction

Dry deposition, which is far more important than wet deposition for highly polluted areas [Furlan and Girardet, 1983a], results from the transfer of pollutant gases and/or particles, including aerosols, from the atmosphere to a surface in the absence of rain and are in general originated in nearby sources, and therefore called short range deposition [Torraca, 1988]. Gases are the most important contributors to dry deposition and their arrival at the surface in question is governed through molecular diffusion or atmospheric turbulence. Gases can react with both the surface of the stone or aerosol particles. Of these, larger particles (>10 pm in diameter) can fall onto the surface through gravity, smaller particles can reach it through atmospheric turbulence while Brownian movement is the most important motion for submicron particles (<0.1 pm). For the latter, the smaller the particle, the faster its deposition rate since the surface acts as a sink and retains the particles by Van der Waals forces. These processes are strongly affected if the particles and/or the surface in question carries an electrostatic charge or if condensation or evaporation processes are simultaneously operative [Camuffo et al, 1987].

The actual deposition process of gases and larger particles (which are the ones that deposit faster) occurs in the boundary layer over the surface and is influenced by the nature of the substrate, its surface conditions and its micro-environment. As is be expected, concentration of gases and of particles affect their rate of deposition. The deposition rate is enhanced by an increase in:

     (a) concentration of the pollutants;

     (b) turbulence of the air;

     (c) roughness and heterogeneity of the receiving surface;

     (d) chemical affinity of the surface for the pollutants;

     (e) moisture on the surface

The relevant concentration of the pollutants is that found in the immediate vicinity, i.e., within some centimeters, of the receiving surface depending on microclimatic conditions. This may be fairly different from that in the nearby atmosphere, at a distance of meters from the surfaces, which in turn changes with the time of day and the season in question.

I.2 Emissions and Sources

A good discussion of sources, sinks and abundance of the most important air pollutants relevant to the deterioration of stone can be found in Chapter 2 of the Amoroso and Fassina *(1983)* book. Apart from *CO2* a normal constituent of the atmosphere whose concentration has increased due to the burning of fossil fuels, the key components involved in the deterioration of stone are the oxides of nitrogen and sulfur. Most of the oxides of nitrogen, NO and NO_2, generally referred to as NON, are produced by combustion engines. In the industrial countries it corresponds to 70-80% of the total amount in the atmosphere [Fassina 1988a, 1991]. But also the resultant nitric acid (HNO_3) can be found in the gas phase [Livingston, 1985; Fassina, l988a]. A discussion of the chemistry of the troposphere and its influence in determining the resulting composition in particualr with regards to assessing the effects of anthropogenic emissions is presented by Ravishankara (1997).

Sulfur oxides result from the combustion of sulfur containing materials, and SO_2 is the key atmospheric pollutant. Data on the increase of emission of this gas over the past century, both from natural (volcanoes, sea spray and biogenic) and anthropogenic sources (combustion of coal, petroleum, ores) is given by Fassina (1991). The residence time of this compound in the atmosphere depends on several factors: its removal by dissolution in rain, its oxidation to 503 in the presence of nitrogen oxides or trace metals, its reaction with ammonia, or its adsorption on calcareous stones where it can be subsequently oxidized.

A more detailed review of the topic can be found in the first volume of the SOS/T reports published by NAPAP [Irving, 1991a]. The volume is divided into eight reports. The first one includes data on emissions of SO_2, NO_X and VOC (volatile organic compounds) which are considered the primary compounds involved in acidic deposition. Both natural and anthropogenic sources of the pollutants are addressed for the US and Canada. For the latter sources, electric utilities are the main contributors the release of SO_2, while both transportation and electric utilities release NO_X. The report also describes the development of anthropogenic emissions data bases and discusses the uncertainties associated with the emissions estimated and the approaches taken for estimating that uncertainty.

The characterization of particulates emitted from both oil-fired and coal-fired power plants as well as the stack gas composition was carried out [Cheng, 1982]. Coal-fired plants liberate more SO_2 and the emitted particulates are larger in size, tend to vary in size, and have relatively smooth surfaces. Particulates emitted from oil-fired plants then to have a spongy appearance, are smaller and more homogeneous in size.

Further and up to date information regarding the location of sources and emissions as well as acid deposition data can be obtained at the EPA data bases (http://www.epa.gov.air) and (http://www.epa.gov/acidrain/ETSadata.html) respectively.

The changes in air pollution with time have been studied extensively by Brimblecombe (1988, 1991a, 1991b) for the case of England, and London in particular [Brimblecombe 1987]. The awareness of changes in air quality can be traced to changes in fuel usage. The concentration of SO_2 and SO_4 in aerosols and in rainwater for several European cities is presented in the first mentioned reference. The improved air quality during the past century can be attributed to the dispersion of sources of air pollutants, thus diluting them. Legislation and improved control methods have also contributed to this end.

From historic records and analysis of the deterioration pattern on the Trajan column, Camuffo (1993) has tried to elucidate the climate and air pollution of Rome throughout the past 18 centuries, as well as the impact of clouds of volcanic aerosols and the formation of dry fog in Italy over the past seven centuries [Camuffo, 1992; Camuffo and Enzi, 1995].

Changes in air pollution, as reflected by the limitation of visibility due to the presence of smoke in Pittsburgh have been studied by Davidson (1979) from mid-nineteenth century to the present. The data presented is completed by the comparison of dustfall for this century and shows that due to the smoke control ordinance established in the late 40's. air pollution has decreased in that city.

Mathematical modeling has been used to relate sources and sinks of pollutants as well as theft regional transport and dispersion, as discussed in the first volume of the SOS/T reports published by NAPAP [Irving 199la]. These reports deal with long range transport, i.e., hundreds of km, of pollutants. Report 2 in this volume concludes that the key complexities in the modeling systems reside primarily in the vertical motion of the gases along their transport paths. This is further complicated by the presence of moisture which raises the possibility of wet deposition and/or chemical reactivity. ft also reviews the air chemistry in both gaseous and liquid phase, and discusses aerosols and particulates, precipitation scavenging and air-surface exchange.

Report 3 in this SOS/T volume presents an overview of the regional modeling methods in which the acid deposition at given receptor sites is related acidic precursor sources for a multistate geographic area. Three types of models are discussed: statistical, Eulerian and Lagrangian. The first type is recommended for screening purposes, the second for examination of control stategies and for providing further insight into the source-sink relation, and the third type is best applied situations where few isolated sources exist.

Report 4 in this same SOS/T volume discusses both the Eulerian regional acidic deposition model (RADM) and engineering models, based on the assumption that the sulfur chemistry can be treated separately. These latter systems can only model control strategies involving sulfur emission sources, without taking into account the effect of other gases such as NO_x and VOCs. The evaluation of the RADM is presented in Report *5*. Since the horizontal grid of the RADM has an 80-km resolution, it is not really appropriate for modeling detailed deposition on buildings.

The various models presented in the above mentioned reports are relevant for what may be called "regional climate" [Camuffo, 1997] over extended distances, and cannot be applied to a particular monument or sculpture since these will be affected primarily by the microclimate in theft immediate vicinity.

I.3 Aerodynamic and Meteorological Factors

A general discussion of the role of climatic factors for the distribution of gaseous and airborne particulates in Europe is presented by Camuffo (199lb). The latter do not contribute as much to the deterioration of stone as gases. The main polluting gases relevant to stone deterioration are SO_2 and NON. Their transport in the vicinity of the stone surface relies on random kinetic motion [Camuffo, 1997]. Under dry conditions, 502 and NO_2 deposition is low as proven in many studies [Gauri et al., 1973; Serra and Starace, 1978] and atmospheric turbulence will evidently increase this rate [Camuffo, 1997]. The gaseous molecules will also concentrate in moisture droplet& For the case of NO_2, lower concentrations are found due to the lower solubility of this gas but its complex dissolution/oxidation chemistry results in HNO_3 production which is dissolved faster. For the case of 502, since the absorption rate is pH dependent, the presence of atmospheric NH_3 will favor its absorption into the liquid phase [Fuzzi and Vittori, 1976]. In polluted areas the gaseous 502 deposition is more relevant than that of sulfate aerosols [Beilke and Gravenhorst, 1978]. The deposition of aerosols is less dependent on the nature of the stone than the deposition of 502, and is far less important [Furlan, 1991].

The properties of dry particle aerosols are summarized in Chapter 3 of the Amoroso and Fassina (1983) book. These range from clusters of a few molecules (? 10^{-3}µm to particles ($40 um The former have a relatively short lifetime because they tend to attach to larger particles, and so do those with a diameter larger than 40 µm because of increased sedimentation rates. Some may have an electric charge due to the inclusion of ions produced by ionizing radiation.

Those particles relevant to dry deposition are discussed by these authors in the following chapter 4 of their book, and range in size from 0.2 to 1.0 p.m in diameter. Brownian diffusion in the boundary layer is the predominant deposition process in the absence of air motion for submicron particles, If the surface is roughened, the deposition rate is increased. However, two other diffusion mechanisms can also operate. The first one is linked a temperature gradient which gives rise thermophoresis, i.e., the movement of the particle towards the colder surface. The second one is linked to a moisture gradient, and in this case, the condensation of moisture enhances the migration of particles towards the condensing surface, called the Stefan flow, while evaporation reverses the flow away from the surface.

In opposition to the thermophoretic effect, the Stefan flow operates on all particles, regardless of size. A discussion of these effects on different particle sizes is given by Hicks (1982) and Camuffo et al. (1987).

A thorough discussion of the mechanism of dry deposition of airborne particles, including gases, can be found in chapter 4 of Camuffo's book (1997). The discussion covers: (1) Brownian diffusion and deposition (main deposition mechanism for particles ranging between 0.00 1 and 0.01 µm (this includes the pollutant gases whose molecules have a diameter in the order of 0.005 µm); (2) thermophoresis and diffusiophoresis, sometimes merely limited to Stephan's flow, which will mainly affect particles between 0.1 and 1 pm; (3) gravitational settling, main deposition mechanism for particles above 2 pm in diameter; (4) electrophoresis and electrostatic deposition, which only increases significantly to deposition under low relative humidity conditions; and (5) aerodynamic deposition which is efficient for particles around 5 µm in diameter. The chapter concludes with discussions on surface adhesion, resuspension of particles and soiling due to microclimate and heating in closed environments.

A probabilistic model for particle deposition and bounceoff was developed by Wu et al. (1992b). The probabilistic model combines knowledge of turbulent bursts with the random properties of turbulent fluctuations. The model predictions for deposition velocities agree with experimental results when the dimensionless particle relaxation times t_p^+ larger than 2. For values of $t_p^+ > 10$ most particles delivered to the edge of a viscous sublayer are able to deposit on the surface, but at higher values the rate of turbulent delivery becomes the limiting factor.

Dry particle aerosols can contain calcium carbonate, *calcite,* which will contribute to an increase of SO_2 absorption and subsequent sulfur deposition on non calcareous stones. They can also contain calcium sulfate, *gypsum,* particles, generally in the 1-2 ?m size, generated from SO_2 deposition on calcareous stones or from wind erosion of exposed gypsum beds, as is the case in Italy [Amoroso and Fassina, 1983]. Aerosols containing hygroscopic salts, such ammonium sulfate, in areas with an ammonia enriched atmosphere; magnesium sulfate, in maritime areas, or sodium sulfate, generated from the combustion of lignin-sulfur compounds or some types of paper manufacture, can serve as condensation nucleus for droplets. The presence of these deliquescent salts will favor their adhesion to the stone surface.

The discussion of aerodynamic factors in dry deposition presented in Report 20 of the third volume of the NAPAP SOS/T reports [Irving l99lb] compares urban to rural areas. In the former, where there is a greater concentration of acidic gases and particles, closely spaced structures create "street canyons" and extra-urban pollutants carried by the air aloft will not be easily deposited. On the other hand, pollutants emitted within the canyons can remain for a long period of time before being removed, and their vertical concentration can vary five-fold. The surface resistance to deposition is considered to be the most important rate-

limiting factor in most cases. However, it is not easily measured and is usually calculated as the difference of the total resistance to deposition and the sum of the aerodynamic and boundary layer resistances. While the aerodynamic resistance to mass transfer is dominated by atmospheric turbulence and operates on meter-long scales, the boundary layer resistance is associated with the laminar boundary layer of an air flow along a surface. It depends on both the aerodynamics and the molecular diffurion properties of the pollutant in question.

The relative importance of aerodynamic, boundary layer and surface resistance is discussed by Wu et al. (1992a). Dry deposition measurements on symmetric airfoils with predictable boundary layer characteristics was carried out in conjunction to deposition on to a bronze equestrian statue in Gettysburg National Military Park and to potted plants at Claremont, CA. The following species were measured: SO_2 gas, and calcium-, lead-, sulfate- or nitrate-containing particulates. Four types of deposition surface materials were used: mylar film uncoated and coated with grease, Nylasorb filtes and paper filters impregnated with potassium carbonate. The latter constitutes a perfect sink surface for SO_2 gas and the overall dry deposition velocities measured are about the same for all locations on the statue. This is explaiend because the boundary layer resistance is smaller than the aerodynamic resistance for this gas due to its high diffusivity across the viscous layer. On the other hand, the boundary layer resistance for particulate sulfate is at least three times as large as the aerodynamic resistance. For ungreased surfaces, rebound of incoming particles and resuspension of deposited particles are both significant. The results from the study appear to indicate that the relative importance of aerodynamic, boundary layer and surface resistance can vary greatly. The latter resistance is highly variable and may often be the rate-limiting factor in the overall dry deposition.

A review of the sizes of particulates reported in the literature for the previous two decades is presented by Milford and Davidson (1985). They report that overall the indicidual distributions of many elements are surprisingly consistent, despite different sampling locations, times and method used. The latter are discussed with regards to the attached experimental error. From the analysis of the data they conclude that those elements with aerodynamic mass median diameter smaller than 2 µm generally have bimodal distributions, while elements with larger mass median diamter present a single peak, with realtively little mass below 1 µm. The paper discusses in particular the distribution of Al, Na and Pb.

An interesting study by Etyemezian et al. (1998) measured airborne concentration of sulfate particles, elemental carbon particles, SO_2 gas and total nitrates (particles and HNO_3 gas) at three different heights of the 42 story Cathedral of Learning in Pittsburgh, PA, for four weeks each season for a year. The results obtained indicate that there are no statistically significant vertical gradients for any of the pollutants which can be explianed by the fact that the pollutants are well mixed before they reach this Indiana limestone building and the lack of nearby buildings which might prevent vertical mixing (see section I.6.2 for further references to this paper).

I.4 Oxidation Mechanisms

There is no doubt that the main contribution to the deterioration of stone is due to sulfur pollutants, among which, as previously mentioned, SO_2 is the key pollutant. The question raised is how SO_2 interacts with the stone, i.e., whether sulfites are formed first and subsequently oxidized or whether sulfates are the only reaction products.

The oxidation of SO_2 can occur in a homogeneous process in the gas phase or heterogeneously in gas-liquid or gas-solid reaction [Amoroso and Fassina, 1983, chap. 6; Fassina, 1988a; Laurenzi Tabasso and Marabelli, 1992]. Of the several mechanisms that can oxidize 502 homogeneously in the gas phase, the most relevant is that involving free radicals in photochemical smog.

For gas-liquid reaction, the absorption of the gas is more rapid than the desorption reaction. Smaller droplets (< 100 µm diameter) have a higher absorption rate (less than 1 s) than larger ones, and the rate-determining step is the oxidation of the SO_2 [Beilke and Gravenhorst, 1978]. Several factors influence this oxidation rate: presence of one or more heavy metals that can act as catalysts and the pH of the droplet/solution which is in turn affected by the presence of alkaline gases such as ammonia. The oxidation of SO_2 to sulfuric acid in the troposhere is a multiphase reaction ocurring in droplets by oxidants such as H_2O_2 and O_3 [Ravishankara, 19971.

For the gas-solid reaction, two possibilities have been postulated. One corresponds to an initial adsorption of the SO_2 on the surface, neutralization to sulfite and subsequent oxidation to sulfate. It has been found that sulfite constitutes a significant fraction of the sulphur of aerosols with diameter in the 1 to 4 µm range [Amoroso and Fassina, 1983]. The second corresponds to the oxidation of the adsorbed SO_2 catalyzed by surface impurities and subsequent sulfation reaction. It has been found on the marble of the Acropolis monuments that around 90% of the surface deposit (formed in absence of water) was gypsum, the remainder being calcium sulfite dihydrate and calcite [Skoulikidis and Papakonstantinou-Ziotis, 1981]

The reaction of gaseous 502 with Carrara type marble (taken from the Cave Hll Cemetery in Lousiville, KY and so designated) has been studied by Gauri et al. [1973] by subjecting the stones to atmospheres containing different amounts of this gas. They found that the rate of deterioration is related linearly to the concentration of SO_2 and that the presence of moisture is crucial for the reaction, since the gas does not react under dry conditions. The reaction products identified under experimental conditions were calcium sulfite hemihydrate and dihydrate as well as some gypsum. The deterioration layer observed ranged in thicknesses between 8 to 10 µm Further studies [Gauri et al. 1982/83] on marbles (Alabama White, Green Mont Vermont, Italian Cremo and Georgia) and their ground powders of known particle size exposed to high concentrations (700-3000 ppm) of SO_2, as compared to typical atmospheric concentrations which range from 10 to 100 ppb SO_2, showed that the

$CaSO_3.1/2H_2O$ is always the initial reaction product under these conditions which, if humidity increases turns partially into gypsum. The reaction rate was found to be dependent on porosity and particle size of the powder, increasing with exposed surface area as would be expected. Studies with somewhat lower concentrations (5-10 ppm) of SO_2 or of NO_2 [Gauri and Gwinn 1982/1983, l982/1983a] again found that $CaSO_3.1/2H_2O$ is the initial product, confirming that SO_2 can react with calcareous stones directly under these conditions. The sulfite hemihydrate is stable unless moisture condenses on it, facilitating the oxidation to gypsum. For the case of NO_2 no nitrates or nitrites were found on the sample, the analysis being carried out by x-ray diffraction.

Further studies [Kulshreshtha, et al. 1989, Gauri et al. 1989] compared the rates of reaction for SO_2 gas with four different marbles: Carrara, Alabama, Georgia and Vermont. The concentration of gas ranged from 10 to 300 ppm and the flow rates from 680 cc/mm to 300 cc/mm, respectively, in an atmosphere equilibrated with liquid water at 20°C. The volumetric rate constant and the molar flux resistance proved to be different from marble to marble. However, when this data was complemented with the mass loss of reacted specimens through leaching in water, all the data could be fitted into a single set of equations, allowing to predict the weathering of marble in a large range of atmospheric SO_2 concentrations.

Studies carried out on travertine exposed to various concentrations of SO_2, ranging from 750 to 4000 ppm, confirmed that the reaction product is only $CaSO_3.1/2H_2O$, and that the reaction takes place in two stages [Götürk et al., 1993]. The first one corresponding to a first order reaction. Experiments at the lower 502 concentration and with varying RH, ranging from 0 to 100%, show that no reaction occurs in the absence of moisture, while at 100% RH mainly gypsum is formed with some sulfite hemihydrate remaining.

Most of the early studies were devoted to understanding the mechanism of the heterogeneous absorption reaction and oxidation of sulphur dioxide on calcium carbonate. Serra (1969) and Serra and Starace (1972, 1978) showed, through radiolabelling of 502 that oxidation proceeds at a fast rate when the gas is absorbed on the active sites of the calcium carbonate surface, the oxidation rate being positively increased by the amount of moisture present. After the absorption phase has been completed, oxidation rate of the sulphur dioxide decreases significantly. Under equal humidity, the amount of active sites on the surface affects the absorption rate.

The kinetics of the sulfation reaction of two kinds of marble, Carrara and Bohemian, radioactively labelled with [85]Kr and exposed to a continuous flow of l000ppm SO_2 at 70%RH was studied [Sramek, 1988]. The preferential accumulation of [34]S at higher oxidation states results in a higher concentration of this isotope in the deposited gypsum. The study found that Bohemian marble accumulated a higher ratio of [34]S/[32]S than Carrara marble, and only slightly less than the original ratio [34]S/[32]S in the SO_2 gas. The calculated rate constants were $9.1x10^{-2}$ and $4.9x10^{-2}$, respectively. Measurements of the sulfur isotope

ratio were also made on gypsum crust samples from different monuments in Prague. A higher ratio was found in the more polluted center of town, this being attributed to the probable sulfation of the stone via an intermediary sulfite due to the higher gaseous SO_2 concentration in the town center.

The presence of ammonia in the atmosphere increases significantly the oxidation efficiency of SO_2 due to increased solubilization of this gas, as discussed for the specific case of Venice by Fassina and Lazzarini (1979).

The oxidation of NO to nitric acid can proceed through homogenous oxidation with ozone, which appears to be the most effective process for NO_2 generation. While during day-time further oxidation is carried out by OH radicals, during night time, ozone continues the oxidation to an NO_3 radical. This reaction does not contribute significantly during day-time because of the photolytical destruction with NO. The NO_3 radical leads to the formation of HNO_3 gas. The overall formation of this gas proceeds at about the same rate for either mechanism [Fassina, 1988a]. It appears that the gas-phase production of nitric acid is the main source of aerosol nitrate [Hoffmann, 1986]. A discussion of the heterogeneous reaction of N_2O_5 to HNO_3 on ice crystals of cirrus clouds in the troposphere and the multiphase reactions involving NO_3 radical in the marine boundary layer in the presence of sea-salt aerosols is presented by Ravishankara [1997].

I.5 Measurement and Monitoring

One of the key point in the measurement of air pollutants is how this is made. As Livingston (1991) discusses, there are several approaches, such as rate of emission at the source, expressed in kg/hour or as air quality, averaging concentrations, in p. $\mu g/m^3$ or ppm_v, either per day or per year; or, as deposition rates. For this last case, the collection method is important and the times between collection, just as critical, given that deposition velocity is not constant [Livingston, 1997a].

Among the first systematic monitoring programs to be established is the NATO/CCMS [NATO, 1985] study based on the German developed IRMA (Immission Rate Measuring Apparatus) method [Luckat, 1976]. Immission rate is the uptake rate of a standardized area, an alkaline liquid surface was used for this study. The report discusses correlations between the immision rates, i.e., and the accumulation of pollutants (SO_X. Cl, F and NON) on stone slabs exposed in twenty five sites in Europe and one site in the USA. It also discusses the validity of the IRMA method which proved useful in areas with uniform climate, i.e., those without drastic changes in atmospheric conditions. The corrosion rate of the stone was also dependent on the flow dynamics over the stone surface and its nature and physical characteristics.

The US site for the NATO/CCMS study was the Bowling Green Custom House in New York City, where other monitoring equipment was also installed as described in Baer et al. (1982). Livingston (1991) presents a good discussion on the various methods of monitoring deposition rates, for both dry and wet deposition. For dry deposition, which is not as easy to measure as wet deposition, two main approaches have been used. The first, an indirect or inferential method, measures ambient air quality and calculates the deposition rate through an equation using an estimated mass transfer coefficient, this being the most difficult point in the procedure. The simplest approximation of this mass transfer coefficient is the so-called deposition velocity. The second approach is the direct method involving sampling the deposited material directly from the object or from test samples of the same material and located at the point of interest.

For sampling dry deposition on surfaces a special milling apparatus was developed [Queisser et al., 1988]. The sampling method proved to be reproducible, however, it will also remove a slight amount of the stone surface. The drilling device has an attachment capable of mearuring the energy required, which could be correlated to the cohesion of the material, Sampling with this method was compared to that of standard Leclerc filters for the determination of the rate of dry SO_2 deposition [Girardet and Furlan, 1982]. It was found that no simple factor can link the two, due to the differences in the nature of the "capturing" surface as discussed in the subsequent section 1.7.

The use of a denuder to measure the concentration of pollutants in the atmosphere has been developed by the Institute for Atmospheric Pollution of the CNR (Consiglio Nazionale delle Ricerche) Italy. The device gives accurate measurements but does not solve the problem of measuring deposition velocities [Camuffo, 1990].

Deposition monitoring and air quality measurments are also discussed in the last three reports of the first volume of the SOS/T reports published by NAPAP [Irving 1991a]. The methods for monitoring acidic deposition under its various forms: dry, droplet and wet deposition are discussed in the sixth report. Among the conclusions reached are that dry deposition of sulfur or of nitrogen compounds is approximately 0.3 to 0.6 of the sum of dry and wet deposition; that the most important sulfur compound involved is SO_2 while for nitrogen it is HNO_3.

The last two reports (7-8) deal with air quality measurements, for the first, and its relationship with atmospheric emissions and deposition, for the latter.

Complementary data on deposition monitoring can be found at the NADP website (http://nadp.nrel.colostate.edu/NADP/)

A transition flow reactor [Knapp et al., 1986; Delopoulou et al., 1991; Sikiotis et al., 1992] was used to determine the concentration of nitric acid and ammonia, as well as nitrates,

sulfates, chlorides and ammonium, sodium and potassium ions in particulate matter in the ambient air of Athens. These measurements were complemented with the evaluation of nitrates on the columns of the Parthenon as well as the measurement, by means of a specially designed reactor [Sikiotis et al., 1992; Delopoulou and Sikiotis, 1992] which included a filter pack and a chamber containing grains of Pentelic marble (their results are summarized in the following section 1.6)

I.6 Dry Deposition Factors and Rates

Livingston (1991) presents a good discussion on the various methods of estimating deposition rates, for both dry and wet deposition. Deposition rate is a function of stone "susceptibility" or "responsiveness" to the pollutant in question, i.e., the capability of a given stone surface to "capture" the pollutant in question, as briefly mentioned in the previous section [Girardet and Furlan, 1982]. This key topic has been further discussed by other researchers, as summarized by Livingston (1997a). Livingston also briefly and critically discusses the various laboratory approaches taken in trying to evaluate deposition velocity. One of the problems encountered when trying to compare laboratory studies is the wide range in concentrations used for the experiments. The reactions occurring under these conditions can be totally different and may bear no relation to the actual phenomena observed on monuments.

The topic of droplet formation and deposition is discussed in section 11.2 of Wet Deposition.

I.6.1 Laboratory Studies

A good discussion of the earlier studies dealing with deposition rates of SO_2 can be found in Braun and Wilson (1970) while Lipfert (1989a) presents a table summarizing the SO_2 deposition velocities measured in previous studies but without attempting to analyze the different methods/units used.

In laboratory studies these rates have been found to be dependent on the degree of the gas phase mixing used in static systems, or gas flow rates in dynamic systems, and increase with higher mixing or flow rates suggesting that the deposition velocities are limited by mass transport to the surface [Judeikis and Stewart, 1976]. The initial high deposition velocity decreases gradually on prolonged exposure to the reactive gas ultimately approaching zero. The velocity is also affected by the nature of the deposition surface (discussed in section 1.7 of this report).

The same effect was also observed for deposition velocities of NO_x [Judeikis and Wren, 1978] and an interesting difference in behaviour pointed out: while SO_2 was quantitatively converted to surface reaction products, this only occurred for NO_2 during the initial period of exposure after which gaseous NO formed. NO was found to have lower deposition rates than NO_2. They conclude that the removal of the reactive NO_x gases (NO + NO_2) by deposition on ground level surfaces in the environment occurs primarily through NO_2-surface interactions.

The condensation of moisture on a surface is an important phenomenon since it favours the deposition of both dry particles and droplets as well as facilitating the oxidation of SO_2. It should be remembered that a surface can provide the roughness or the presence of salts that can act as condensation nuclei. Therefore, the high supersaturation needed for droplets formation in the free atmosphere as stated by the Kelvin equation is not required [Camuffo et al., 1987].

The laboratory study by Johansson et al. (1988) shows that apart from humidity the presence of NO_2 may influence significantly the rate of SO_2 uptake. They postulate a first reversible adsorption step and as favourable adsorption sites are occupied the adsorption rate drops. At the same time, a slow reaction to produce $CaSO_3.2H_2O$ takes place. A steady-state rate of SO_2 deposition would correspond to the rate of conversion to sulfite. This corresponds with the findings of Gauri discussed in the previous section 1.4. When NO_2 is present, the oxidation of the adsorbed SO_2 results in the formation of sulfate (gypsum). The study also shows that NO_2 deposits on the surface though no crystalline component was found.

Simulations in an environmentally controlled exposure chamber were used to study the effect of NO and SO_2 (both around 300 ppm) at different humidities on finely crystalline limestone from quarries near Jerusalem [Peleg et al., 1989]. The study was complemented with field exposure tests (see next subsection I.6.2). From the study it appears that heterogenous oxidation of SO_2 is the most important path for the formation of gypsum, while the formation of $Ca(NO_3)_2$ is unaffected by changes in RH but decreases in absence of UV light. The presence of hydrocarbons appear to be important for the oxidation of NO.

The research carried out on monuments by Furlan and Girardet (see next subsection 1.6.2), was complemented using an atmospheric simulation chamber [Ausset et al., 1996; Girardet et al., 1996] to study Jaumont limestone and Berne molasse, two stones that been previously used in outdoors exposure tests [Furlan and Girardet, 1988]. The stone samples were exposed "naked" and covered with either fly ash or soot particles. It was found that after 1 year of chamber exposure in real-life conditions (125 ppb SO_2, 50 ppb NO_2 at 79% RH and 13°C) the results obtained are comparable to those observed in site tests. Only a slightly higher SO_2 deposition rate was observed for the Jaumont limestone (10.0 $g/m^2.y$) than for the Berne molasse (8.3 $g/m^2.y$). The presence of fly-ash appeared to increase the SO_2 deposition velocity for the Jaumont stone after the first half-year, but not that for the Berne molasse.

Soot particles appeared to protect the surface from sulphur deposition. The sulphur penetrates into the stone to a depth of about 0.8mm.

Further laboratory studies with a simulation chamber [Girardet and Furlan, 1996] confirmed that the reactivity of stones to SO_2 can be strongly influenced both by the relative humidity, as already noted, and by temperature. The study used five different stones, Berne and Villarlod molasses, Jaumont and Beaune limestones, and Carrara marble exposed to 75 ppb of SO_2 at different RHs and temperatures (-10°C to 25°C). It was found that for the marble and the less porous limestone (pink Beaune) no noticeable SO_2 uptake is found at lower RH, the threshold for marble being higher than for the limestone. The other stones show high reactivity even at low humidity and decreasing temperatures. The deposition values calculated from the measured flow of sulfur on these stones in situ ranged from 0.11 cm/s for the Beaune limestone to 0.26 cm/s for the Berne molasse. Comparing these values to the laboratory uptake curves at in situ RH and temperature conditions it was found that the were within the range confirming that these simulation tests reproduce actual conditions. The reactivity of the stones to SO_2 has been found to be a varying function of RH. While Carrara marble has an exponential function Berne molasse has a linear dependence. The Jaumont limestone and the Berne molasse were used in another chamber experiment [Girardet et al., 1996].

Another climate chamber study tested Pentelic and Carrara marble, Vicenza limestone and Pietra Serena (a calcareous sandstone), which were also used in a field exposure test (see next section) and other stones, e.g., granites, monzonites, soapstones, and materials, e.g., calcareous renderings and glass [Henriksen, 1994]. The test was carried out with a mixture of SO_2 and NO_2, both in the concentration range of 350-450 $\mu g/m^3$ The deposition velocities measured ranged from around 1 mm/s for the calcareous renderings and Vicenza limestone, through 0.6 mm/s for the Pentelic and Carrara marbles and 0.4 mm/s for red and grey granites, to 0.3-0.2 mm/s for monzonites. No deposition velocity could be measured for the sodium glass. A linear relationship was determined between deposition velocity and RH.

A laboratory study was conducted to quantify the dry SO_2 deposition on Indiana limestone (Salem limestone) and Vermont marble (Shelburne marble) in relationship to relative humidity and surface moisture [Spiker et al., 1992; Spiker et al., 1995]. It was found that the surface resistance to SO_2 deposition appears to be an exponential function of RH and the rate of SO_2 deposition is controlled by the amount of water adsorbed on the surface. Deposition of SO_2 on limestone is larger and more susceptible to the RH than marble, reflecting the influence of porosity and roughness.

Desorption of deposited SO_2 was followed with TPD, temperature-programmed desorption on Polish Pinczów limestone [Ceckiewicz and Kozlowski, 1989/90/91]. The method differentiates between $CaSO_3.1/2 H_20$ and $CaSO_4.2H_2O$ allowing to follow the reaction under dry or wet conditions. The effect of water repellents or silica gel sols was shown to reduce the attack of SO_2.

The reaction of dolomite with SO_2 was studied by Tambe et al. (1994) by exposing dolomite rock slabs to atmospheres containing SO_2 ranging in concentration from 8 to 21 ppm SO_2. The exposed samples developed a nearly impermeable crust of gypsum and epsomite. However, porosimetric data showed that after removal of the crust, the stone had increased porosity. The deterioration pattern, hard crust, underlying "cavernous" area and sound stone, is similar to that described by Domaslowski (1982) and found on Austrian calcarenites [Charola and Koestler 1985/86] as discussed in section III.2.

Another laboratory study on the interaction of SO_2 with a Spanish dolomite (Laspa) was carried out in an Atmospheric Flow Chamber [Grossi et al., 1994]. The chamber, while exposing the stone to a 2.5 ppm SO_2, allowed for half of the samples to remain dry while others were exposed to artificial rain. The amount of sulfate deposited onto a dry surface appeared to be proportional to its specific surface area, but no deterioration was observed. The deposition of SO_2 was significantly enhanced by the wet surface, and in this case, much gypsum was formed. The highly soluble magnesium sulfates were only found in the run-off water.

Climatic chamber studies in which an air flow (0.5 m^3/h) with 10 ppm SO_2 was circulated over granite (Figueiras) tests samples joined with mortar [Rivas et al., 19971. Some samples were kept dry while other were kept damp through water wicking. It was found that dry deposition of SO_2 can lead to the formation of gypsum and thenardite, the process accelerated in the wet samples.

Böke et al. (1996a) studied the effect of different particles, such as clay, activated carbon, metal oxides and chlorides, on the sulphation of calcium carbonate powder. The reaction chamber used a flowing atmosphere with a concentration of 3500 ppm SO_2 at 85%RH. The various types of clays added, at 1% concentration, did not appear to change the total amount of sulphur reacted, though slight differences in the amounts of calcium sulfite hemihydrate (main reaction product) and gypsum, were noted. For activated carbon, the relative amount of gypsum formed increased, although still less than the sulfite formed. When *0.5%* metal oxides (MnO_2, V_2O_5) were added, complete sulphation was achieved (an increase of 20% reaction) with gypsum the only reaction product. For other metals oxides (TiO_2, NiO, Fe_2O_3, SiO_2) no differences were observed with regards to the control. For the case of metal chlorides-also added at 0.5%, $MnCl_2$, $CuCl_2$ and $CoCl_2$, increased the sulphation by 10%, and gypsum was the only product. However, with lower concentrations, 0.1% and 0.05%, calcium sulfite hemydrate was also found with the gypsum. Iron, nickel and sodium chlorides increased the sulphation, with calcium sulfite hemihydrate the main product, and some gypsum present, whereas practically no gypsum formed on the control.

A similar experimental setup was used to test the effect of surfactants-cationic, anionic and non-ionic-, on the sulfur uptake of calcium carbonate powder [Böke et al., 1996b]. A flowing atmosphere with 1000 ppm SO_2 was passed over the samples at *85%* RH. The main

reaction product was calcium sulfite. At the higher surfactant concentration (1.5%) all of them decreased the total sulfur deposition (as sulfite) by about 40%. At the lower concentration (0.5%) only the anionic type (sodium oleate) proved effective decreasing the amount of sulfur deposit (sulfite) by 60%. The surfactants did not have any effect on the oxidation of the sulfite hemihydrate formed.

Sikiotis et al. (1992) and Delopoulou and Sikiotis (1992) used a specially designed reactor (sampling train) holding Pentelic marble grains to which a filter pack could be added to filter out all particulates so as to determine the effect of pollutant gases alone or pollutant gases and particulates. They found that altough the SO_2 concentration was much higher than that of particulate sulfates, the sulfation of marble by the SO_2 gas is one order of magnitude less than that by particulate sulfates. They also claim that the NO_3 found on the marble is $Ca(NO_3)_2$ and that this salt is produced either by the reaction of the marble with nitrous acid and its subsequent oxidation to nitrate, or by oxidation of adsorbed HNO_2 to HNO_3 and subsequent reaction with the marble. The amount of $Ca(NO_3)_2$ found when the reactor operated without the filter pack was three times as much as when it operated with the filter pack. These unexpected results, in which sulfation rate is larger for sulfate containing particulates than for SO_2, even when this gas is at higher concentrations, might be explained by the experimental design in which the air is forced to flow through a bed of marble chips.

Experiments with a parallel plate denuder [De Santis et al., 1994] were designed to study the heteogeneous reaction of Thassos marble with SO_2 by itself and mixed with NO_2. By measuring the inlet and outlet concentrations of SO_2 at different RH and with or without the presence of NO_2, it was possible to relate the decrease in concentration with a surface removal constant K and the deposition velocity. The presence of NO_2 enhances the deposition at 90% RH, but does not affect it for lower RH (50%). The values obtained in these experiments would apply to the maximum rates of dry deposition.

Another experiment [Sikiotis and Kirkitsos, 1994] was based on passing gaseous HNO_3 over the reactor in which a known amount of ground stone, with three different particle sizes in the ranges 0.2-0.5mm; 0.5-1.0mm and 1.0-2.0mm, was held. Three different stones were tested: Pentelic marble, Portland limestone and Baumberger sandstone. Plots of the retention of HNO_3 vs RH, mass of grains, diamater of the grains, concentration of the acid and flow rate are presented. The results show that above 50% RH there is practically total retention, although the level of HNO_3 used was at least an order of magnitude higher than that occurring in polluted atmosphere (approximately 54 $\mu g/m^3$) below that relative humidity, each stone differs in the absorption. For the case of the Pentelic marble, the retention of the two larger ranges of particle diameter is significantly less than for the smaller range. For Portland limestone, the lowest value was obtained with the larger particles, then the middle one and the highest was for the smallest size. For the Baumberger sandstone, the larger size gave the highest absorption while the middle and smaller particle range gave lower absorption. This has been attributed to the heterogeneity of the stone.

An atmospheric flow chamber was used to evaluate the dry deposition of SO_2, NO_2, and NO (with and without 03 as an oxidant) on to different stones [Johnson et al. 1991]. The experiment was carried out on samples of Leinster granite, Massangis Jaune, Portland limestone, Mansfield dolomitic sandstone and Pentelic marble, at room temperature and 85%RH, with gaseous presentation rates ranging from $l.6x10^{-2}$ µg/cm^2.s for SO_2 to $0.75x10^{-2}$ µg/cm^2.s for NO. It included wetting some of the stones with drips of demineralized water. Except for Pentelic marble, weight increases were recorded for all stones under dry conditions. When drip wetted, increases were only observed for the SO_2 containing mixtures (except when mixed with NO) for the limestones and the sandstone. The drip water produced erosion channels which were deeper for Pentelic marble. The study was complemented with wet deposition in a spray cabinet and this is discussed in section. 11.3. Stones that had not been wetted showed a weight increase which varied with the type of stone. Mansfield dolomitic marble gave the maximum weight increase which in turn depended on the mixture of gases used. NO or NO_2 gave the smallest increase while the largest increase corresponded to a mixture of NO or NO_2 + SO_2 and O_3. With water dripping, only limestones and sandstone showed weight increase. Pentelic marble showed weight decrease for all conditions. This was related to differences in porosity, 0.3% for Pentelic marble to 15% for the limestones and the sandstone.

Deposition velocities of NO, NO_2, HNO_2 and HNO_3 as well as PAN on the calcareous Ihrlersteiner sandstone [Behlen et al, 1996] were measured in a chamber at 80% RH. Concentrations of these gases ranged from 264 ppb for HNO_2 to 174 ppb for HNO_3 and 32 ppb for PAN with flow rates ranging from 2.0 1/mm for NO_2 to 1.4 1/mm for HNO_2 to 2.1 l/min for PAN. After an initial phase the pollutant uptake by the stones becomes constant and the deposition velocity can be calculated from the difference in chamber entrance to exit concentrations. These range from 1.8 cm/s for HNO_3 to under 0.001cm/s for NO and 0.006cm/s for PAN. Nitric acid and NO_2 are the main gases responsible for the formation of nitrates on sandstones. The pollutant uptake is determined by the deposition velocity, the atmospheric concentrations and the duration of exposition.

The resistance of protective coatings on calcareous materials was checked in a climatic chamber [Cimitàn et al., 1994]. The study, which reports the progressive sulphation of calcium carbonate powder with time of exposure (at 98% RH and 10 ppm SO_2), found that the initial reaction rate was slow, it then increased reaching after about 20 days an almost constant value. This is interpreted as a reaction barrier and the possibility of protecting the surface is postulated in terms of inhibitors containing electron acceptor or donor groups which could interfere with the adsorption process. First, powder samples were treated with either lead acetate, thiourea or p-nitroaniline. The final conversion rates observed were 0.28%CaSO$_4$/d, 0.23%CaSO$_4$/d and 0.07%CaSO$_4$/d, respectively while for the pure CaCO$_3$ control the rate was 0.07%CaSO$_4$/d. The actual measurements were of total S held by the surface. Then mortar disks were prepared to hold the calcium carbonate powder and for some samples a water repellent (Rhodorsil RP 224) was added during the mixing. Other samples were brushed on the set surface with p-nitroaniline by itself or followed by brushing

with the water repellent. The best result was obtained from the .p-nitroaniline treated sample. The water-repellent appears to enhance the absorption of SO_2 and samples prepared by inclusion of the water-repellent were the worst The growth of gypsum was followed by SEM examination.

The deposition of SO_2 or NO_x has been shown to be very dependent on both the nature of the stone and the moisture present. The type of porosity in the stone will affect the moisture uptake of the stone itself and hence influence the deposition of the gaseous pollutants {Johnson et al., 1991].

I.6.2 In-Situ Studies

The issues dealing with deposition processes are discussed in Volume III of the SOS/T reports prepared by NAPAP [Irving 1991b]. In Section 2 of the SOS/T 20 Report, the dry deposition processes at various scale levels, such as urban, micro-urban and structural, are discussed. Material-specific considerations are also considered.

The discussion of dry deposition processes at urban scale addresses the different resistances encountered, such as aerodynamic, boundary layer and surface; the aerodynamic and the meteorological factors, and, the modeling methods used for urban areas. The urban microscale deposition evaluation deals with the microscale aerodynamic, roughness and meteorological factors, while that at structural scale discusses the aerodynamics of building surfaces, microclimate factors, particle deposition and their measurement.

The material-specific considerations affecting deposition take into account the surface resistance, moisture, chemistry and physical characteristics, as well as the effect of biological colonization.

The report considers that deposition processes at urban and urban micro-scale are fairly well understood allowing the application of numerical models which take into account the major controlling factors: concentration, turbulence, energy balance, and, to a lesser extent, moisture regimes. The meteorological and pollutant concentration measurements required for these models are routinely made. However, spatial and temporal resolution is lacking. Deposition at a structural scale is still mainly descriptive.

With regards to the sulfur dioxide fluxes to buildings and structures, the presence of edges and corners will increase turbulence and exposure to pollutants, although protecting portions of the surface in some cases. The presence of projections and carved ornaments tends to increase turbulent transfer, increasing the extremes of temperature and moisture ranges, both above and below the projection, while shading the latter from solar radiation and incident

precipitation. The presence of surface moisture enhances the deposition of SO_2 to all materials. An increase of surface roughness or colonization by biological growth also enhances deposition.

In an site exposure study by Peleg et al. (1989) the concentration of SO_2 and NO_x in Jerusalem were measured at 10 m above street level (0.005 and 0.025 ppm, respectively) and found to be about four times lower than at street level. The study, complementing a laboratory accelerated ageing tests described in the previous subsection I.6.1, found that the concentration of gypsum on the actual walls, even in areas exposed to direct washout, was much higher than could be extrapolated from the simulation tests. The level of nitrates found on the wall, lower than that of gypsum by a factor of about five, is less than expected and can be explained by its greater solubility. The authors conclude that the damage to stones can not be linearly accelerated by increasing the concentration of pollutants.

The deposition of "dry" sulfur was measured on samples of a calcareous sandstone, Villarlod blue molasse, exposed in various protected areas [Furlan and Girardet, 1983b, 1983c]. It was found that amount of sulfur deposited in urban areas approximately doubled that found in rural areas, 1.6 to 0.8 $gS/m^2.y$, respectively. They also confirmed that the flux of "dry" sulfur was far more important than the flux of "humid" sulfur. This research was continued for the case of the molasse d'Ostermundigen, another calcareous sandstone, measuring the deposit on buildings of known construction date, ranging from 1869 to 1925 [Furlan and Girardet, 1988]. For comparison, the current deposition rate was measured on samples of the same stone. For great urban centers, such as Zurich, no modifications appear to have occurred in the past 60 years, while other centers such as Geneva and St.Gall, significant increases have occurred, while in other centers, such as Lausanne, the current deposition rate is only slightly above the mean of the past 80 years. Further studies [Furman and Girardet, 1992] obtained deposition velocities for dry sulfur flux in Lausanne ranging from 0.26 cm/s for the Berne molasse to 0.11 cm/s for the Beaune pink limestone (see references to these authors in next section 1.7). Studies on molasse de Berne [Connor and Girardet, 1992] confirmed that this stone is particularly susceptible to deterioration by gypsum originating from oxidation of gaseous SO_2 rather than from deposition of aerosol sulfates.

The field test study described by Henriksen (1994) compared sulfur deposition on four stones (Carrara and Pentelic marble, Vicenza limestone and Pietra Serena, a calcareous sandstone) set in two exposure sites, Oslo and Borregaard. The first is an urban site with an annual mean concentration of 6.4 $\mu g/m^3$ of SO_2 and 51.9 $\mu g/m^3$ of NO_2. The second is an industrial site in which Cl_2 is also an important pollutant. The annual mean concentrations for the gases were of 28.3 $\mu g/m^3$ for SO_2 and 17.4 $\mu g/m^3$ for NO_2. The surface of the samples was milled with a special device and the depth of sulfur penetration determined. It was seen that for both sites most of the deposit was to be found in the first 300 μm. The deposition velocities calculated ranged from 6 mm/s for Vicenza limestone to around 2 mm/s for Pietra Serena with both marbles at around 2.6 mm/s in Oslo. In the more polluted Borregaard, the calculated deposition velocities ranged from 11 mm/s for Vicenza limestone to 7 mm/s for

both the Pentelic marble and the Pietra Serena, while it was only 4.4 mm/s for the Carrara marble. These results were compared to the previously described chamber studies and are discussed in the following section 1.7.

Samples of Saltrio stone, a marly dolomitic limestone, were exposed in Milan, near the Politecnico, a polluted urban area, for nearly three years. Exposure times were divided into five long periods, separating hot months from the cold ones characterized by high pollution values. The main decay product was gypsum and it was found that this stone was less resistant than Carrara marble. Correlations between the measured dry deposition and the expected values calculated from deposition on the sampler are made and were observed to increase linearly [Realini et al., 1997].

In samples exposed at Aachen [Wittenburg and Dannecker, 1992] dry deposition velocities for SO_2 ranged from 0.09 cm/s for Brazilian soapstone to 1.76 cm/s for a calcareous sandstone (Ihrlerstein).

A short discussion of the problem is presented in Chapter 6 of the Buildings Effects Review Group Report (1989) which reviews studies on SO_2 and NO_x deposition. For the former, the review concludes that aerodynamic resistance is the principal factor governing its deposition, but under lower humidities the surface resistance increases significantly. This last factor has not been studied as thoroughly. The case of NO_x is even less well understood, particularly in urban areas. The report concludes that there are still significant uncertainties in the understanding and specification of the turbulent transfer of pollutants to urban surfaces which limit the accuracy of calculations of deposition building and material surfaces.

The concentration of airborne pollutants, sulfate particles, SO_2 gas and total nitrates (particles and HNO_3 gas) was measured by Etyemezian et al. (1998) using multistage Teflon filterpacks placed at three heights, fifth and sixteenth floor and the roof, on the Cathedral of Learning in Pittsburgh, PA. The desing of the filterpacks maintained a flow of 1 liter/min. No significant difference was observed in the concentration. The deposition flux of SO_2 was measured only on the two floors mentioned by means of cellulose filters impregnated with K_2CO_3. They ranged from 0.6-1.0 cm/s, the average deposition for the higher floor being 0.85 ± 0.13 cm/s and 0.69 ± 0.07 cm/s for the lower floor. Part of the difference was attributed to differences in exposition site, since more exposed areas on the 5th floor also gave systematically higher results during the year-long study. The deposition velocities measured appear to be constant throughout the year.

I.7 Effect of the Stone Nature on Dry Deposition Rates

The uptake of SO_2 by any surface is strongly influenced by the ambient humidity. Early studies measured the uptake for limestone and attributed the differences observed between the stone's matrix and the surrounded fossils to differences in their physical characteristics [Spedding, 1969a]. Spedding (1969b) also evaluated the absorption of isotope labelled SO_2 on various materials found in the laboratory such as concrete, painted surfaces, corroded iron, plastic and paper. The results obtained for concrete and mortar confirm the previous data published by Gilardi (1965) for various construction materials: clay brick, mortar, sandstone, marble and granite.

In an interesting study Braun and Wilson (1970) discuss the deposition of SO_2 on weathered surfaces and fresh surfaces of weathered limestones and found no difference in the deposition rate (about 3 mg/m^3.h) for SO_2 concentrations of 1.0 mg/m^3 (— 0.4 ppm). For higher concentrations of SO_2, ranging from 3-5 mg/m^3, the rate deposition increased a tenfold (from 1.6 mg/m^3.h to 15 mg/m^3.h) suggesting that for outdoors conditions the limiting factor is the diffusion rate of SO_2 from the air to the surface.

Judeikis and Steward (1976) report a laboratory study which determined deposition velocity of gaseous SO_2 on materials such as cured cement, stucco, adobe clay soil, sandy loam soil and asphalt, under turbulent atmospheric conditions so that the velocity was only limited by adsorption and chemical processes. The rates ranged from 0.04 cm/s for asphalt to 2.4 cm/s for cured commercial cement formulation. Judeikis and Wren (1978) also studied the deposition of NO_x on the same soils and cured cement. The values measured ranged from 0.21 cm/s (NO) and 0.32 cm/s (NO_2) for cured cement to 0.19 cm/s and 0.60 cm/s respectively, for sandy loam soil. An interesting result is that the deposition rate for NO_x gases is apparently relatively independent of oxygen concentration and relative humidity.

The nature of the surface plays a key role in the deposition of gases and particles. A study by Degranges et al. (1978) describes the different behaviour of three types of calcareous stones, ranging from a marble to a tufa, with regards their absorption of SO_2 gas as studied by chromatographic techniques. While the marble does not absorb any significant amount, a limestone shows some absorption when first exposed the gas and the tufa has totally different behaviour absorbing a large amount of SO_2. In this last case, it could be demonstrated that sorption occurrs at two different surface energy levels.

The NATO/CCMS study [NATO, 1985] observed that the Baumberg sandstone, which has a calcareous binder, absorbed twice as much SOx than the Krensheim Muschelkalk, a relatively pure limestone. This was attributed to porosity and pore structure differences which, as measured by BET, resulted to be 9.6m^2/g and 0.3m^2/g, respectively.

The dry deposition on four types of stone was studied by Furlan and Girardet (1988). The stones were: a Swiss calcareous sandstone (Molasse Villarlod), two French limestones

(Pouilleney and the more porous Jaumont, Metz) and Italian Carrara marble. These test stones were located in various cities and sites in Europe and Washington, DC. and sampled after one year. The amount of "dry sulfur" varied significantly between the stones and increased from the marble to the limestone-with increasing porosity-to the calcareous sandstone which was the most affected. However, the deposition on the marble appeared to be different in comparison to that of the other three stones. The deposition of the "dry" sulfur is superficial and does not penetrate into the stone. Further studies [Furlan and Girardet, 1992] evaluated the flux of dry deposition of sulphur on different stones ranging from siliceous ones, like gneiss and sandstones to calcareous sandstones, limestones and marble. It was found that the order of reactivity increased from the siliceous stones, through the marble and limestone, while the calcareous sandstone (molasse de Berne) was the most reactive. Good correlations between the dry deposition of sulphur on the stone and the concentration of SO_2 in the atmosphere was obtained. The velocity of sulphur deposition ranged from 0.26 cm/s for the molasse to 0.11cm/s for the Beaune pink limestone. The authors [Furlan and Girardet, 1993] point out that for a stone like the molasse de Berne, deterioration appears when sulfur deposits reach $25g/m^2$.

Another study [Wittenburg and Dannecker, 1992] exposed four different sandstones-a very porous sandstone (Herzogenrath), a quartzitic sandstone with siliceous cement (Ober-kichner), a clay rich sandstone (Sander) and a calcareous sandstone (Ihlersteiner)-and a Brazilian soapstone for a month in a rain protected environment at the Cathedral in Aachen. The dry deposition velocities for SO_2 measured range from 0.09cm/s for the soapstone to 1.76cm/s for the calcareous sandstone. The different deposition velocities reflect the effect of the stone nature on this phenomenon.

A study with both chamber experiments and in-situ analysis used isotope measurements to determine the origin of the sulfur in the gypsum layers [Torfs et al. 1997a]. Chamber experiments were carried out to evaluate the S-isotope fractionation for SO_2 deposition on to glass fiber filters impregnated with K_2CO_3, or three different limestones: Balegem (40-60% calcite with quartz), Gobertange (70-90% calcite with quartz) and Massangis (>90% calcite). All three stones have a porosity of about 10%. The chamber was kept at 76%RH and used a $6x10^6 \mu gSO_2/m^3$ (≈ 3000 ppm). The field tests involved sampling existing crusts on monuments in Antwerp, Belgium, constructed from the above stones, and sampling the atmospheric SO_2 near them as well as gases released form the most important anthropogenic emitters, such as fuel-oil heating of houses, industrial fumes and vehicular diesel-oil exhaust fumes. Relatively large variations of the $^{34}S/^{32}S$ ratio have been found in the gypsum crusts on monuments depending on the location, i.e., town center, suburbs or surrounding areas, with higher ^{34}S being encountered in the center of town. The isotopic composition of crusts coincides geographically with that in the atmosthere, the crusts being generally "heavier" than the sorrounding atmosphere. This was also observed in the chamber experiments and attributed to the fact that the equilibrium between the isotopes and the two chemical species, SO_2 gas and HSO_3 dissolved in the water film is displace towards an enrichment of ^{34}S in the water soluble species.

A laboratory study [Johansson et al., 1988] compared the behaviour of a limestone (red from Kinnekulle, Sweden), Carrara marble and Roman travertine. The study first measured the amount of moisture absorbed by these three stones when exposed to an approximately 95% RH environment. The values were 0.5%, 0.003% and 0.03% respectively. The samples were then exposed to different concentrations of pollutants (1.6ppm SO_2, 3.1ppm NO_2 and a mixture of 1.6ppm SO_2 + 3.1ppm NO_2) at 90%RH and 22°C and the weight increases measured. The results show that the weight increase for limestone and travertine is similar for equal exposure times for the case of the mixture of SO_2 + NO_2. However, when SO_2 is by itself, a smaller weight increase was noted, especially for the marble and the travertine. No significant weight increase was observed for any of the materials with 1402 by itself Analysis of the surfaces by XRD showed that in the presence of SO_2 alone, $CaSO_3.2H_2O$ was formed on all materials, but for the case of the limestone a minor amount of gypsum was also present. Upon exposure to the mixture of gases, gypsum was found on all materials without any trace of the sulfite salt. No crystalline corrosion product was detected on any of the surfaces after exposure to NO_2 by itself, but in the leachates, the presence of both nitrites and nitrates was confirmed on all exposed surfaces.

Results from field tests and climate chamber tests (see previous sections I.6.1 and I.6.2) were compared for four different stones: Pentelic and Carrara marble, Vicenza limestone and Pietra Serena (a calcareous sandstone) [Henriksen, 1994]. The significant difference in the deposition velocities measured in the chamber experiments and those calculated from the field data were attributed to fluctuating conditions in the latter, particularly with respect the amount of foggy days during autumn. It is of interest that while the Vicenza limestone always showed the highest deposition velocity, that for Pietra Serena varied significantly. The deposition velocity for Pentelic marble appears to be more related to the concentration of pollutant which is not the case for the Carrara marble, confirming the results obtained by Furlan and Girardet (1988) discussed above.

The effect of nitrogen oxides in the deterioration of stone has been addressed by Livingston (1985) who compiled the information of all studies reporting the presence of nitrates in the deterioration products of calcareous stones. From the analysis of the reviewed data the conclusion reached is that the effect of these nitrogen oxides appears to be minor compared with that of SO_2. In another paper he brings together conclusions from various studies relating to the different reactivity of stones to sulfur dioxide [Livingston, 1988]. The influence of the mechanical resistance to weathering, the textural factor, differences in mineralogy, particle size and porosity are discussed.

Following confirmation of the presence of nitrates on the Parthenon columns, particularly during the dry season, laboratory studies of the effect of gaseous nitric acid on different stones, such as Pentelic marble, Portland limestone and Baumberger sandstoned [Kirkitsos and Sikiotis, 1995] have shown that these act as good sinks. The more porous stones, i.e., limestone and sandstone, deteriorate to a similar extent at any given relative humidity, while the marble is increasingly vulnerable with higher relative humidities (>50% RH).

I.8 Thy Deposition Modeling

One of the first models suggested for the heterogeneous reaction between SO_2 and calcium carbonate was presented by Vittori and Fuzzi (1975) and Breccia et al. (1975). The influence of calcium carbonate dissolution in the moisture droplets (buffering the pH and thus icreasing the absorption of SO_2 into the liquid system) and the catalytic effect of atmospheric particles deposited on the surface on the oxidation of SO_2 was demonstrated. Studies by Sikiotis et a!. (1979) and Fassina et al. (1979) confirmed the influence of atmospheric particles in the catalytic oxidation of SO_2, particularly iron oxides.

An explanation of the deterioration of calcareous stones was proposed by Gauri and Gwinn (1982/1983) based on their laboratory studies. They consider that the initial reaction product of SO_2 with the calcareous stone is $CaSO_3 . 1/2H_2O$ which then oxidizes to gypsum forming an impermeable crust. This crust is considered the main cause for deterioration of the stone. This research was continued by working out a mathematical model for the kinetics of the reaction between SO_2 and $CaCO_3$ in marble [Gwinn and Popli, 1982] that would fit the experimental data observed, where $CaCO_3$ reacts form $CaSO_3 . 1/2H_2O$ as confirmed by x-ray diffraction The reaction rate was initially linear, followed by a diffusion controlled rate. The amount of conversion was governed in most cases by the grain size of the marble. From calculations with the equation proposed the depth reached by the reaction was of less than 10gm, in good agreement with optical microscopy data and XRF and XRD data [Gauri et al., 1973]. Further studies by Gauri et al. [1988] carried out on Georgia marble exposed to 10 ppm SO_2 atmosphere at 100% RH confirm that the sulfated crust grows outwards of the marble surfcae through migration of calcium ions from the interior which react at the surface with the gas thus leaving a more porous layer of stone immediately below the surface, following the pattern described by Domaslowki [1982].

The NATO/CCMS study established the statistical correlation functions between the pollutant deposited and immissions measured with the IRMA apparatus [Luckat, 1976]. An power law function ($y = a.x^b$ where y is the amount deposited, a is a correlation coefficient, x is the measured immission, and b is a factor that varied between 0.6 to 0.8) was found to fit well for SOx deposition on Baumberger sandstone (with a correlation factor of around 0.83), while for the Krensheim Muschelkalk limestone, a linear function ($y = a + bx$) was found to fit better (correlation factor 0.60). No correlations could be drawn for other pollutants.

The review study by Livingston (1985) on the influence of NOx on the deterioration of calcareous stones suggests that no simple relation can be established for the rate of deposition of these oxides and that perhaps a better correlation could be obtained on the basis of the concentration of nitric acid in the atmosphere and the deposited nitrates.

The unorthodox theory proposed by Skoulikidis to elucidate the mechanism of the reaction between SO_2 in aqueous solution with marble is based on an electrochemical model [Skoulikidis et al. 1979, 1981a, 1981b, 1982, 1987, 1991, 1993]. The sulfation of marble

a potentiometric SO_3 sensor with gypsum as a solid electrolyte at room temperature are briefly described. The sensor, which in contact with ambient air on one side and on the other with various concentrations of SO_3, taken directly from oleum—fuming sulfuric acid— through air flows ranging from 200 to 500 Nml/min. It detected the changes in SO_3 concentrations through differences of 40-45 mV after some 20 minutes stabilization. However, the functioning of the second half cell based on a solid $CaCO_3$ electrolyte has yet to be confirmed.

Preliminary analysis of data from the National Exposure Programme carried Out for four years [Butlin et al., 1992a] proved that data sets of the unsheltered samples could be fitted into a range of linear equations. A linear equation containing the average atmospheric SO_2 concentration, rainfall and rainfall acidity can account for over 60-65% of the variation in surface recession for Portland stone and for over 70-75% for White Mansfield stone. The relative importance of each term depends on the location. At remote sites with high rainfall, degradation is dominated by dissolution of the stone by rain. In high pollution areas, the SO_2 term is much more important and may account for 50% or more of the damage. A second paper [Butlin et al., 1992b] presents an equivalent linear equation that relates weight loss to SO_2 and NO_2 concentrations-this last term having a negative coefficient as yet not fully explained-, rainfall and rain acidity. The NO_2 term is relatively unimportant for Portland stone but more important for the White Mansfield stone, while the rain term is less so. The equations postulated have correlation coefficients of 0.604 and 0.727, respectively.

The rate constants for adsorption, desorption and chemical reaction of SO_2 with marble, as well as other parameter for the gas-solid reaction were measured by reversed flow gas chromatography, RF-GC, [Katsanos and Vassilakos, 1991]. The experiment used Pentelic marble ground to mesh 22-30 and 100-120 and dry air as carrier gas at $0.283cm^3$/s or $0.583cm^3$/s velocities and different temperatures. The adsorption constant appears to decrease with increasing flow rate for a given temperature and the decrease is greater for smaller particle size. For the smaller particle size most other parameters also decrease for increasing flow rate, and the chemical reaction constant gives negative results for the higher temperatures. It is speculated that a chemidesorption step could be occurring. Further studies [Vassilakos et al., 1992] explored not only the effect of SO_2 on geometric shaped objects in Pentelic marble, as well as that of NO_2 (only on a marble sphere) and for mixtures of both gases [Vassilakos and Salta, 1993]. It was found that for SO_2 the shape had negligible influence on all physicochemical parameters measured. Upon repeting the experiment on the same objects after careful washing it was found that most parameters changed, except for the cylinder. The distribution equilibrium constant was found to depend on the geometrical form and this unexpected result was explained as being due to representing the ratio of the solid-gas interface to gas concetrations, rather than the ratio of bulk solid to gas concentrations. For the case of NO_2, all parameters measured are roughly three orders of magnitude smaller than that for SO_2. The mass transfer in both gas and solid phase are activated processes for NO_2, but apparently this is not the case for the surface adsorption reaction. This latter gas appears not to have a synergistic effect on the SO_2

results first in the formation of a porous gypsum film that is usually less than 300 Å, where the gypsum is formed at the calcite/gypsum interface. The growth of this film follows a linear equation and its activation energy was calculated to be 14 ± 1.5 Kcal/mol. The reaction is proposed in terms of a galvanic cell, where the $CaCO_3$ acts as the anode:

$$CaCO_3 \longrightarrow Ca^{++} + CO_2 + 1/2\ O_2 + 2e^-$$
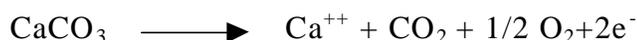
while the SO_2-O_2-H_2O mixture acts as the cathode:

$$SO_2 + \tfrac{1}{2}\ O_2 \longrightarrow SoO_3 \text{ and}$$

$$SO_3 + \tfrac{1}{2}\ O_2 + 2e^- \longrightarrow SO_4$$
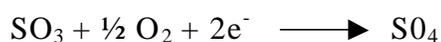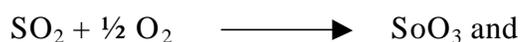
The galvanic cell $Pt/CaCO_3(s)//CaSO_4.2H_2O(s)/Pt, SO_2(g), O_2(g)$ was constructed and claimed to function as such. The semi-conductor nature of these minerals (calcite, gypsum) is based on the fact that the first is a cation conductor and the second an electron conductor at high temperatures (over 100°C) [Parkhomenko, 1967].

As the gypsum film increases in thickness, its porosity decreases, and the reaction rate determining step is the migration of Ca^{++} through the layer with a mechanism similar to that described for tooth decay [Cussler and Featherstone, 1981]. The new gypsum forms on the top of the first film thereby destroying any surface detail. This reaction follows a parabolic equation and its activation energy was calculated to be 18 ± 1.5 Kcal/mol.

The two mechanisms described are equated, in both their thermodynamics and kinetics, to the Wagner equations for metal oxidation layer growth. As proof of this comparison of SEM photomicrograph of crystal growth on metals and marble is made'.

On the strength of the above theory, the failure of conventional protective treatments is discussed and new artificial patinas proposed [Skoulikidis et al. 1993], some of them based on Fe_2O_3 -specially prepared with n-semiconductor properties-in a Acryloid B72 solution.

Confirmation of the hypothesis postulated by Skoulikidis has been found partly in the functioning of SO_2/SO_3 sensors. These are based on concentration cells using a solid electrolyte, such as alkaline or alkaline earth sulfates, requiring operation at 500°C to assure sufficient ionic conductance and reasonable response time [Atzeni et a!., 1994]. Tests using

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[1]Unfortunately, the SEM photomicrograph of the "gypsum" crystals growing on the surface of a marble protective coating [Fig.s 11(1979), 12 (1981a), 49 (1991)] is mis-interpreted. The original micrograph [Lewin and Charola, 1978] was taken from the interface of a sandstone/powdered sandstone and nitrocellulose polymer replacement and the nature of the crystals was not identified.

adsorption, but decreases the SO_2 desorption rate constant by a factor often. Following this experimental work, the theoretical analysis of the interaction of two pollutants in the gas phase and on the monument surface as well as the calculations required using RF-GC and the appropriate computer programs are presented by Arvanitopoulou et al. (1994).

A kinetic study of the SO_2 reaction with dolomite determined that the extperimental data, modeled on the unshrinking unreacted core model fit the half-order rate model, however, the first-order ratemodel expresses more accurately the weathing of dolomite in outdoor conditions [Gauri et al., 1989; Tambe et al., 1991]. The correlation coefficients for the experimental data fitted to a half-order reaction rate is of 0.98, while for the first order reaction rate it is 0.95.

Dry deposition of SO_2 on a thin water layer, using NH_3 as a pH regulator, was measured in a wind tunnel [Adema and Heeres, 1995]. The concentrations above and in the water for SO_2, HSO_3^-, $SO_3^=$, NH_3 and NH_4^+ were calculated by Fick's first law and were accurate enough to derive an adequate kinetic equation for the oxidation of sulfur by both oxygen and ozone. A kinetic equation for the surface oxidation was developed. The oxidation with either O_2 or O_3 was described through reaction with an activated HSO_3^- or $HS_2O_3^-$ surface complex. The experimental results seem to indicate that the oxidation occurs at the gas-liquid interface and that the presence of NH_3 or catalysts is not necessary for the oxidation.

The linear relationship between the deposition velocity of SO_2 (from a mixture of SO_2 and NO_2) on Pentelic marble and relative humidity was obtained empirically from laboratory data [Henriksen 1994]. The equation derived had a correlation coefficient of 0.98.

A model to evaluate the rate of growth of a gypsum/calcium nitrate crust on marble was developed by Yerrapragada et al. (1994). The experimental procedure exposed polished slabs of Carrara and Georgia marble in protected outdoors environments in six sites in Jefferson county, KY. The surface of the exposed samples were analyzed by X-ray photoelectron spectroscopy and the solubilized surface deposit analyzed by ion chromatography. The diffusion coefficients and surface rate constants as well as the effective stoichiometric proportions of SO_2 and NO_2 were determined. These were found to be applicable for prediction of crust thickness or, if the crust thickness is known, for calculating the concentrations of SO_2 and NO_2. The correlation coefficients for the plots of the crust thickness versus time obtained in the various sites ranges from 0.95 to 1.0. It was also found that Georgia marble was less reactive than Carrara marble. Data from samples of monuments in Los Angeles cemeteries confirm an increase in the ratio of nitrate to sulfate for younger crusts reflecting the increase of NO_x in the atmosphere.

II. Wet Deposition

II.1 Introduction

Wet deposition is concerned with the incorporation of pollutant substances in cloud droplets, also called "occult deposition" (or rain out), or in regular precipitation, also called "wet-only precipitation," "acid rain" (or wash-out). Although the acidity of the rain was blamed for the damage induced to stone, in particular calcareous stones, it was found that the pH of rain decreases as rainfall continues. Camuffo has studied this in the particular case for Padua [Camuffo et al., 1988] and summarized the situation for Venice [Camuffo et al., 1984]. Wet deposition will only affect the exposed surfaces of a building while dry deposition attains all of them [Furlan and Girardet, 1988]..

Rain is more efficient in scavenging air-borne pollutants than cloud droplets. Its acidity, as well as the turbulent character of the runoff, will attack the stone surface. But a strong rain will also wash away from the stone surface the accumulated dry deposit. This is not the case for a soft drizzle, which does not remove the deposit but provides sufficient moisture to chemically activate this deposit thus turning out to be far more damaging than "acid rain." [Camuffo, 1991a]. In rural areas, i.e., those with low pollution, wet deposition can be just as important as dry deposition [Furlan and Girardet, 1983a].

The pollutants incorporated in wet deposition are usually produced by distant sources, i.e., long range deposition [Torraca, 1988]. The efficiency of "occult deposition" and "acid rain" depends on drop formation and intensity of precipitation as well as on the vertical distribution of trace substances in the atmosphere. It would appear that the main source of sulfate in rainwater results from the oxidation of anthropogenically generated SO_2. However, the mechanism of the incorporation of this pollutant in the rain appears to be mainly through SO_4 particles within clouds and not by direct dissolution of the gas [Amoroso and Fassina, 1983, chap. 4]. Other contributions, such as seawater sulfate, are much smaller even in coastal areas.

In northern and central Europe, the great frequency of rainfall makes wet deposition important. Measurements of the acidity of rain water for Como, northern Italy, gave a yearly average of pH 4.2, lower in winter months due to fuel combustion. The authors, Rocchi and Mosello (1979) have shown it to be linked to the amount of sulfate ions present. However, it was found that the acidity of rainwater could not to be attributed exclusively to the emission of sulfur compounds; that sulfate transport only contributes partially to it, and, short-range or micro-climatic factors can affect it significantly [Camuffo, 1990; Camuffo, 1991b].

Studies of the variation in pH during summer storms near the continental divide in the US, followed by continuous monitoring have shown that the minimum pH (~ 4.1) was found near of slightly after the maximum rainfall intensity [Reddy et al. 1 985b]. The wet-only

precipitation was about 0.5 pH units lower than the bulk precipitation, which included the dry deposition. This difference in pH was attributed to neutralization by the particulate matter. The concentration of sulfates in wet deposition in Western US was found to be linearly related to the SO_2 emissions of non-ferous metal smelters in neighbouring states in a four year-long study [Oppenheimer et al., 1985] confirming the long range transport of pollutants by wet deposition.

II.2 Fog and Droplet Formation

As mentioned above, a light drizze or fog does not wash away the accumulated dry deposition from the surface of the stone, but increases its time of wetness. This in turn increases both the available time for chemical reactions and the capture efficiency of airborne gaseous and particulate pollutants. Occult precipitation is particularly important in areas with special climatic conditions such as Venice and California. Studies of chemical composition of fogs in the latter [Waldman et al. 1882] have shown that the ratio of NO_3 to $SO_4^=$ is about 2.5 for Los Angeles, while in rain water the ratio was about 1. For Bakersfield, an area in the San Joaquin Valley which has oil fields in the southern part of the valley, and hence higher sulfur emissions for a non-urban area, the ratio was about 1. Dominant ions in the fog water were NH_4^+ H^+, NO_3^- and $SO_4^=$.

Free droplet formation is a complex process. For homogeneous nucleation to occur the relative humidity is above 100%, i.e. the air has to be supersaturated in water. In the free atmosphere moisture will nucleate on a solid particle serving as a condensation nuclei. If the particle is partially soluble, the effect of this solute will affect both the surface tension and the vapor pressure of the drop thus influencing the critical equilibrium curvature radius of the drop "embryo" and its potential of actually developing into a water droplet. One of the most common condensation nuclei is provided by NaC1 from sea spray. These nuclei will start adsorbing water molecules, will become delisquescent and hygroscopic finally developing into a drop when their radius increases above the critical value [Camuffo et al., 1987; Camuffo 1997].

The deposition of these droplets on the stone surface can result from various effects: Brownian, thermophoretical and the Stefan effect The first one is an efficient mechanism for the smaller droplets (<0.1 µm), and its effectiveness is increased if the surface is already wet. Thermophoretical deposition occurs when the stone surface is cooler than the surrounding air, so that particles between 0.1 and 1 µm (those that have a high Knudsen number) within the region of this thermal gradient will be "pushed" on to the surface. This effect is not important for larger droplets which will be affected more by condensation phenomena and the resulting convective movement (Stefan's hydrodynamic flow). For

droplets with diameters of around 8-10 µm, inertial deposition is the main mechanism in operation and finally gravitational sedimentation is the main effect for large droplets in the absence of wind. A good discussion of this topic is found in Camuffo et al. (1987).

The main mechanisms that will define the final chemical composition of a droplet when the pollutants come in contact with dispersed atmospheric liquid are: nucleation scavenging, scavenging of gas and particles during the evolution of the dispersed system, chemical reactions in the dispersed liquid phase, and microphysical evolution of the system. These are summarized and discussed by Camuffo (1990).

A discussion of chemical composition of fog and cloud water in various areas in California is given by Hoffmann (1986). The key mechanisms for the acidification of fog were found to be: (a) scavenging of acidic precursur aerosol; (b) scavenging of gaseous nitric acid; and (c) oxidation of reduced sulfur compounds to sulfate. The aqueous phase oxidation of sulfite to sulfate is due to hydrogen peroxide, ozone and oxygen catalyzed by trace metals. Aqueous phase producton of nitric acid is unimportant. The relative concentration of nitrates and sulfates in the fog reflect the emission patterns in the vicinity. The presence of sulfur (IV) - aldehyde adducts explain the high concentration of sulfur.

The composition of fog water in Venice and Stevan, 1992] was studied in relation to the damage to stone. It was found that fog had higher concentrations of pollutants which can be due to its having a larger surface area than rain drops. Average concentration of chlorides and sulfates can be 7-16 times higher in fog than in rain. This is attributed to the fact that fog mainly collects local air pollution.

Measurements of maritime aerosols over the North Atlantic [Gravenhorst, 1978] have shown that excess sulfate was present, mainly for the lower size range of large particles ($1.0\mu > r > 0.1\mu$) and that for particles smaller than 0.5 µm radius, ammonium and protons were the counter ions. The amount of $(NH_4)_2SO_4$ present in particles, both in maritime and continental aerosols, was shown to be of minor importance for giant particles (r>l µm), increasing in importance with decreasing particle size, and becoming the main constituent for Aitken particles ($r < 0.2\mu m$) [Jaenicke, 1978].

As summarized by Laurenzi Tabasso and Marabelli (1992) fine particles in coastal aerosols can contain sulfates originating from homogeneous oxidation of SO_2 in the gas phase (particles with aerodynamic diameter, ?, between 0.17-0.25 µm), or from the oxidation of $SO_2.H_2O$ in water (? between 0 .60-0 .6 5 µm), and ammonium nitrate in particles (4< 2.5 µm) resulting from the homogenous gaseous phase reaction between NH_3 and HNO_3. Coarser particles are due to the reaction of SO_2 with marine aerosols, with probable formation of Na_2SO_4, while nitrates result from the reaction of HNO_3 and $NaCl$.

In Report 6, Vol. I of the SOS/T NAPAP reports [Irving, l99la] the concentration of hydrogen, sulfate, nitrate and ammonium ions was found to be three times larger in droplet deposition (which is most significant at elevations above 1000 m) than for wet deposition. This could possible be attributed to the hygroscopic of the salts formed. For wet deposition it was found that except for the hydrogen ion, a slight decreasing trend was observed in the concentration of the dissolved ions, such as sulfate and nitrate. Areas in the northeast US and the southeast Canada show maximum deposition of individual inorganic chemical species. This study concludes that the research and monitoring carried out in the 80's is inadequate to address mass balance of sulfur and nitrogen species on a regional scale, and that monitoring would have to include urban sites to be able to reach such a goal.

II.3 Hydrodynamic Factors and Dissolution Mechanisms

Among the first studies trying to elucidate the influence of hydrodynamic factors of acid rain washing over monuments and its relation to the deterioration of calcareous stones the one by Guidobaldi (1981) should be mentioned. The laboratory experiment differentiates the corrosion due neutralization of the acid and that originating from mechanical erosion of the solution flowing over the stone surface. The amount of Ca^{++} removed by mechanical erosion can be equivalent to that dissolved by acid action for pH above 4. At lower pHs this effect is reduced. Guidobaldi also evaluated in the laboratory the influence of rainfall frequency. The study concluded that, at a macroscopic level, no significant differences were observed for a given amount of rain-fall, regardless of whether this was a continued occurrence or divided into a number of events which allowed the stone to dry out between them.

From studies carried out by Snethlage (1981) it was found that the rate of dissolution of dolomite, as compared with calcite, decreased proportionately with decreasing concentrations of sulfuric acid. Also, the amount of mineral dissolved was one fourth at the lower acid concentration (10^{-3} M H_2SO_4). It was found that dolomite dissolved congruently, i.e., the same amounts of Ca^{++} as of Mg^{++} went into solution and that the rates of dissolution were the same for calcite and for dolomite, except for the initial acid attack which is a lot stronger on calcite than on dolomite.

A general discussion on the dissolution reaction and the various factors affecting its rate as well as the contribution of the crystallizing gypsum to the overall deterioration is presented by Charola (1988). Another discussion summarizing the effects of acid deposition on Vermont Shelburne marble and Indiana Salem limestone is presented by Ross et al. (1989) (see also section III.3).

The recession of the surface of Vermont marble samples was correlated with rainfall quantity in a study by Reddy et al. (1985a). The changes in rainfall-runoff composition were followed and the recession of the surface calculated on the basis of the amount of Ca^{++} removed. In a further study [Reddy et al. 1986] the recession of this marble was correlated to the hydrogen ion deposition in a linear equation. The recession is calculated from the amount of Ca^{++} measured in the run-off water and converted to an equivalent volume of removed rock. A related study [Youngdahl and Doe, 1986] on Vermont marble and Indiana limestone, measured changes in roughness and weight on specially prepared samples.

Laboratory studies of run-off water from limestone and marble samples sewed to define the linear relationship between the concentration of Ca^{++} in the collected water and that of H+ in the "rain" [Baedecker and Reddy, 1993]. It is suggesed that the amount of granular material collected for either stone is independent of the pH of the solution flowing over the stone (see reference to these authors in section III.4).

The analysis of run-off water from two comparable statues, both in Carrara marble and two obelisks, one in Carrara marble and the other in Pennsylvania blue marble, in the Gettysbrg National Militay Park, PA, was correlated to stone mineralogy and roughness and to environmental data [Sherwood and Dolske, 1992; Dolske, 1995]. It was found that the dry deposition of sulfate is slightly higher for the coarse-grained Pennsylvania marble. The rate of Ca^{++} removal is more dependent on the shape, surface complexity and size of the catchment area used than on the nature of the stone, for this particular pair of marbles.

Run-off analysis from field sites in rural and urban New York sites and a Washington, DC., site, are reported by Sherwood and Reddy (1988). Both Vermont Shelburn marble and Indiana Salem limestone samples were exposed with roughened inert glass plates serving as controls. The analysis show that the net calcium in the run-off from marble in rural Nwe York for rain events with incident pH>4.5 is 12.4% higher than for events with incident pH>4.3. For the case of limestone, because of its higher porosity, the results are not as easy to interpret, but the net amount of sulfate is three times that of marble at the same site.

The complete overview of these studies is presented by Irving (l991b) in Section 3 of the NAPAP SOS/T Report 19. The recession for Indiana limestone and Vermont marble, exposed at 30° from the horizontal, has been estimated to around 25-45 µm/y and 15-30 µm/y, respectively. The wet deposition of hydrogen ion in rain was found to account for approximately 10% of the chemical erosion, while the dry deposition of sulfur dioxide contributes around 5-20% with the dry deposition of nitric acid contributing approximately 2-6%. The balance corresponds to the natural carbonate dissolution from atmospheric carbon dioxide. The contribution of dry deposition of SO_2 increases significantly when the stone slabs surface present higher angle inclinations, such as 60° or 85°. The report also presents the development of a kinetic model, CHEMTRAK, for the dissolution reaction of carbonate rock.

An experimental study on the effect of acid rain, simulated by sulphuric acid solutions of pH 4.8 and 2.6, was carried out on the compact Istrian and the porous Vicenza limestones [Zendri et al., 1996]. The setup allowed for both the chemical dissolution and the impact of rain drops. Samples were placed at 60° and 2 liters of the acid solution sprayed on them for 20 minutes. Every four cycles the samples were dried. The run-off was analyzed for Ca^{++} concentration which was considered the "chemical" decay. The collected fragments lost by the samples were considered the "physical" deterioration. It was found, for both levels of pH, that the chemical decay increased with the number of cycles-more for the lower pH-and more for the Vicenza stone than for the Istrian. However, the physical decay at pH 4.8 started off identical for both stones as the number of cycles continued, it increased in steps for the Istrian stone due to loss of fragments in between stylolithic planes. At pH 2.6, the Vicenza stone follows a parabolic function, due to loss of the cementing material, while the Istrian stone starts with a higher loss but does not increase as much with the number of cycles.

The ionic strength of synthetic acid rain percolating through pieces of coquina, a very porous stone composed of sea-shells and calcareous sandstone cemented together by calcium carbonate was found to contribute as significantly as its acidity to the dissolution of the calcite in the stone [Rands et al., 1986].

The dissolution mechanism for calcite and its polymorphs, aragonite and vaterite were studied in the laboratory [Koutsoukos and Orkoula, 1997]. This was complemented with controlled atmosphere (100 ppm SO_2 in nitrogen) tests with Pentelic marble samples, some treated with KH_2PO_4 or EHDP, a phosphonic acid, and periodically sprayed with distilled water and the run-off analyzed. Also water run-off from samples exposed to urban atmosphere on the Patras campus (Greece), some of them also pre-treated with potential dissolution inhibitors. Under the experimental conditions, a surface controlled process, i.e., the diffusion of a crystal building unit from the active site to the, crystal surface, appears to be rate determining step in the dissolution of calcite, its polymorphs and Pentelic marble. Samples exposed to SO_2 showed an initial rapid loss of material followed by a slower constant weight loss. Marbles protected by EHDP and inorganic phosphate had a lower loss in the second stage. Specimens exposed outdoors showed similar results as those obtained in the controlled atmosphere. The rainwater at Patras ranged in pH from neutral to alkaline, suggesting that a surface diffusion controlled mechanism, i.e., diffusion of a crystal building unit from the active site to the crystal surface, was operative for the dissolution.

Graphical methods for the resolution of the total Ca^{++} loss into its components originating from acid rain, dry deposition and karst dissolution by application of electrolyte theory and carbonate equilibria are described by Livingston (1992). From the analysis it would appear that for urban sites, dry deposition is the dominant factor rather than acid rain. Even in rural areas, karst dissolution can be more important than acid rain (see reference to this paper in section III.4).

A field study exposing various types of stones at two sites in Germany with different air pollutions levels was carried out [Steiger et al, 1993]. For two years, complete run-off data were obtained for seven kinds of stones. The experimental results are presented for two calcareous sandstones (Ihrler and Anröchte) and a limestone (Auer). The relative contribution of dry SO_2 deposition and acid rain for the total Ca loss of these stones show that acid rain contributes approximately 74% in rural areas and only 21% in polluted areas. (see reference to this paper in sections III.2 and IV.2).

A study on the weathering of Pentelic marble under atmospheric conditions in Antwerp, Belgium was carried out by Delalieux et al. (1997). It served to develop damage functions from the material loss, based on the amount of Ca^{++} measured in the run-off water. These are discussed in section III.4.

Another study carried out in Belgium reports on the exposure of Massangis limestone (calcite content >90%) to different monitored areas ranging from urban to rural and including coastal areas [Van Grieken and Toils, 1996]. Run-off water, dry and wet deposition were measured for newly quarried stones both untreated and treated with different water repellents. The effect of these treatments decreased after two years' exposure. The data obtained served to develop a damage function which is discussed in section ffl.4.

An exposure study in England, which concentrated on Portland limestone set out in thirteen locations, was used to develop a physico-chemical model for stone loss rate [Webb et al., 1992]. The model does not apply to the very wet site in Scotland, but for the other sites a good fit to the stone loss data was obtained using the dry deposition velocity measured at one site - since variations in dry deposition velocity between the various sites did not appear affect stone loss-, the theoretical acid neutralization relationship and the calculated natural solubitily equilibrium of $CaCO_3$. The measured stone loss, determined by weighing, was of 0. 14g/m^2.d and equivalent, by calculation, to 24 µm/y recession.

A chamber study where samples of Leinster granite, Massangis Jaune, Portland limestone, Mansfield dolomitic sandstone and Pentelic marble were subjected to repeated spraying with artificial acid rain (pH *3.5* prepared by mixing H_2SO_4, HNO_3, $(NH_4)_2SO_4$, Na_2SO_4, $NaNO_3$ and NaCl) was used to complement a dry deposition study (discussed in section 1.6.1) [Johnson et al., 1991]. The limestones and the sandstone show a continuing and unchanging reaction from pH change in run-off water. However, the Ca^{++} concentrations decrease with exposure time. For both these types of stones weight increases are reported, and all anions were found to be retained by all stones. For the granite, both pH and CA^{++} concentration decreased in the run-off, while the marble showed weight decrease in spite of retaining anions.

Further studies by the same team [Haneef et al., 1992] used the same exposure chamber to spray the artificial acid rain previously described (average run-off rate of 2.5x10-6 ml/cm.s) to individual and coupled pairs of samples of Leinster granite and Portland limestone. The study showed that for single stones, after 90 days exposure, the amount of Cl^- and NO_3^- retained in either type of stone was similar, whereas the calcareous stone retained about twice the amount of SO_4. For coupled stones, the amount of SO_4 retained was increased significantly for both limestone and granite when they were the lower stone in the couple (more information on this paper is presented in section III.2).

III. Deterioration Mechanisms

III.1 Introduction

The deterioration caused by "acid rain" on stone is very difficult to characterize unequivocally since apart from the increased deposition of particulates in urban areas, there is no unique characteristic that differentiates this deterioration from others. The stone itself is an active partner in the reaction and thus different stones will behave differently. For carbonate rocks, the NAPAP study (Irving, 1991b) concludes that the contributions of "acid rain" to their chemical weathering ranges between 5 to 20% for dry deposition of SO_2, between 7-26% for dry deposition of HNO_3 and around 10% for wet deposition. A general discussion of meteorological and microclimatic factors in the deterioration of stone is given by Camuffo (1994). The formation of the ubiquitous black crusts in protected areas is also not a simple accumulation of gypsum and much research has gone into trying to understand the mechanims of their formation. The assessment of the economic costs of the damage is presented in the last section of this chapter.

III.2 Influence of Stone Nature

Among the first studies observing differences in deterioration in calcareous stones is the paper by Marchesini (1969) who compares the effects of air pollution/acid rain on Greek marbles and Istria stone in Venice. For the first material he describes the three deteriorated layers that can be distinguished above the sound material: dark surface deposit, highly sulfated calcite crystals and sulfation edges around calcite crystals. The two first layers tend flake off, the sulfation edges on the calcite crystals facilitates their decohesion giving rise to "sugaring" In the case of Istria stone, due its compact nature and lower porosity its surface is less reactive, leading "whitening" of the surface but no in-depth deterioration. However, this stone can have natural veins and dishomogeneities which serve as an entry for pollutants. The orientation of these veins with regards the exterior surface is critical for their durability.

A discussion of the different detorioration patterns observed for different calcareous stones, such as crystalline marble, Istria limestone, clay containing Verona limestone, calcarenites, is presented by Rossi Manaresi (1991). It is complemented by the discussion presented by Biscontin (1991).

A study by Weber (1985) reports changes in weight (in g/m^2.year) obtained from the analysis of different stone samples exposed in situ, where half were protected from and half were exposed to rain. The stones ranged from a sandstone (Purkersdorfer Sandstein), to a marble (Laaser) and including porous limestones-such as Aurer, Breitenbrunner, St.Margaretner,

Zogelsdorfer and Mannersdorfer-and less porous ones such as Adneter and Untersberger. Loss of weight correlated fairly well with the porosity of the stone, and was minimal for the sandstone, as would be expected.

An SEM study of calcarenite stones from monumental buildings in Vienna or its outskirts was carried out by Charola and Koestler (1985/86). For samples of the latter, more rural area, the typical crust formation with an underlying area of increased porosity and decohesion, typical of a diffusion mechanism [Cussler and Featherstone, 1981; Domaslowski, 1982] was observed. In more polluted areas, the prevalence of gypsum crystallizing between calcite grains, crystal boundaries with accompanying etching of the calcite crystal surfaces was noted. The preferential dissolution of smaller calcite grains explains in part the sugaring effect and greater susceptibility to deterioration of these types of stones.

The deterioration of three different Belgian limestones, leper, Balegem and Gobertange, used in Flanders' historical monuments have been studied [Nijs et al., 1988]. The three stones are of marine origin and contain sand-sized detrital quartz, glauconite, calcareous fossils and a calcitic cement. However, variations in this composition leads to their different texture: leper limestone is characterized by big nummulites, surrounded by a coarse calcite cement. The Balegem stone has an important amount of fine-grained sand (25-50% w/w) and a fine calcite matrix. And the Gobertange stone has a lesser amount of coarser sand (10-20% w/w) and a higher calcite content (75-90% w/w). Upon weathering, the latter stone remains white, while the Baelegem becomes yellowish-brownish and the leper stone turns a rusty brownish, due to their higher iron content. These stones perform well in rural areas, but in polluted cities their resistance is curtailed. The more susceptible is the leper stone while Gobertange is relatively the more resistant one. According to the authors the resistance decreases with decreasing quartz and glauconite content.

A laboratory study comparing Indiana limestone, Vermont marble and a dolomite containing grey micrite from the Onondaga formation in New York [Neal et al., 1986] compared their dissolution when acid solutions, of various pH prepared from nitric acid, were sprayed on them and the run-off water collected. The Ca^{++} concentration in the leachate was highest for the Indiana limestone, less for the marble and least of all for the micrite. The study also measures the depth increase of engraved letters on the micrite at pH 3 which shows an initial fast change, attributed to the weakening of the stone from the engraving process, followed by a much slower depth change. It also presents measurements of the depth of carved letters of both marble and granite tombstones from the US Government Military Veterans! Administration. Surprisingly, the average letter depth versus stone date gave similar values for marble and for granite.

The deterioration patterns observed on limestone and marble monuments are summarized by Camuffo (1990) as resulting from the three ways water can wet their surface: (1) run-off associated with "white areas" where the surface is eroded and covered with reprecipitated

spatic calcite crystals; (2) "black areas" resulted on surfaces without run-off but where percolation and windborne droplet deposition occurred; and (3) "gray areas" formed in absence of run-off, percolation and/or droplet deposition. These last are not chemically affected but merely covered by a layer of dust and particles.

The Cracow case study (Haber et al., 1988) studied three different limestones, called respectively Pinczow, Jurassic and Debnik, from various monuments in and around this town. The Pinczow limestone is a soft, Miocene detritic rock, formed ofr crushed lime reef fragments held together in a calcitic, marly or argillaceous matrix. The Jurassic limestone is a white-greyish compact stone, consisting of very fine crystalline calcite, micrite and/or sparites and which hold some fragments of shells or other limestones. The third stone is the black Debnik limestone, of paleozoic organic sediment, the color being due to the presence of bituminous materials. The stone occurs in different types depending on mineral composition, texture and structure. It was found that this latter stone deteriorated along cracks, where water could penetrate due to sedimentary discontinuities and where gypsum had been found to deposit. This results also in the loss of what the authors call "chipping", loss of lens shaped chips, which develops primarily when the exposed surface is parallel to the sedimentary plane because of the nodular nature of the stone. The more compact varieties as well as the Jurassic limestone, which has a more uniform structure, were found to be very resistant to weathering. The weathering of the softer Pinczow limestone results in the formation of a hard gypsum crust on the surface through leaching processes and the disaggregation of the subsurface.

The effect of pollution on the main types of stone in the Cologne cathedral were studied by Mirwald et al. (1988). The stones range from a trachyte (Drachenfels/Siebengebirge), a volcanic rock, to sandstones (Schlaitforfer and Obernkirchener) and a limestone (Krenskeimer Muschelkalk). The trachyte tends to deteriorate through exfoliation, and the neighbouring limestone blocks, contribute sginificantly to this problem. The latter is affected by a leaching and dissolution process and erodes away where exposed to direct water action. Less exposed parts are covered with a black crust. The Schlaitdorfer sandstone, which can contain up to 15% clays and 10% dolomite, is the most affected material and also tends to exfoliate in some areas. On the other hand, the Obernkirchener sandstone, containing only 10% clays and no calcareous material, is the most resistant material, though its surface turns black upon exposure.

Mother German field study exposed thirteen types of stones at two sites in Germany with different air pollutions levels [Steiger et al, 1993]. For two years, complete run-off data were obtained for seven kinds of stones. The experimental results are presented for two calcareous sandstones (Ihrler and Anröchte) and a pure silicate sandstone (Obernkirchner). The partitioning of sulfates in the interior of the stone and the run-off, is dependent on the ability of the stone to absorb water, the amount of driving rain and ambient concentration of SO_2 (see reference to this paper in sections II.3 and IV.2).

In an interesting laboratory study [Haneefet al., 1992], coupled stones of different nature were exposed to cyles of artificial acid rain and drying (see section II.2). The stones were Leinster granite and Portland limestone, with porosities of 12.9% and 0.03% by volume, respectively. The lower stone projected some 2.5 cm from the upper one (2.5 cm x 2.5 cm). It was observed that maximum deterioration occurred on the lower stone, in the region immediately adjacent to the upper stone. This was explained by the longer time of wetness by acid spray solution and run-off, compared to the average exposed surface. An increased retention of all ions in the lower stone of the couple as compared with the same stone by itself was noticed, in particular for sulfate ions which ranged from 3 to 10 times the value retained for each stone by itself

III.3 Surface Deterioration and Black Crust Formation

The localized formation of gypsum black crusts on calcareous stones and their growth mechanism has been studied by Camuffo et al. (1982, 1983, 1987). It is suggested that differences in thermal expansion of the gypsum crystals on calcite favor the disruption of the stone surface. The relative contribution of chemical agents, microclimate and surface geometry has been summarized as follows for the case of calcareous stones having microporosity, such as marbles and compact limestones:

> (1) rain water washing over a surface will have a solubilizing effect which is increased by turbulence and low pH.

> (2) water also mobilizes any compounds that are found on the surface by dry deposition thus increasing the initial pH of the resulting solution.

> (3) water from fog or dew is in general insufficient to "activate" any dry deposit on or to dissolve the calcite of the stone surface.

For more porous limestones these processes can be significantly different.

Laboratory studies by Weber et al. (1984) and Weber (1985) compare the result from artificial weathering with an SO_2 enriched atmosphere and that obtained by simple sulphuric acid sprayings. The first one results in sulfate deposits up to nearly 1 mm within the stone pores, similar to the deposits actually found in the limestone of Viennese monuments, while the second only produced a surface deposit. Limestones containing a certain amount of marls, such as the Lorettostein, show the influence their presence has in the fixing of sulfur compounds.

The alteration phenomena for Swiss sandstone (molasse de Berne) can be differentiated depending on whether the stone is exposed to rain water, resulting in blistering and exfoliation or contour scaling, or protected from rain water, resulting in surface decohesion to a depth to 1 to 3 mm [Furlan and Girardet, l983a]. The authors compare data from various publications on dry and wet depostion. Further studies [Felix, 1986] confirm that in areas exposed to driving rain, where contour scaling occurs and the highest sulphur concentration is found at depths of 5 and 20 mm whereas in areas that are only wetted, a gypsum surface crust of 200-400 μm forms and flaking occurs only for the 1-2 mm surface. The role of water in the distribution of sulphur within the stone is emphasized. The research line was continued [Furlan and Girardet, 1992] exposing test pieces of this stone to different environments for a year (see reference to these authors in IV.2 and also various stones in a same site to evaluate their reactivity to sulphur pollutants (see reference to these authors in section I.7).

Carbonaceous particles, resulting from oil combustion in particular, are very active in forming black crusts when they are wet since they both contain sulphur compounds and catalysts, they can absorb SO_2 from the atmosphere and can serve to nucleate gypsum crystals. Thus the gypsum in the crust is partly due to the transformation of the calcareous surface and partly contributed from particle deposition and nucleation [Camuffo, 1990; Del Monte, 1991].

The analysis of carbonaceous particles responsible for the black colour of the patinas and crusts formed on monuments is discussed by Sabbioni et al. (1996). Three main sources of carbon can distinguished: (a) deposition of atmospheric particles containing elemental and organic carbon compounds; (b) biological weathering resulting in the formation of oxalates; and (c) calcium carbonate, from underlying materials such as stone and mortars. The analysis of black patinas from monuments and buildings in Bologna and Rome were found to contain mostly non-carbonate carbon (90%), and within this, elemental and organic carbon were the most important contributors. Of the organic carbon, oxalates have the highest concentration while other organic compounds, such as formates, n-alkanoic acids, polycyclic aromatic hydrocarbons, ethyl esters, which can serve as tracers of specific anthropogenic sources of urban pollution.

Analysis of fly-ash in the atmosphere in Arles and in the black crust on St.Trophime has been reported by Ausset et al. (1992) and Bannery et al (1993). The authors try to establish the trajectory of these particles and their origin, which in part is due to vehicular exhaust but mainly is due vegetable biomass, attributed to industrial sources since at the time of sampling no large forest or pasture fires had occurred.

Analysis of the spherical micro-particulates in black crusts on the tuffeau of the Saint-Gatien Cathedral in Tours were also carried out [Derbez and Lefèvre, 1996]. The fly-ash is divided into smaller smooth surface particles, 80% of which are constituted by silico-aluminate compounds, and larger porous, skeletal particles, which also contain at least 55% of other

metal oxides, and three other types of spherical particles in smaller concentrations. The particles found within the black crusts are compared with the microparticulate collected from the atmosphere and found to match exactly. The larger part of the fly ash originates from carbon combustion and brought in by continental or marine air flows. Their smaller size results from the fractioning over a longer transport and are not of local origin. On the other hand, the larger porous, skeletal particles result from local combustion of heavy fuels.

The black crusts on a local porous calcareous sandstone with a high content of fossil rests from the Rueda cloister, near Zaragoza, Spain, are described [Gisbert et al., 1996]. The spherical particles found embedded in the 2-mm black, botryoidal crusts can be divided into 40% silicoaluminates, 20% iron oxide particles, 27% mixed particles and 13% calcium containing particles. The authors distinguish three layers in these crusts describing the morphology and sizes of the gypsum crystals found in them. The fly-ash originated mainly from the Eseatrón thermal electric central, 2 km from Rueda, which operated on coal from 1952 to 1987. A similar study was carried out by Esbert et al. (1996) from the gypsum crusts formed on the Hontoria limestone of the Burgos Cathedral. Five types of particles are described: (a) small spheres ($< 5\mu m$) from fuel oil combustion in domestic heating; (b) small smooth spheres mainly composed of iron oxides, generated from both fuel oil or coal combustion; (c) smooth spheres of aluminosilicate composition from coal combustion; (d) subspherical particles with large holes containing lead, zinc, iron and other elements, from the combustion of petroleum; and (e) skeletal particles of carbonaceous nature attributed to the combustion of industrial fuel.

The various organic pollutants found included or sorbed in black crusts taken from the Custom House, Dublin, Ireland, and the Mechelen catedral, Belgium, are described by Saiz-Jimenez (1991).

The formation of black gypsum crusts on both Carrara marble columns and capitals and the Pennsylvania blue marble, on the Merchants Exchange Building in Philadelphia, PA, was observed for protected areas. In less protected areas, a thin orange soft alteration crust was formed [McGee, 1992]. The alterations were examined only by optical and SEM microscopy and their morphology described No elemental composition is given nor any other analytical technique was used for their characterization. Analysis of run-off water showed that the sulfate concentrations obtained from the Carrara marble columns is larger than that from the Pennsylvania marble [Dolske, 1995]. The concentration of sulfates in also showed a spatial pattern depending on the position of the collecting surface (column) in the building. Higher concentration were obtained on the south side, closer to the street facade, than on the north side. No such relation could be established for the concentration of nitrates in the run-off. The author correlates the concentration of sulfates and nitrates measured to the value calculated from estimated dry deposition.

Laboratory experiments of accelerated ageing with sulphuric acid rain spray have shown that differences in the habit of the gypsum cyrstals formed resulted depending on the presence of

treatments, such as acrylic, water repellent, etc., had been applied to the stone surface [Tucci et al., 1985].

A laboratory experiment where Indiana limestone samples were soaked in sulfate solutions (unfortunately the cation was not identified) of different concentrations and dried at different conditions to determine the accumulation of sulfate within the stone. It was found that this process is slow and no correlation could be established between transport efficiency and drying [McGee and Mossotti, 1992].

A paper by Reddy and Leith (1994) with the misleading title of "Dry Deposition of Sulfur to Limestone and Marble", develops a predictive model for sulphur transport into limestone and marble based on unsteady diffusion into a semi-infinite slab to describe the temporal and spatial surface distribution of sulfate in these stones. The diffusion model assumes that a saturated gypsum solution is present in pores at the stone surface and that sulfate is transported into the stone's interior by molecular diffusion. The model fits the field data obtained from the NAPAP study.

Further studies, which also give the mineralogical characterization of both the marble and limestone used in these exposure sites [Ross et al., 1989], examined them by light and SEM microscopy (see section II.2). The black appearence of the gypsum crust formed on the underside of the exposed stones from the NAPAP study was attributed to the presence of carbonaceous particles. The authors present a general discussion of the various factors contributing to the deterioration of these calcareous stone by acid deposition and suggest that the most significant deterioration factor is the salt build up on and within the stone

Analysis of thin black crusts on non-calcareous stones [Nord and Tronner, 1992] such as quartz-cemented sandstone, granite or brick, have found that apart from sulfates, chlorides and carbon, certain elements, such as iron and phosphorous are also enriched in that layer. In particular the enrichment of iron through acid leaching from secondary iron minerals, such as pyrite, limonite, jarosite, glauconite, hornblende and micas. This latter mechanism also occurs in rural areas and and the very thin black "crust" formed on the stones can be considered a natural weathering. Mother study differentiates black crusts from thin black layers on granite [Begonha and Sequeira Braga, 1996]. The analysis of these surface alterations on monuments in Oporto, Portugal, describes the first as forming on areas exposed to water but not run-off. The gypsum crystallizing on the surface is essentially washed away but the deposition of cabon and iron rich particles is easily retained by the humid surfaces. The black crusts, formed in sheltered areas are mainly constituted by gypsum.

The deterioration of Istrian limestone [Maravelaki et al., 1992] was studied from samples taken from different monuments in Venice. Two types of samples were differentiated, black crusts from protected areas, and white surface deposits from washed areas. In the black crusts, the loss of carbonate occurs in the first 1-2 mm, while for the white ones, although the

loss is smaller yet goes further in depth increasing porosity and facilitating further deterioration. In these white deposits oxalates were also found which require further study. The black crusts were further differentiated [Felix and Maravelaki, 1992] into dendritic crusts, formed in the protected areas, where gypsum constitutes 50-80% of the volume of the crust and contains embedded black microparticles, i.e., fly ash; and compact ones, formed in areas where water flows over them. Under the dendritic crusts the stone presents microfissures parallel to the stone-crust interface. These crusts form by surface deposit. On the other hand, compact crusts are a continuous biogenic layer of as yet unidentified organic nature, dark brown in colour over a second discontinuous layer of crypto- or microcrystalline gypsum which penetrates into the actual stone. In this crust, no black particles are observed. The compact crusts are believed to form through reaction of the gaseous SO_2 with the stone after the biogenic brown layer has formed.

The sulfate crusts on white and grey Naxos marbles from the archaeological site of Delos, Greece, were examined [Chabas and Lefèvre, 1996]. The analysis confirmed the presence of gypsum with traces of thenardite. Two types of fly-ash, small (2 µm) with smooth surface and large porous ones (10 µm), were found with the former in greater number than the latter and also collected on the air filters. The sulfur deposited on these filters was analyzed and the contributions from marine, land and anthropogenic originated sulfur calculated. The result shows that the main contribution is from anthropogenic sources, while land originated sulfur is negligible. The marine contribution is from sulfate aerosols.

III.4 Damage Functions

As defined by Benarie (1991) damage functions are a mathematical relationship between rates of material deterioration and damage causing factors. The fitting of experimental data to a theoretical damage function is discussed, emphasizing that time as damage factor is many times ignored. He discusses the equation developed by Lipfert (1989b) and the calculated stone loss range. However, the physical meaning assigned to this equation may not be justified on a theoretical basis [Livingston, 1997a].

Livingston (1997a) gives a comprehensive summary of the development of these damage functions which relate the acceleration in the rate of damage associated to changes in pollution level. They can be approached through physicochemical theory, laboratory tests, field studies or an epidemiological approach from measurements on actual monuments. The objective of developing damage functions can serve at least three purposes: express quantitatively the cause and effect relationship between the pollutant and the damage observed; predict the remaining life of a particular object exposed to a given air pollution level; and, predict how changes in air-pollution level will affect the lifetimes of monuments. For the latter a dose-response function is also needed. This is described in another paper

[Livingston, 1997b] which discusses the need for air pollution standards for architectural conservation. From the examples cited, it would appear that at levels for current human health effects standard, stone deterioration is not significantly greater than natural or background rates.

Several damage models have been developed. These can be based on mass loss, such as the study by Webb et al. (1992) which used Portland limestone exposed at thirteen different sites in the U.K. The model presented, which includes a factor for evaporation gave a correlation coefficient of 0.88 when comparing calculated to measured values for data of all sites in the study. When excluding data from a very wet Scottish site, an improved the correlation coefficient of 0.92 was obtained.

The 4-year materials exposure program carried out at the Building Research Establishment in Watford, England, measured the mass loss of sheltered and unsheltered calcareous stones, Portland limestone and White Mansfield dolomitic sandstone. The dose-response functions for the weight loss of the exposed samples was found to be a function of the concentration of SO_2 and the H^+ concentration in the rain, for the sandstone. For limestone another term is added taking into account the amount of precipitation. Through statistical analysis it was found that mass loss of the unshelted specimens depended on both dry SO_2 deposition and time of wetness as well as on the load of rain acidity. In sheltered specimens, the weight gain is a function of dry deposition only [Kucera et al., 1995].

Damage models can also be based on chemical denudation [Livingston, 1986; Reddy, 1988, Baedecker et al., 1992], i.e, measurement of total Ca^{++} measured in the run-off. The latter study also compares measured physical recession of the limestone and marble from five NAPAP sites. The measured recession rates ranged from around 15 to 30 µm/y for marble and from 25 to 45 µm/y for limestone, while those calculated from run-off data ranged from 6 to 10 p. µm/y for both stones. The difference obtained is attributed to grain loss from the surface. This phenomenon is tentatively correlated to dry deposition of SO_2 (see reference to these authors in section II.3).

From run-off water analysis of Massangis limestone exposed at five sites with different environmental conditions, Van Grieken and Toils (1996) developed a general "damage function" from partial least square regression analysis of the net calcium loss of the stone with variables which include, among other, rain-fall amount, run-off volume, RH and concentrations of $SO_4^=$, Cl^- and Mg^{++}; which were found to be the most significant ones. The correlation coefficient obtained was 0.52 (see reference to these authors in section II.2)

Damage functions were developed from the material loss, expressed as $CaCO_3$ or stone loss, based on the amount of Ca^{++} measured in the run-off water, of Pentelic marble samples exposed to out-door conditions in Antwerp, Belgium, over a two-year period [Delalieux et al., 1997]. The damage functions include the concentration of other ions in the rain water, such as Cl^-, $NO3^-$, Mg^{++} K^+ etc. It was found that $SO_4^=$ and HCO_3^- ions have the largest

influence on the variation of Ca^{++}.. Most Ca^{++} loss occurs during autumn and winter, where the time of wetness is longer and the ambient SO_2 concentrations higher. It was also found that Na^+ and K^+ were retained during some seasons and lost during others, but no explanation has been found. The surface recession was calculated from the run-off data and the weathering rate obtained was of about 10 µm/year

Other models have used actual surface recession [Feddema and Meierding, 1991; Meierding, 1993]. The latter study relates a damage function computer modeled on 100-year mean SO_2 inputs to maximum mean face-recession rates from Vermon marble tombstones at 18 American cities and 3 rural sites. The correlation coefficient obtained was 0.77 (further reference to these studies is given in section IV.4) A study by Livingston and Baer (1985/86) discusses the uncertainties associated with the actual measurement of recession or roughness of surfaces.

To derive better damage functions not only chemical denudation, mass loss and surface recession need to be measured but also residual dry deposition on the stone surface. These data need to be complemented with pollutant deposition velocity and other parameters such as evaporation loss. Livingston (1992) also suggests resolving total Ca^{++} loss into its components due to acid rain, dry deposition and karst dissolution through the application of electrolyte theory and carbonate equilibria. This step should be carried out before attempting regression analysis of the data. He illustrates the point using data from run-off measurements taken at Mechelen Cathedral, Belgium, Bowling Green, NYC, Washington Cathedral and the Adirondacks, and shows that for urban areas, dry deposition is the dominant factor (see reference to this paper in section II.2).

Two studies based on different approaches are reported by Holland (1995). The effect of air pollutants (SO_2, NO_x, VOCs, O_3 and PM1O, i.e., particulate matter less than 10µm in diameter, including nitrate and sulfate aerosols) was analyzed through the "impact" pathway methodology, which follows the logical progression from emission to impact and subsequent valuation. The methodology is most complete for assessment of damages to human health, materials and crops, and least complete for natural ecosystems. These are better addressed through a "critical load" approach which is not at all suitable for materials. It was found that to describe the atmospheric chemistry and transport of acidifying pollutants including PM10, analysis to 1000 km or more had to be run to account for 80% of the total impact of an individual power station.

An approach for quantifying additional maintenance and repair costs for materials, stone included, due to SO_2 and NO_x emissions in Europe is described by Mayerhofer et al. (1995). The total economic damage was calculated by comparison between the present air pollution as calculated by the Windrose Trajectory Model and SO_2 concentrations and acid depositions valid at the moment for the north of Ireland. The authors suggest that the International Cooperative Program (ICP) of the UN-ECE is the best souce for European damage functions.

For natural stone, the ICP function gives higher results than the Lipfert (1989b) function but lower than the Butlin (1992b) function.

Moisture transport in Indiana Salem limestone could be predicted through application of fundamental principles of air and water flow in porous media [Leith et al., 1997]. Moisture flux boundary conditions were specified based on surface energy balance and measured meteorological parameters from the Newcomb, NY NAPAP site. Model-predicted wetting and drying behavior of the limestone corresponded well with measured laboratory data and the periodic changes in moisture contents, predicted by the model and also measured in the field, is strongly dependent on the bi-modal pore size distribution of this material. Application of the model to the transport and accumulation of sulfate can only be done for infinite exposure times since only constanct concentration boundary conditions at the stone surface are used. Further studies to determine the exact mechanism of sulfate/carbonate chemistry under well controlled conditions are suggested.

IV. Site Studies

IV.1 Introduction

The site studies summarized in this chapter have been divided into field tests, those which essentially are case studies of buildings and monuments around the world and those which have concentrated on tombstones. These may prove useful for future reference when evaluating any new damage.

IV.2 Field Tests

The studies by Girardet and Furlan (1979, 1982) and Girardet and Felix (1981) of the behaviour of calcareous sandstone samples located on site on various monuments served determine the influence of atmospheric conditions and compare urban rural conditions. In a first approach, on rain protected sites, the deposition results from atmospheric transport of calcium sulfate particles. The deposition in urban sites can be significantly higher (an approximately twentyfold increase in sulfate deposition was measured) than that in rural areas. However, the exposure of the building and its surface topography have a strong influence on the rate of deposition. The deposition of the particles is strongly influenced by the nature of the surface (stone samples vs. saturated paper filter system), the deposition being significantly higher for the latter. The deposition rate measured in 1979, approximately $1.3 g/m^2$.year in urban atmosphere (Lausanne) was similar the average rate over the past 70 years.

A study by Weber (1985) reports the results obtained from three urban exposure sites in Vienna of different stone samples: quartzite sandstone, a marble, two compact limestones and several porous limestones. On each site, half of the samples were protected and the other half exposed to rain. The monthly mean values of SO_2 measured at the sites are reported, the average mean values ranging between 84 to 55 mg/m^2.year. The results are reported as weight gain (for protected samples) or weight loss (for those exposed to rain) in g/m^2.year. Calculations on the basis of the different bulk densities of the stones, the theoretical surface erosion was calculated to be 6.2 mm per century, agreeing with actual observations for monuments.

Twenty-five exposure sites were chosen in London and south-east England as reported in the study by Butlin et al. (1985). The two-year study used Portland stone and Monks Park stone, the latter a less durable limestone, and changes in weight and surface roughness complemented chemical analysis. They did not find an increase in weight for samples protected from rain but the weight loss of those exposed correlated with the environment,

rates in London being significantly greater (around 25%) than those in rural areas. Weight loss of protected samples leached with distilled water was half of that of the exposed ones, suggesting that the effect of wet deposition and rain contribute about 50% to the total loss of mass. In the short term, weight loss of the exposed samples increased over time as the stone weathered and can be attributed to increased roughness. Among the conclusions drawn is the suggestion that contemporary rates of erosion in central London are greater than historic ones (which might be attributable to the weathered state of the monuments). Little evidence was found for a major role of NOx in the decay mechanism of these limestones.

Short-term exposure trials in Venice for two different stones, Antrim hard chalk from Northern Ireland and Portland stone from southern England are reported by Whalley et al. (1992). The samples were located in both protected and exposed areas, and were examined after one year. The results show that Portland stone is etched even in protected areas although to a lesser extent than for the exposed ones. The surface of the protected Antrim chalk is sulfated. Little evidence of particulate mailer is seen, indicating the improved environment in Venice.

A follow-up study on Portland stone exposed in two sites in Venice, and two in the neighbourhood, Marghera and Porto Marghera, also in pairs of protected-exposed samples, evaluated their deterioration after one year [Smith et al., 1994]. After one year, even in the most rural environment (Marghera) definite acid etching occurs and gypsum is found even on the rain-exposed surfaces where also gypsum particles are found which appear to be deposited there by the rain. These have not been reported previously and their origin is as yet uncertain. The paper does not link the damage to the local environmental conditions.

Run-off water was collected for analysis from test stones of Mansfield dolomitic sandstone, Pentelic marble and Leinster granite exposed at Antwerp. Statistical techniques were used to process the large amount of collected data and only preliminary results are given [Sweevers and Van Grieken, 1992]. Among these is the cumulative Ca^{++} loss which is larger for marble, followed by the sandstone and least for granite. However, if this is considered as a ratio of the Ca content in the stones, granite has an initial increase which then very slowly decreases, while sandstone has a much higher loss than marble. The cumulative loss of $SO_4^=$ is practically identical for the sandstone and the marble.

A field exposure program at two sites in Germany, Holzkirchen, Bavaria and Duisburg in the Ruhr area, was carried out for 13 different stone materials [Steiger et al, 1993, Steiger and Dannecker, 1994]. Run-off and rain-fall data were collected for one year, and the cumulative total input through wet or dry deposition was calculated. The authors take into account that part of the precipitation is taken up by the stone by capillarity, and suggest that fluxes rather than excess concentrations in the run-off water be used, to accurately determine the net amount of a species removed from the stone. One of the remaining questions is how much sulfate penetrates into the stone.

A two-year research program was carried out in Germany in which sixteen monitoring campaigns near historic monuments, each lasting four weeks [Wittenburg and Dannecker, 1994]. Samples of three sandstones (a siliceous one, Obemkirchen; a clay-rich one, Sander, and a calcareous one, Ihrlerstein) and PVC-foils were exposed but protected from precipitation. The sulfate deposition ($ng/cm^2.d$) correlated well with the dry deposition velocity of SO_2. When the concentration of SO_2 is low, the dry deposition velocity is high for all stones, but with higher concentration the deposition velocity decreases, particularly for the non-calcareous sandstones. On the other hand, the latter stones are better sinks for ammonia, but the ammonium input could not be correlated with the ammonia concentrations. The paper also discusses the deposition of nitrates, which is higher in summer due to the enhanced photochemical reaction between and hydroxyl radicals. The total flux of NO_3^- results from different sources, such as NO_2, HNO_3 and particulate nitrate. It was found that although NO_2 concentrations were higher (average $52\mu g/m^3$) the total input is predominated by HNO_3 ($1.5\ \mu g/m^3$). Contributions by particulate nitrates are minor.

Another set of field campaigns, each of 8-weeks length, were carried out at different historical buildings in Germany [Behlen et al., 1996] to measure dry deposition of NO, NO_2, HNO_2 and HNO_3 as well as PAN. The same three types of sandstones mentioned previously were used. Except for HNO_3, the ambient concentration of nitrogenous species was lower during the summer in Halberstadt than those measured in Stralsund in winter. Nitrate enrichment was more in summer than in winter, and the best sinks proved to be the Sander stone (clay-rich sandstone) and the the Ihrlerstein (calcareous sandstone) respectively. These data seem to confirm that HNO_3 is mainly responsible for the deposition on stone. This study also describes chamber experiments which are summarized in section I.1.6.1.

The preliminary results after a nine-month exposure of four different marbles in seven locations in Europe are reported. The marbles studied were: Carrara and Laas (Italy); dolomitic Ekeberg, (Sweden); and Pentelic (Greece). The seven locations were: Arles, Göteborg, Messina, Moscow, Munich and Stockholm. In situ measurements of changes in gloss, roughness, color, water absorption and ultrasonic velocity are reported. The observed surface changes appear be due to selective dissolution of calcite inclusions and the exposure of tremolite crystals rather than from dissolution attack as for the other marbles. For the latter, typical preferential dissolution patterns reflect the surface reaction controlled dissolution kinetics which occurs at pH>4.5 and lower temperatures. These results are in accordance with the NAPAP study.

Four locations in eastern US were used for on site experiments to study the acid-rain increased dissolution of two types carbonate rock, Indiana limestone and Vermont marble [Reddy et al. 1986]. The amount of rainfall and its pH, in the North Caroline site was related to the surface recession which is calculated through a linear equation to the hydrogen ion deposition. A further study [Baedecker and Reddy, 1993] suggests that at high flow-rates, the incremental effect of hydrogen ion concentration in the rain could be significant. A more complete description of the 10-year study on acidic deposition in eastern US is given by

Baedecker et al. (1992). The program compared data from weight loss, laser-moiré interferometric profiling and Ca^{++} concentration in run-off water from the previously mentioned limestone and marble on samples exposed at an inclination of 30°. Recession calculated from the physical methods (gravimetry- profilometry) was higher (~15-30 µm/y for marble, ~25-45 µm/y for limestone) than that based on run-off data (~6-10 µm/y for both stones). The difference is attributed to the loss of solid granular material from the surface, although the collection of this material cannot account for all the difference. The amount of granular material appears to be related to dry deposition of SO_2. It was found that approximately 70% of the dissolution of these stones, exposed at 30°, can be attributed to karst dissolution. At higher angles, the relative contribution of dry deposition is significantly enhanced.

IV.3 Actual Buildings and Monuments

A study case of the Sint-Rombouts cathedral in Mechelen, Belgium, is described by Keppens et al. (1985) and Roekens et al. (1986). The location is in the center of one of the most polluted areas in Europe. The original stones were Balegem and Gobertange limestones and replacements were made with Euville limestone which proved to be less resistant. The atmospheric sampling was done with devices for total, wet and dry deposition and were located at two different heights (33 and 96 m) on the building itself and at 2 m at a close-lying meteorological station (St.Katelijne-Waver). The pH and Ca concentrations were found to be higher for total deposition (pH 7, Ca^{++} ~ 8 ppm) than for wet deposition samples (pH ~ 6, Ca^{++} ~3 ppm) because of the contribution of $CaCO_3$ dust from nearby restoration works. While the values for total deposition at the meteorological station were lower (pH ~ 4, Ca^{++} ~ 2 ppm). It was also found that the concentration of NO_2 at 33 m was twice as large as that at 96 m, as could be expected from the motor-vehicle contribution.

Another Belgian case-study corresponds to the O.L.Basilica in Tongeren [Roekens et al., 1988]. The 14th century monument is constructed in Maastricht limestone, a light yellowish, porous, soft, Late Cretaceous stone, composed of sand-sized fossils and particle of microcrystalline calcite. The stone formed a 1-mm thick surface layer, a black grypsum crust in areas protected from the rain, and a grey colored surface layer composed of recrystallized calcite with gypsum in the pores, in areas exposed to direct rain-fall. For south-facing walls, the latter had a thin green layer below it Gypsum was found to penetrate several millimeters into the stone. In some instances, powdering took place behind the outer crust, which resulted in flaking of the surface crust, especially at rounded areas and corners.

St. Paul's Cathedral in London was also the subject of a case study [Butlin et al., 1985]. The Cathedral, built in Portland stone, was monitored over a three-year period. The study concentrated in the analysis of rainwater runoff on the NE roof court and one of the key

findings was that the main source of sulfate and nitrate, whose concentrations increased as the water passed over the stones, was the rain water itself.

The effect of air pollution on the Lincoln Cathedral in Lincoln, England, constructed mainly in a local oolitic limestone which weathers in a similar fashion to Porltan limestone [Butlin et al., 1988]. The authors found that the sources of pollution in the area had changed considerably over the last 100 years, with distant sources now making a more significant contribution to pollutant levels. The detachment of surface flakes by blistering in some of the black (relatively protected) areas is determi ned by the architectural feature and nature of the stone.

The Stephansdom in Vienna was studied by a mutidisciplinary group [Saliger et al. 1985/86]. The various stones used in the construction and various reconstruction campaigns, the last one corresponding to the 1945 after the second world war, are mentioned and range from limestones of the pre-Alps, used during Roman times, to limestones and calcareous sandstones of the Leithagebirges, such as the Au, Breitenbrunn, St.Margarethen, Mannersdorf stones, and the Tertiary quarries north of Vienna. Of these, the StMargarethen limestone has been used extensively in the restorations since the mid-nineteenth century. Three sites were chose to install the previously mentioned IRMA apparatuses to measure every fortnight the deposition rate of SO_2. The winter months give the highest values through the contribution from heating (SO_2 concentrations around 130 mg/m^2.d) and the yearly average was around 2-3 g/m^2.y. The concentraton of nitrites-nitrates as well as that of chlorides was an order or magnitude less. A correlation between the mass change of standard stone samples (quartz sandstone, porous limestones, dense limestones and marble), one set protected from rain and the other exposed, to the sulfur immision measured with the IRMA apparatus, was established. All protected stones gained some weight, while all those exposed to rain, lost weight. Whereas the weight loss, higher than expected from a quantitative transformation of all SO_2 to gypsum and its dissolution, correlates well with the SO_2 immission rate, such a correlation cannot be established for the weight gain of the protected samples. Nonetheless a general trend was observed where higher weights were obtained for samples on the site where the highest SO_2 concentrations were found. The study also comprised electron microprobe analysis of weathering crusts, about 30µm in thickness, found on porous limestones, since these deteriorate faster, from the cathedral itself The inhomogeneous nature of the crust, essentially constituted by gypsum, but containing such foreign particles as quartz, feldspars and iron oxides, was shown. These tend to be in higher concentrations towards the outer side of the crust. In samples without a weathering crust, gypsum was found growing between limestone grains, indicating water transport which dissolving some Ca^{++} from the stone, reacts in situ with the gaseous SO_2. No diffusion of the pollutants into the stone was observed for either type of sample, with or without a weathering crust. The study also discusses the biological colonization patterns.

The problem posed by air pollution to the Swedish heritage is briefly summarized by Gullman (1992). The booklet reports on the progress made in preserving the deteriorating

heritage, ranging from rock carvings to stained glass, and including building stones. Two chapters are devoted to this last material, giving information regarding the documentation, characterization of the deterioration and future perspectives.

The deterioration of the Cologne Cathedral due to atmospheric pollution and its effect on the different stones used in its construction is discussed by Mirwald et al. (1988). The Alte Pinakothek and the Allerheiligenhoikirche in Munich, as well as Schioß Schillingsfürst, and Kloster Birkenfeld served as a thorough case studies [Snethlage et al., 1996a to d]. The history of the buildings, war damages, reconstructions, stone characterization, its deterioration and mapping as well as conservation measures are described.

Air pollution affecting the city of Cracow and its monuments is discussed by Haber et al. (1988). They found different deterioration mechanisms depending on the nature of the limestone, either compact or soft. A significant difference in the amount of deterioration was found depending on whether the monument was located in the high polluted environment near industrial zones or in rural areas.

The deterioration of the Lioz limestone of the Jeronimos Monastery in Lisbon, Portugal, was studied and its immediate environment monitored in five places which presented different orientations and exposures [Aires-Barros et al. 1991]. Relationship between the local climate and the exposure of the monument are pointed out. The rain water is not very acid (Ph ~ 5.5 - 7.2) and the concentration of the main ions present decrease as follows $SO_4^=>Cl^->NO_3^-$. The highest average concentration of pollutant in the air is NO_x although individual values are very variable and is attributed to the fertilizer and ammonia factories nearby.

The deterioration of the Marcus Aurelius' Column in Rome, particularly areas not washed by rain, was correlated to the amount of SO_2 and suspended particulates in the air [Brocco et al., 1988]. The concentration of the various gaseous pollutants and suspended particles were measured in various locations in Rome itself, at different heights on the Column, and are reported for the years 1970 to 1986. The concentration of SO_2 was highest during the winter months (due to domestic oil heating), although its concentration started declining in the winter of 1984 due to regulations which required sustitution of fuel oil with diesel oil of lower S content. On the other hand, particulate matter increased reflecting increasing traffic and higher number of diesel engines. However, the high concentrations of NO_x measured year round is not reflected in the presence of nitrates, however, the authors consider that NO_2 can enhance the oxidation of SO_2, especially in the presence of metal and carbon particles which can act as catalyzers.

A similar study was carried out for the Trajan Column [Camuffo and Bernardi, 1993] which analyzed the microclimatic factors affecting both dry and wet deposition on this column. A simple correlation between the observed stone deterioration and pollutant concentration cannot be drawn. It was found that rainwater is a very important deterioraton factor, particularly when it runs along the surface of the column causing severe dissolution, except

in areas where oxalates protect the surface. The dissolution of the marble is due to the chemical activity of both dry and wet deposition and the hydrodynamics of the run-off. Other factos regarding particulate deposition and the changing air-flows around the column are discussed.

Two monuments in Rome, the basilica of Santa Maria Maggiore and Teatro Marcello, and two in nearby Tivoli, cloister at Villa d'Este and Villa Adriana, were used to monitor the air quality and the surface damage to the stone [Lorusso et al., 1996; 1997]. The paper reports the data collected during 20-3 0 days in three seasons, winter '94 to summer '94, for SO_2, NO and NO_2 and total suspended particles, as well as the greying level of both vertical and horizontal travertine slabs, by brilliance measurements using two different spectrophotometric color meters for comparison. The greying of the surfaces increased during the monitoring, and more for the horizontal than for the vertical ones.

A summarized description of the studies carried out on different monume nts in Rome, from the two above mentioned columns, to the Fountain "del Tritone" and the Colosseum, is given by Laurenzi Tabasso and Marabelli (1992).

The microclimate at the Ducal Palace of Urbino, constructed in brick with architectural stone (either an oolitic or a fossiliferous microcrystalline limestone) features and their weathering are discussed in a paper by Bernardi et al. (1985)

The effect of air pollution and other natural weathering factors on the deterioration of the stones of Saint Mark's cathedral in Venice was reported by Fassina (1988b). He found that the degree of sulphation is highest in the areas where running water produces dirty streaks and where thick black crusts are formed (amounting to 60-70% sulfates), while on black surface deposits the amount of sulfates is lower (30-40%). This is still higher than the degree of sulphation measured 20 years ago which was in the order go 20-40%, even though the SO_2 concentration decreased in recent years, showing the "memory" effect of the stone. A study concentrating on the climate in Venice and non-traditional treatment of meteorological data relating the stone weathering to the frequency of climatological events was carried out by Camuffo et al. (1997).

The effect of environmental conditions to the collection of art work in the Campo Santo in Pisa is described by Baracchini et al. (1992). The analysis of the data allowed for a better maintenance program. The various crusts and surface deposits found on the stones of the "leaning" Tower of Pisa were characterized and discussed in a paper by García-Vallés et al. (1997)

The effect of the surrounding atmosphere on the cathedral of Barn, Italy, has been studied [Torfs et al., 199Th]. Samples of surface crusts, both from the interior and the exterior were analyzed. The deterioration in the interior of the cathedral can be attributed to the action of chlorides from the marine environment, but the exterior black crust can be attributed to

anthropogenic sources. The presence of heavy metals in the aerosols point to this source. However, the high concentration of gypsum in the crust cannot be attributed to aerosols but rather to dry deposition of SO_2.

The analysis of crusts, encrustations and surface deposits from the Sanctuary of Demeter in Eleusis, Athens, was carried out by various instrumental techniques [Fassina et al., 1994; Moropoulou et al., 1994]. Five different stones, ranging from a grey micritic limestone to a white marble, were identified and the deterioration patterns evolved as a funtion of textural and structural characteristics of the building stones. Rusty, yellow patinas formed on washed out areas, firmly attached black grey crusts on areas in contact with water and black loose deposits in protected areas. A cementitious coating was also identified and had formed from pollution from a nearby cement factory.

The deterioration of the Temple of Augustus in Ankara in relation to the local air pollution and climatic conditions is discussed by Caner et al. (1988) as well as the measures suggested to protect it. Mother study [Böke et al., 1992] analyzed gypsum crusts on travertine buildings constructed in Ankara in the last fifty years. It was found that the crusts contained considerable amounts of clays, organic matter and iron oxides, apart of gypsum. The amount of gypsum was found to be in direct relation to the age of the building.

A study on the possible effect the installation of a new oil refinery in Mathura, near the Taj Mahal at Agra, is discussed in at least three papers [Gauri and Holdren, 1981; Bose, 1988; Sharma and Gupta, 1993]. The first paper compares the ionic composition of weathered marble crusts from this monument to that of the Field Museum of Natural History in Chicago. Although sulfates and nitrates are below detection limits for the first monument, the various problems increased air pollution will produce in it are discussed. The second paper describes other air pollution sources already existing at Agra at least for the past thirty five years, such as two thermal power plants, a railway marshalling yard, and industries in the vicinity of Agra, including 250 foundries, most of which are situated NW, windward of this and other monuments such as the Agra Fort and Akbar's Tomb. The third paper gives data for the ambient air quality, average suspended particulate matter and SO_2 concentration, at Agra measured over the 1989-199 1 period. The measured sulfation rate was found to be particularly high for January 1991 (242 mg/m^2.day) as compared with the same month the previous year (83 mg/m^2.day) and attributed to the impact of the burning oil-wells duing the Gulf war. Microscopical analysis of the surface did not reveal any sulfation, but mainly a deposit of particulate matter.

The deterioration of the Schenectady City Hall (NY) is studied by Cheng and Castillo (1984). The surface crusts were examined and show that for the marble of this monument (Vermont) the deterioration under this crust continues although the amount of atmospheric pollutants had decreased over the past ten years.

IV.4 Tombstone Studies

Tombstones have been frequently used in studies aiming to determine the rate of deterioration of stones. However, evaluation of the data may not be as simple as it would appear, as discussed by Livingston and Baer (1985/86) (see reference to this paper in section (III.4). In another paper [Livingston and Baer, 1988] they suggest that the most appropriate use of the data obtained is for the identification of more durable types of stones, or for screening studies to identify time periods or geographical areas with significantly different damage rates.

Among the first studies carried out in the U.S., those of Matthias (1967) and Rahn (1971) should be mentioned. The first one deals with brownstones, Portland arkoses sandstones in Middletown, CT, given that meteorological records for that area are available since 1800. The measurement of the depth of inscription of the number 1 was used, for tombstones facing different orientations. It was found that: tombstones from between 1810-1820 lost 2.4/64th inch (approx. 1 mm), those between 1860-70 lost 1.6/64th inch (approx. 0.6 mm) and those between 1895-1905 had lost 1.4/64th inch (approx. 0.5 mm). The most weathered tombstones are always those facing west, which are 67% more weathered, while those facing south and east are 50% and 16% more weathered respectively, in the past 145 years. The 0.2% by volume annual increase in CO_2 in the atmosphere for the past sixty years is discussed as well as increased traffic pollution, though no measurements of the latter were made.

The study by Rahn (1971) compares deterioration rates for different stone types in tombstones at the West Willington cemetery, CT. The degree of weathering increases from granite<schist<marble<sandstone, the latter two being very close in value assuming a constant weathering rate over 100 years. The author compares this data to the topography in New England, which follows the same trend.

The study carried out by Baer and Berman (1983) concentrated on marble tombstones in National Cemeteries. The marbles were mainly from four sources: Vermont, Georgia, Massachusets and Mississippi, although the latter is maingly quarried at Taledega, AL. The Massachusets Lee marble are dolomitic, the Western Vermont and Mississippi are fine grained, and the Georgia Tate marble is coarse grained. Both depth and thickness of incription were measured The study concludes that for equal high annual precipitation levels, urban environment causes more damage and that the local sources dominate the deposition of damaging pollutants. They also concludethat finer grained marbles weather more rapidly than coarse, medium grained stones or dolomitic marbles. The weathering rates measured range from 3.6mm/100 years (Philadelphia, PA) and 2.8mm/l00 years (Cypress Hills Cemetery, NY) for urban sites to 1.7mm/100 years (Long Island Cemetery) in suburban areas.

The climate and pollution of the Delaware valley in relation to the deterioration of marble tombstones in different cemeteries in the area is described by Feddema (1986). Tombstones of mainly two different marbles were considered: Vermont (very fine grained) and Pennsylvania Blue (coarser grains and with silicate minerals veins). Only two examples of Georgia marble (larger grains) were included. Although the weathering was not the same for these marbles, the surface recession, measured taking the polished, unexposed bottom of the tombstone as reference, resulted similar for all of them. Vermont marble showed greater dissolution rates in urban areas than Pennsylvania Blue and only occasionally showed some scaling. For Pennsylvania Blue two main types of weathering were observed: granular disintegration, occurring in rural areas, and exfoliation, in urban locations. The exfoliation pattern has been attributed to the formation of a gypsum crust. The mechanism for the separation of this crust is discussed in theory but no analyses were carried out to confirm it.

Further studies on tombstones are reported by Feddema and Meierding (1991) and Meierding (1993) who studied Vermont and Pensylvania marbles in various cemeteries throughout the US, but mainly in Philadelphia. The study followed the methodology described above and relates the SO_2 air pollution to the damage observed on the stones. A damage function was derived for Vermont marble based on a century of pollution emissions (see reference to these studies in section III.4). The primary cause of the accelerated marble decay, as esfoliation, in urban atmosphere is dry deposition of SO_2 from local sources.

Gauri et al. (1990) report their findings from a study of tombstones in the Kentucky-Indiana region. The results from three of the 21 cemeteries studies are reported. These are Cave Hill and Resthaven, Louisville, and Grove Hill, Shelbyville. Scrapings from the marble surfaces were obtained, and only tombstones in Georgia marble were used for the study, although this marble does not react as fast as Vermont marble. The study plotted the time contours obtained from the presence of gypsum on dated tombstones. The map clearly shows that these contours coincide with the emission of SO_2 pollution in the western Louisville area. It shows the variation between high-risk area (sulfate is present on tombstones as soon as 1 to 5 years), to very low risk area (over 15 years exposure are required before the presence of sulfate is observed on the stone).

Studies of tombstones were carried out by Grimm (l993a, 1993b) in Germany. The first one examines the Petersfriedhof at Straubing at the edge of the Danube river,. The most important monuments in the 500-year old cemetery are mentioned, the different types of stones used identified and usage frequency over time plotted for the six most common ones: Solnhoffen Plattenkalk, light colored granite from the Bavarian area, Rosenheim granitmarmor, Kelheim Donaukalk, Muschelkalk and Carrara marble. The Solnhoffen Plattenkalk, a homogeneous dense limestone shows good weathering characteristics, The Bavarian granites, on the other hand, have not weathered as well, frost-thaw, wet-dry and temperature cycling as well as biological colonization being the main deterioration factors identified. The Rosenheimer is a grainy limestone, particularly susceptible to weathering both by sugaring as well as spalling. The Kelheimer limestone, being dense only weathers by

dissolution, and in some instances shows microkarst dissolution features. The Carrara marble loses its polish rapidly but otherwise weathers relatively slowly through carbonate dissolution. The green sandstone from Regensburg (Regensburger Grunsandstein) is very susceptible to deterioration, in part due to its heterogeneity, through the presence of clay minerals and its calcic-dolomitic contents. This composition leads to sugaring and even to alveolar deterioration. From measurements and statistical treatment of data the surface loss was estimated to be around 1.5 mm/200 years for the granite. For the case of the Solnhofener limestone, the deterioration rate per decade was shown to be linear, not progressive.

The second paper by Grimm (1993b) describes the St.Johannis cemetery in Nürnberg where light colored to red colored sandstones (Burgsandstein) were used. The Worzeldorfer variety of this sandstone was used from the 16th century, while only in the 19th century were other stones, such as Muschelkalk and black Swedish basalt, used. The sandstone weathered fairly well, deterioration patterns depending on the local source for the stone.

V. Conclusions and Future Research Lines

> *First, of course, there 's the things you don 't know;*
> *Then there 's the things you do know but don 't understand;*
> *Then there 's the things you do understand but which don 't matter*
> *"Simple Simon" A.E. Coppard*

The conclusions that can be drawn from this survey of the literature on acidic deposition on stone research can be summarized into the following key points:

- dry deposition of gaseous pollutants (from short range transport) is the key factor in the deterioration of stone, particularly calcareous ones.

- SO_2 is the main contributor, among gaseous pollutants to deterioration probably because it results in the formation of slightly soluble gypsum;

- wet deposition contributes only in part to the deterioration mechanism, except in rural areas with high rainfalls where it can be a main factor together with karst dissolution;

- fog or occult deposition can be particularly important in areas with special climatic conditions, such as Venice or Los Angeles;

- particulate deposit contributes mainly to the soiling of the stone, when emissions are lowered, soiling will eventually be washed away;

- calcite dissolution mechanism is transport controlled by H+ concentration below pH 4 and surface reaction controlled for pH>4;

- each stone has a particular susceptibility to SO_2 attack, i.e., reactivity, which has to be determined experimentally to be able to derive dose-response and eventually damage functions;

- gypsum crusts will contribute to the deterioration, particularly through dissolution and penetration into the stone matrix.

Of the many research projects described in the publications reviewed, the work carried out by Furlan, Girardet and co-workers stands out through its comprehensive approach, clear definition of objectives, balanced approach through laboratory and field-studies and experimental designs that gave results that could be compared to actual field data.

Much information and data can be found in this review, and even some contradicting results. As an example, the laboratory experiments of Böke et al. (l996a,b) on the influence the presence of clay and other siliceous components in the stone may have on the deposition of SO_2 can be cited, since these are in contradiction to in situ exposure studies carried out by Furlan, Girardet and coworkers.

Although advances in the understanding of the damage induced by acid precipitation on stone have been made, many areas still require closer analysis. Among these is the question of whether calcium sulfite is formed prior to oxidation to gypsum or if this is only a question of conditions, such as extremely high concentrations of SO_2.

Mother issue is the influence of NO_x on the oxidation of SO_2, since the exact mechanism has not been elucidated. The respective influence and interaction of the various nitrogen compounds also requires further study.

Issues such as pore size distribution, its effect on moisture condensation, and the consequent difficulty of defining "time of wetness", is an area that urgently needs to be addressed following a systematic study. Some studies have found that the deposition of SO_2 and NO_x is very dependent on both the nature of the stone and the moisture present [Johnson et al., 1991]. Since the stone porosity will affect moisture uptake and distribution within its matrix, further understanding of this process is urgently needed. This may help shed light in the interpretation of many of the results summarized in this review and for the design of future studies.

The influence biofilms may have in the retention of moisture on one hand, and their capability of acting as sinks for gases or particulates is another area that requires investigation.

The reactivity of the different stones needs to be investigated, both on an empirical basis as well as following the exchange dynamics between atmosphere/stone as suggested by Frlan and Girardet (1993).

The formation of black, exfoliating crusts, as described by Domaslowski (1982), appears to occur preferentially on more porous stones. This observation needs a systematic study to confirm it as well as to explain its mechanism.

The crystallization of gypsum in the surface crusts, its habit and morphology has not been adequately explored. The influence of the presence of organic pollutants, or compounds applied to the surface of the stone, on the crystallization habit of the gypsum and whether differences in morphology can affect the deterioration rate require further studies.

A more appropriate term for what is called "memory effect" is "previous history." If a stone has suffered damage from previous deterioration mechanisms, its resistance to damage is obviously diminished. As shown experimentally, its reactivity to pollutants is still the same [Judeikis and Steward, 1976]. However, current erosion rates on buildings in central London are greater than historic ones [Butlin et al. 1985] due to their weathered state, i.e., previous history.

As stated by Camuffo (1995) "chemical weathering is not directly related to the concentration of pollutants in the air, but to the combined action of the pollutants deposited on the monument surface, when microclimatic or meteorological factors may trigger some deterioration process."

The areas where research would apparently best serve to advance the understanding of the problem of acid precipitation on stone are briefly listed below:

• stone/moisture interactions;

• definition of time-of-wetness relevant to the dry deposition of gaseous pollutants;

• stone/atmosphere exchange dynamics;

• rationale for the formation of exfolating gyspum crusts;

• elucidation of the variation in crystallization habits of gypsum in black crusts.

All of these points have a common element: water. Once a clear understanding is gained as to how water interacts with stone, from a molecular to a macroscopic level, a better picture of the deterioration mechanisms of stone will be obtained.

Great Neck, NY, March 1998

VI. References

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