Assessment of the state of knowledge on the long range transport of air pollutants and acid deposition, update 1989. Part 7, effects on man-made structures

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ASSESSMENT OF THE STATE OF KNOWLEDGE ON THE LONG RANGE TRANSPORT OF AIR POLLUTANTS AND ACID DEPOSITION UPDATE 1989

PART 7

EFFECTS ON MAN-MADE STRUCTURES

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SUMMARY

This report attemps to answer specific questions posed by Environment Canada. This is being done at a time when a large part of the research in this area, that undertaken by the U. S. NAPAP, is at an unfinished state being analysed and not yet fully documented. Because of this situation, the authors are compelled to make certain conclusion that may turn out to be at variance with those conducting the investigation. This report cannot address and discuss all the conflicting views that the literature on this subject presents because of lack of space and time.

SCIENCE AND TECHNOLOGY

In general there has been significant progress made in advancing the science and technology of corrosion and deterioration of materials by understanding of processes and reactions derived from coordinated laboratory and field studies.

METHODOLOGY:

Advances in monitoring of deposition of pollutants and progress of reactions by :
- run-off analysis
- chamber studies
- analysis of surface layers
- analysis of products of corrosion and deterioration

NEEDS :

- methods to monitor NO_x deposition on structures

DAMAGE FUNCTIONS :

Metals :
- reasonable functions have been derived for standard flat specimens exposed at various sites
- some progress has been made to adapt this relation to various shapes but not yet applicable to materials on

structures because of possible variation in distribution of time-of-wetness and pollution deposition.

Organics and paints :
- no damage function has been developed

Stone and masonry
- various damage functions have been proposed yielding recession rates that may account for stone loss from exposed samples but their application to materials on structures has not been verified. As in the case of metals variation in distribution of time-of-wetness and pollutants will need to be accounted for. Those damage functions do not apply to the scaling mode of failure.

DAMAGE ASSESSMENT

Cost assessment : various estimate of cost due to acid deposition ranging from $2 to $20 per capita/year have been proposed, based on surveys and use of damage functions. Most workers agree that these estimates may be in error by as much as an order of magnitude.

It can be concluded that an accurate estimate of the cost that can be attributed to different levels of pollutants is far from being realized.

7.1 INTRODUCTION

This section of the 1990 Assessment document for the Long Range Transport of Air Pollution Program is prepared as an update of the report prepared by Sereda (1986). Therefore, this report must be read in conjunction with that published in 1986. Conclusions drawn in the 1986 report will not be repeated unless results of subsequent research indicates changes. For this report, literature searches were confined to the period 1985 to 1989 inclusive.

7.1.1 Conferences and Symposia

During this period a number of very important conferences and symposia were held in North America and in Europe which addressed the state of the knowledge pertaining to effects of acid deposition on man-made structures and materials.

7.1.1.1 Dean, S.W. and Lee, T.S. (eds.) (1987)

These symposium proceedings sponsored by ASTM include 26 papers covering the following areas : materials performance, environment characterization and tests methods. Of particular significance are the papers that deal with documentation that addresses the question of establishing damage functions based on data pertaining to microclimatic factors. Reference to some of these papers will be made in the text.

7.1.1.2 Baboian, R. (ed.) (1986)

These proceedings include 29 papers subdivided in the following areas : measurement and monitoring of atmospheric pollutant deposition; metallic corrosion; masonry deterioration; degradation of organics and economic effects. This symposium, sponsored by the ACS, covered most of the major topics and references to various papers will be made in the text.

7.1.1.3 Roswall, J. and Aleby, S. (eds.) (1988)

These proceedings of the symposium, sponsored by the Swedish Institute of Classical Studies, held in Rome, Italy, represent a good complement to the previously mentioned symposia, because it addresses the technical as well as the philosophic and social questions regarding conservation and restoration of objects of cultural heritage. It deals with materials in actual structures or monuments. Included are studies on monuments in Ankara (Temple of Augustus), deterioration of build environment in Greece, decay of architectural monuments in the City of Crakow, stone deterioration on the Cathedral of Cologne, deterioration of architecture in Scandinavia and deterioration of the Cathedral Well in Göteborg. Because of the serious limitations in studying the performance of materials on structures, especially those that may be centuries old, it is understandable that most of the observations reported are qualitative, not quantitative. Evidence of dramatic material deterioration is recorded, but projection of performance into the future is limited because of the lack of data on levels of pollution in the past. It may be surprising that Krumbein (1988) argues for letting buildings age naturally, as people do, without restoration.

7.1.1.4 Mansfeld, F. et al. (eds.) (1986)

This symposium, sponsored by the Electrochemical Society, presents some papers that deal with the problem of quantifying atmospheric parameters that contribute to the corrosion of metals.

7.1.2 European Cultural Heritage, Newsletter on Research (Benarie 1987).

Commission of the European Communities, Directorate General for Science, Research and Development, has begun in 1987 to publish a European Cultural Heritage Newsletter on Research. It is a useful compilation of research in progress and provides summaries of the significant reports and publications.

7.1.3 U.S. National Acid Precipitation Assessment Program (NAPAP)

This program, involving laboratory and field investigations, was carried out during the period 1982 to 1989. It is scheduled for completion in 1990, and results of this work are in the final stages of analysis and compilation in reports. The authors of this update are priviledged to have personal contact with researchers involved in this program. Although some of the results have been published, most of the results are available only in EPA reports to which reference will be made in the text.

7.1.4 Reviews

An annual review of the acid precipitation literature is provided by the Nordic Council of Ministers. Chapter 8 deals with materials. These chapters, apart from being written by a highly-respected scientist in this field, are very useful since they mention less well known, but nevertheless interesting work being done in Scandinavia (Kucera, 1986, 1987, 1988).

Another interesting review was made by Graedel and McGill (1986), where they showed very clearly the susceptibily of all kinds of materials to deterioration by pollutants in a variety of situations : in the presence of fog, rain, dew, particles, etc.

Other reviews are cited later in this report.

7.1.5 About the authors

It is fortunate that J.J. Hechler, of the National Research Council of Canada, co-author of this report, has been actively engaged in research in this area and his published and unpublished work will be cited to indicate the nature of his results. He has also participated as a reviewer of the NAPAP as well as being a member of various international and Canadian committees coordinating research in this area, thus bringing a "sense" of the views of peers regarding these difficult problems.

7.2 RECORDED EVIDENCE OF THE EFFECT OF ACID DEPOSITION ON BUILDING MATERIALS

As stated by Sereda (1986), many physical and chemical processes, resulting from material interaction with environment, are responsible for material deterioration. Studies involving acid deposition continue to try to isolate and measure this effect alone, with the hope that when a damage function is derived, that it will be possible to determine the economic loss due to pollution. It is the authors' belief that it may not be possible to separate completely the different effects observed in deterioration of materials. Understanding the different processes, however, will assist in making better decisions regarding selection of materials in design and enable successful repairing and restoring of existing structures. Research in laboratories and at testing sites must be supported by extensive field studies. Only by a multi-phase approach can one hope to reduce the estimated $11 billion repair and maintenance cost of the Canadian construction industry which has a current value of about $80 billion.

7.2.1 Atmospheric corrosion of metals

7.2.1.1 Is there a unique value for "corrosivity" of each site ?

The fact that the value of "corrosivity" applies only to a particular metal and a particular site as discussed by Sereda (1986), and as such is of limited use, has not deterred its application as an index of levels of severity of a location from the standpoint of corrosion and deterioration. In Australia, King et al. (1982) and King (1988) provide corrosivity maps for Melbourne and other sites, listing values of corrosion loss of steel in μm/y.

Dean (1988) describes the collaborative exposure program (ISO CORRAG) organized within the International Standard Organization by the Technical Committee 156, Working Group 4. This program begun in the fall of 1986 aims to establish a classification system for atmospheric corrosivity based on :

- measured characteristics of the atmosphere : temperature, relative humidity, SO_2 concentration and deposition, NaCl deposition and time-of-wetness.
- exposure of standard panels of zinc, copper, steel and aluminium.

Currently, this organization defines four SO_2 pollution categories (levels) P_0, P_1, P_2, P_3 and P_4 to apply to the following

ranges of SO_2 concentration ($\mu g/m^3$) : <12, >12 to 40, >40 to 90 and >90 to 250. For each category, from results obtained at 37 sites located all over the world and covering a wide range and combination of climatic and pollution parameters levels, the exposure program will determine the range of observed corrosion rates for four metals. Thus the "corrosivity" as determined by a range of climatic and pollution parameters levels and the corresponding range of corrosion rates (guiding values) will be given. Although some fine tuning is lost in this procedure, a better (if not ideal) knowledge and forecasting of the corrosion rates for these metals might result for engineering purposes. Four ISO standards are currently under preparation (Anon. 1989a). Such standards have been in use in Chekoslovakia with some success (Vrobel and Knotkova,1987).

7.2.1.2 Recorded evidence

Since 1986, several national and international exposure programmes were started over large and small geographical areas including the measurements of climatic, meteorological and pollution parameters.

The most extensive large scale study is the United Nations Economic Commission for Europe Cooperative Programme on Effects on Materials including Historic and Cultural Monuments. This programme gathers data on metals, paints and stones from 39 sites over Europe, Canada and the U.S.A., covers a wide range of climatic and pollution parameters levels and is expected to last 10 years. The results of the first year 1987-1988 indicate a very pronounced effect of the sulphur dioxide on the atmospheric corrosion of several metals, especially carbon steel and nickel. As stated previously, the variation of corrosivity from one site to another is different from one material to another, and different dose-responses are expected for different materials. (Anon.,1989b).

Results from an 8-year exposure program at 11 sites in Sweden and Chekoslovakia (Kucera et al., 1987), show again the influence of the sulphur dioxide on the long term corrosion of carbon steel, zinc, copper and aluminium in the temperate climate zone along with the influence of chloride in the marine atmospheres. For carbon steel and zinc, the sulphur dioxide deposition rate and exposure time explain most of the measured corrosion, showing the importance of the effect of that particular pollutant.

The U.S.A. National Acid Precipitation Assessment Program (NAPAP) with 5 sites in the northeastern states studied the same metals from 1982 to 1989 (Cramer et al., 1988a; Cramer et al. ,1988b; Flinn et al. 1986). From a variety of exposure types

(boldly exposed, sheltered, ...) to separate the effects of dry and wet deposition, sulphur dioxide appeared to be an important factor contributing to damage for steel and copper (Carter et al., 1987). Results for zinc, galvanized steel and galvalume (a Zn/Al coated steel) showed that sulphur dioxide had also an important effect but was less well defined. In this programme, a synergetic effect of sulphur dioxide and nitrogen oxides is suggested for zinc when atmospheric conditions favor the oxidation of sulphur dioxide into sulphuric acid, i.e. relatively dry conditions and a high deposition rate of NO_2 (Cramer et al. 1988a). This seems to be the only evidence of such a synergetic effect from field tests up to now.

This definitive effect of SO_2 was also shown on several other large scale programmes, for instance in Spain (Costa and Vilarassa, 1987; Espada et al., 1987a; Espada et al. 1987b).

Several field studies over small areas were also performed mainly over industrialised areas and showed clearly a decreasing corrosion rate of several metals with distance from local pollution sources (Kulis and Knotkova, 1986; Haagenrud et al., 1986). In the latter study, performed in Norway on an urban/rural area of around 900 km^2, excellent correlations were obtained between the corrosion rates of carbon steel, zinc, copper and aluminium and SO_2 concentrations and the time-of-wetness. At the rural sites, SO_2 is responsible for 15-30 % of the corrosion over one year of exposure and for 75-80% at the industrial sites.

The "corrosion map" of Melbourne based on the corrosion rate of carbon steel over two years also shows clearly some small regions of enhanced corrosivity related to local pollution sources emitting SO_2 (King and Gibbs, 1986).

On a much smaller scale, bronze statues have been studied. The corrosion of some parts of the Statue of Liberty have been attributed to acid deposition (Baboian and Cliver, 1986). Pitting was observed on the 52 replicas of the "Hiker", an outdoor bronze statue found in the the Northeast of the U.S.A., and attributed to pollutants particulate deposition (Sherwood et al., 1987). Acidic deposition has also been identified as part of the corrosion of automobiles which is mostly caused by deicing salts (Turcotte et al., 1986).

Except for these statues, all measurements and observations of the effect of acid rain were made on small flat metallic samples exposed on racks. No systematic studies of the effect of acid rain are reported in the open literature on metal used on real structures. Some general aspects of this effect are reported by Kucera and Mattson (1987). It is noteworthy to mention that these authors describe these effects as being important for specific real life exposure (having generally nothing in common with samples on racks) for which the effect of

acid rain is enhanced compared to flat samples (i.e. gutters, overhangs, ...). Apart from the influence of the sample geometry, some interesting effects due to the combination of several pollutants would certainly be noticed as did Button and Simm (1985) during their too short survey of type 316 stainless steel in London, U.K. where they suggested an inhibiting effect of oil based contaminants from vehicular traffic on panels where normally pitting and rust staining were expected.

7.2.2 Indoor corrosion of metals

The rapid development of electronic applications, automatization, data handling, ... and the increase of miniaturization has revealed that moisture and sub-ppm levels of the common pollutants (SO_2, NO_2, Cl_2, H_2S. ...) can cause severe premature failures of electronic equipment. Recent studies have shown that all common corrosion mechanisms can be found on surfaces where pollutants can only be detected by highly sophisticated analytical techniques. Localised corrosion, stress corrosion, bimetallic corrosion, ... happen at concentrations well below what human beings can tolerate (Leygraf et al., 1986). A methodology based on measuring surface concentration of various pollutants to assess the degree of corrosivity is also presented (Sinclair and Weschler, 1986). This problem is currently being addressed on a very large scale within the U.N. E.C.E. Programme mentionned earlier.

7.2.3 Soil and water corrosion of metals

If acidification of atmospheres and its corrosion enhencement has been studied for some time, the effect of acidification of soil and natural water on the corrosion of real structures has only been reported recently. The following is a brief summary of three recent reviews (Kucera, 1986b; Kucera, 1988b; Anonym, 1989c).

The main effect of acidification of natural waters is to reduce its bicarbonate concentration, therefore reducing the stability of its pH which then can fall rapidly with only small additions of acidic species. A sufficiently low pH presents increased corrosion risks for several metals. For instance, the following degradation occurs:
- deterioration of the passive protective layers inside water pipes (cast iron, steel, galvanized steel, copper)
- perforation of copper pipes through pitting

- corrosion of road culverts, steel pilings, ...
- corrosion of concrete pipes
- increase of microbiological corrosion through increase of nitrate and sulphates
- etc ...

These acidification effects have been found to account for around 30% of the cost of insurance cases involving water damage in houses through corrosion in Sweden and Finland. Further huge expenditures are expected for prevention protection (e.g. cathodic protection).

Corrosion in soil is a complicated process influenced by a great number of factors such as type of soil, moisture content, aeration, electrical conductivity, etc ... , leading to very different corrosivities. Soils are generally all sentitive to acidification but at various degree. In Sweden during the last 30 years, an average decrease in soil pH of 0.7 unit (a five-fold increase of acidity) has been measured and not only on the surface. The corrosion processes also can be very different. A decrease in soil pH probably does not affect the corrosion of copper, lead, aluminium or stainless steel since other parameters control their corrosion. Carbon steel, cast iron and zinc corrode more for any decrease in pH. Corrosion of many underground structures is therefore enhanced. A short list includes water supply lines, tanks, electric groundings, well jackets, etc ... and economic consequences are expected to be important since the amount of buried metallic structures is quite high.

7.2.4 Organics, protective coatings and plastics

Most studies of paint deterioration prior to 1985, dealt with failure due to UV irradiation, moisture and temperature effects, and largely ignored any contribution of pollutants, except that of acid leaching of ZnO and $CaCO_3$ pigments.

Current work completed and in progress, especially the early NAPAP (Edney et al., 1988a), tried to account for the observed erosion (used as the only measure of deterioration) solely due to pollution, ignoring processes caused by environmental factors other than pollution. This program did not include the influence of the substrate, using stainless steel panels coated with different paint formulations. It is certain that effects of acid rain act in combination, probably synergetically, with other effects of such factors as UV irradiation, moisture, temperature and the influence of the substrate. The NAPAP has been significantly altered in response to criticisms of a review panel and Smith et al. (1987) who

pointed out the limits of these early programs, and drew attention to mechanisms of failure involving peeling, cracking and discoloration (aesthetics) which may require repainting in a much shorter time than would be indicated from erosion data. These authors, based on probabilitic approach, suggest that the NAPAP approch may underestime the damage by an order of magnitude.

The most recent report of the NAPAP, Balik et al. (1989) and Moran et al. (1989) describe chamber studies involving coatings on wood and painted steel, where exposure to SO_2 and NO_x is combined with exposure to UV irradiation and control of humidity and temperature. This preliminary work aimed at developing instrumental techniques involving sophisticated state-of-the-art instruments to measure chemical and physical effects on polymer coatings. Techniques tried were Fourier transforms IR spectroscopy (FTIR), dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC), contact angle and electron spin resonnance (ESR), X-ray photoelectron spectroscopy and gel permeation chromatography (GPC).

As part of the NAPAP, Williams (1986,1988), Williams et al. (1987,1989) studied the effect of acid deposition on wood weathering and adhesion of paint to wood in order to show the effect of the substrate. Moran et al. (1989) are studying the effect of acid deposition on metal substrate, especially steel, and how this may influence the paint failure.

7.2.5 Cementitious materials : stone, brick, masonry and concrete.

As stated by Sereda (1986), stone represents a very small part of commercial construction materials but because it is the main material at risk on heritage buildings and monuments, it receives a great deal of attention. In the past five years research in this area has been very active. The NAPAP included stone (Shelburne marble and Salem limestone) and considerable results have been obtained on laboratory chamber studies and field exposure of test samples at five exposure sites. Youngdahl and Doe (1986) and Mossotti et al. (1987) presented the preliminary results giving analysis of $SO4^{=}$ and Cl^{-} in the surface layer removed from the samples and giving recession values as obtained from weight loss data. Surface roughness was also studied by laser holographic profiling. Surface recession values thus obtained, were about the same as values obtained from run-off chemistry as shown by Reddy et al. (1986) and Reddy and Youngdahl (1987). This work showed a linear relation between carbonate-rock surface recession rate and hydrogen ion loading to

the rock surface.

Jaynes and Cooke (1987) studied stone weathering in Southeast England by exposing 12 samples each of Portland stone and Monk's Park stone for two years at 25 sites. The sites represented a range of SO_2 levels from 11 to 119 $\mu g/m^3$ for a mean 56.2 $\mu g/m^3$. Central London had SO_2 level of 74 while rural areas had SO_2 level of 49 $\mu g/m^3$. Two series of samples were exposed at each site, one set exposed boldly to the weather while the other set was sheltered from rain. The sheltered samples showed weight loss of one third of that experimentally experienced by boldly exposed samples. The ratio of weight loss observed was 1.47 : 1 for Portland stone and 1.35 : 1 for Monk's Park stone when comparing results for Central London to rural. In the period 1955 to 1965, Honeyborne and Price (1977) obtained weathering rates for Central London of 29 μm/year and 9.94 for Garston. In the present study, the weathering rate for Central London was 16 μm/year and 10.3 for the rural site. Clearly a significant decrease in weathering rate has occured in a period of about 25 years, reflecting the decreasing SO_2 concentration.

A number of case studies were carried out in Europe. Roekens et al. (1987, 1988) and Leysen et al. (1987), involving the Saint Rombout Cathedral in Mechelen, Belgium, where areas of wall 28.5 cm by 45.5 were washed with spray of deionized water which was collected and analysed for particulate matter and dissolved ions. Rain water close to the wall collected and analysed showed values of pH which were high, being mostly in excess of 5.6 and higher than those found in total deposition in a village six kilometers away. The authors concluded that acidity was neutralized by dust and eroded calcite. High level of calcium ions was found in all run-off water and in rainwater collected. The authors conclude that there is no direct attack on stone by the acids in rainwater.

Reggio Emilia Cathedral in Bologna was studied by Del Monte and Sabbioni (1986). Analysis were made of the crust and the conclusion drawn that impact of air pollution seems to prevail over natural weathering processes including biological processes. Sulphation was widespread and its effect was found in nearly all samples analysed. Some evidence of biodegradation by algae and lichens was confirmed by oxalates being present but activity of these agents decreases as pollution concentration increases. Del Monte et al. (1987) analysed samples from surface of a number of monuments and structures and confirmed presence of minerals derived from oxalic acid produced by lichens and algae and showing that in these instances the biodegradation is responsible for most of the damage.

Camuffo and Bernardi (1988) studied the 700 year old Orvieto Cathedral showing photographs and stating that this

monument is quite well preserved despite active lichens flourishing on the side walls and despite incidents of condensation induced physico-chemical processes. It is stated that pollution is very low although no SO_2 concentrations are given. It may be concluded that this negative evidence of damage on a very old structure, in an area where pollution is low, can be used as further evidence that where pollution level is high and damage occurs, that pollution is the main cause of stone deterioration.

Deterioration on tombstones has, for many years, served as evidence of pollution damage. Feddema and Meierding (1987) measured recession rates on tombstones in the urban Philadelphia region. Recession rates were quantitatively estimated by comparing upper and lower slab thicknesses. Exfoliation of stone, (involving only the original polished surface layer) is documented, showing that such failure began occuring about 1930, increased rapidely between 1940 to 1960 with a mean exfoliation percentage changing from 5 to 35%. Contour map of percent of face exfoliated in the greater Philadelphia region corresponds roughly with contour map of annual mean pollution concentration ranging from 25 $\mu g/m^3$ to 50. The exfoliation damage is much greater than that caused by recession of the surface. In the past twenty years, the SO_2 concentration has decreased in Philadelphia and decrease in percent exfoliation has been noted. Concentration in the center of the city was 1.5 ppm in 1956, 0.9 in 1964, 0.38 in 1978 and 0.18 in 1980.

Mirwald et al. (1988) document the deterioration of the Cologne Cathedral showing evidence of very serious stone damage attributed to pollution. Pollution levels were measured and correlations between SO_2 immission and SO_2 deposition for different types of stone used were found. This work and that described by Brocco et al. (1988) for a similar study in Rome is representative of the type of studies, involving measurements of pollution at a particular location, and the corresponding detailed analysis of deterioration on a structure, that can yield the most useful results. These types of studies can help understand the factors that must be considered when making decisions concerning preservation and restoration of any given structure.

There were no reported studies of concrete deterioration due to acid rain in the period under consideration. One study by Kong and Orbison (1987) involved laboratory tests using cylinders immersed in solutions of nitric and sulphuric acid in the ratio 2/1 and pH of 2, 3, 4 and 5. This is hardly representative of atmospheric conditions.

7.3 MECHANISMS FOR ACID DEPOSITION EFFECTS ON MATERIALS

Studies carried out by the NAPAP were designed to yield a damage function or dose-response relationship for metals, paints and stone with the hope that the effects of pollution can be quantified and a dollar value can be assigned to this process. This objective was to be achieved by exposing standard samples at 5 sites and observing various changes to these samples, to be correlated with parameters representing the environment including pollution. The simplicity of this approach was realized early and various additional measurements were undertaken such as analysis of the runoff from surfaces of the samples, chamber and laboratory studies to determine surface characteristics and such factors as deposition velocities for SO_2 and NO_x, and in the case of paints, to observe effects of substrate, and changes in the polymer characteristics due to pollution. Thus it became clear that the mechanisms of reactions had to be understood to enable interpretation of results and to provide prediction of what may happen in similar or other situations. Perhaps the most useful methodology to help understand mechanisms, involved the analysis of the runoff from samples and analysis of various ions in the surface layers and deterioration products.

Various other reported studies included observations at actual structures where results would not yield specific data to formulate mechanisms because too many processes occur at the same time. However, the observations may come closer to provide a guide to future action.

7.3.1 Metals

7.3.1.1 NAPAP

By far the most extensive studies were performed under the National Acid Precipitation Assessment Program in the U.S.A. Basically two series of experiments were performed : a) traditional field exposures combined with innovative controlled covering of the samples to determine the relative importance of dry deposition versus wet deposition and b) laboratories experiments in controlled atmospheres to determine the influence of a variety of pollutants and their combination. This program is almost completed. The huge amount of data which has been generated has only been analysed partially. The main published results can be summarized as follows :

Field studies

(Cramer et al.,1988a; Edney et al., 1988a and b; Spence et al., 1986a; Spence et al., 1986b; Carter et al., 1987; Flinn et al.,1986)

Four types of corrosion experiments were conducted :
i) weight loss samples were exposed at five sites
ii) precipitation run-off from large panels on one site was collected to determine the wet and dry deposition inputs to the corrosion film and their effect on film dissolution
iii) weight loss samples having either the skyward or the groundward side masked were exposed at two sites
iv) other weight loss samples were exposed but sheltered during rain : half of these were kept dry, the other half were sprayed with pH 5.6 deionized water in an amount equivalent to the precipitation.

At all sites extensive gathering of climatic, environmental and meteorological data was performed in order to establish damage functions.

Zinc and galvanized steel. Wide dispersion in the corrosion rates for short-term exposures (1 year and less) showed the importance of environmental conditions on the initial corrosion rates. After one year, these variations are damped out and the long-term corrosion rate correlated well with the average ambient SO_2 concentration. The average corrosion film weight increased with exposure time without providing increased protection. Skyward side corroded consistantly more than the groundward side. Sheltered specimens also corroded less than the boldly exposed specimens. This was explained by the run-off measurements. The zinc run-off was directly proportional to the H^+ load and was explained by a quantitative dissolution of $Zn(OH)_2$ and $ZnCO_3$. Dissolution by other acidic species (SO_2) is also possible. In bold exposure, the sulphur concentration reaches a saturation limit of 6% by weight which suggests that the effect of SO_2 on weight loss may be limited. The corrosion of zinc was explained by a model where the corrosion product formed in short time exposure weathers with time into a film consisting of two layers. The outer layer, sensitive to the weathering factors continues to grow while the inner layer, which is stable, controls the corrosion process. This inner layer reacts with SO_2. On one site with high ambient NO_2 concentration and low time-of-wetness the increased corrosion rate was suggested to be due to the synergetic effect $H_2O+NO_2+SO_2 \rightarrow H_2SO_4+NO$. The dry and wet deposition experiment showed that for zinc dry deposition

increased relatively to wet deposition with time. The dry SO_2 flux retained by the corrosion product increasing with time showed the substantial capacity the weathered zinc corrosion product has for adsorbing SO_2.

Copper. Among the few published results, those corresponding to the efforts made to separate the wet and dry deposition are the most interesting. At the low polluted site, the copper weight loss was the same for boldly exposed samples, sheltered and those sprayed, a result showing no effect of the wet acid deposition. At the higher polluted site, the boldly exposed samples had higher corrosion loss than the sheltered and sprayed samples, these two last samples having about the same weight losses. These preliminary results show that sufficiently low pHs seem to enhance the corrosion of copper. The deposition velocity of SO_2 remained constant with time.

Carbon steel and weathering steel. Again the most interesting results correspond to the wet and dry deposition studies. For the two sites, high and low pollution, the corrosion rates for panels boldly exposed, covered and sprayed were almost the same, suggesting no important global effect of wet deposition. Single-sided corrosion rates seem to support these results although at the same site the groundward side corroded more than the skyward side. The dry SO_2 deposition rate decreased with time for the weathering steel but increased when compared to the wet deposition SO_2.

Aluminium. No special effect of acid rain has yet been reported.

Laboratory tests.

The laboratory studies were conducted in a specially designed chamber where samples could be cooled sufficiantly to provoke the formation of dew on the exposed surfaces whose run-off has been analysed. Only galvanized steel was studied. (Edney et al., 1986a, 1986b).

SO_2. In the absence of artificially created dew, on a freshly prepared surface, the SO_2 dry deposition leads to an adsorbed monolayer. In the presence of dew, the adsorbed SO_2 is much higher and the corresponding run-off shows that each SO_2 deposited dissolves one Zn. Several experiments were performed on panels with solutions with different pHs and different exposure times showing that dissolution of Zn is a function of initial pH and depends also on the exposure history. If exposure time increases, less zinc is available for dissolution, which could be explained by the two-phase corrosion layer.

NO_2. The deposition velocity of NO_2 was found to be very small,

around 5% of the SO_2 velocity. The dew composition corresponds to $Zn(NO_2)_2$ (which is unstable) which might explain why nitrates/nitrites are not easily detected on metals.

Polypropylene/NO_2. A series of experiments included polypropylene in order to simulate the dissolution of Zn by photochemical smog. The mixture was irradiated and a complex mixture of gases containing O_3, NO_2, HNO_3, HCHO, CH_3CHO and $CH_3C(O)OONO_2$ was obtained in quantity, generally higher than in real life. A significant amount of Zn in the dew could not be accounted for by NO_2^- and NO_3^- suggesting that $HCOO^-$ is present in the dew, and suggesting that carbonyl compounds contribute to corrosion.

Polypropylene/NO_2/SO_2 mixtures. SO_2 concentrations were changed while NO_2 and polypropylene concentrations were kept constant. Zinc dissolution is enhanced when SO_2 concentration is increased. The results also suggest that HNO_3 and HCHO contribute to the dissolution rate, a contribution which might be masked in the atmosphere where SO_2 concentrations are high.

Special studies (Edney 1989)

An interesting study was conducted on galvanized samples having different geometric shapes in order to determine the effect of geometry and exposure history on the uptake of gases and the impact of the dissolution of zinc. These samples (including gutter, pipe, chain-link fencing) weathered or not, were exposed boldly on one site, covered during rain, and only exposed to dry deposition. Periodically they were rinsed with deionized water and the run-off analysed. Accumulated run-off samples were different : the pipe run-off was twice the gutter run-off. The preliminary results show that geometrical shapes play an important role in the adsorption of SO_2, and that the SO_2 uptake per unit area decreases as the total area increases.

7.3.1.2) Other studies related to NO_2 and SO_2 effects on metals

Effects of SO_2

Mikhailowski and Solokov (1986) reviewed the mechanisms by which SO_2 enhances the corrosion of metals. Experimentally they show that in slighly acidic and deaerated solutions, the dissolution of iron is enhanced by a small amount of sulphites. They explain this by an additional formation of OH^- and $S^=$ during the reduction reactions of SO_2, these species being absorbed on iron promote the oxidation of Fe to Fe^{++}. The same general mechanism can be applied to other metals like Zn, Ni and Al.

Several chamber studies in well controlled atmospheres were conducted (Takazawa, 1985; Henriksen and Rode, 1986; Ericsson and Johansson, 1986) at concentrations generally higher than ambient concentrations (1-100 ppm). They all confirmed that SO_2 increased the corrosion of Zn, Al, Fe, Cu and Ni provided that enough humidity is present (relative humidity RH>50%) to allow adsorption of SO_2 on the metal surfaces.

Effects of NO_2

The same chamber studies, stated above, all showed that NO_2 increases to some extend the corrosion of Al, Zn, Fe, Cu and Ni regardless of the RH values. At concentrations somewhat higher than ambient this effect is smaller, but according to Takazawa increases substantially for all metals when the concentration increases over 10 ppm, which is already several orders of magnitude higher than real concentrations. This effect also increased substantially, around three times, from 65 to 95% RH. For all metals the corrosion due to NO_2 is always much smaller than for SO_2. These effects were all determined by measuring the weight increase of the corroded samples. One study (Whitbeck and Jones, 1987) used an electrochemical technique which showed that NO_2 at concentrations of 10-160 ppm inhibited the corrosion of iron at RH ranging from 20 to 75%.

Effects of NO_2+SO_2

In a preliminary work, Johansson (1984) showed that under certain conditions the addition of NO_2 to SO_2 can provoke some devastating corrosion effects on metals. This aspect has been studied further. Takazawa (1985) found that the weight increase for a mixture of 1 ppm NO_2 + 1 ppm SO_2 at 95% RH is slighly smaller than those obtained with 1 ppm SO_2 alone for Zn, Al, Fe, Ni and copper. This suggests that NO_2 inhibits slighly the corrosion induced by SO_2. However at the 100 ppm level that inhibiting effect disappears completely for Fe, Ni and Cu but remains for Zn and Al. Henriksen and Rode (1986), at concentrations around 0.5 ppm and RH of 95%, showed that this inhibiting effect appears only for steel and aluminium. The corrosion rates remain the same for Zn with or without NO_2 added to SO_2 but the inhibition effect disappears completely for Cu and Ag. They explain that NO_2 forms NO_2^- and NO_3^- which are known to act as corrosion inhibitors for metals whose corrosion layer is mainly made of their oxides. Therefore metals like Cu, Zn and Ag are not "protected" by NO_2. Ericsson and Johansson (1986) in a more complete study showed that RH is the important parameter. At 50% RH, NO_2 increases considerably the corrosion of steel due to

SO_2 providing that its concentration is higher than 0.2 ppm at the 3 ppm SO_2 level. At 90% RH, the addition of NO_2 inhibits slighly the SO_2 corrosion. For the other metals Cu, Zn and Al at the 1 ppm level and at 90% RH, NO_2 increases the corrosion due to SO_2.

Discussion

For NO_2 large uncertainties and contradictions still exist. First, the reactivity of the nitrogen oxycompounds are highly reactive which renders the study of their action much more difficult to understand. In field studies, there are no satisfactory techniques to measure over long periods their deposition rates which is now generally aknowledged as the parameter to measure and not concentration when degradation of materials are concerned.

The discrepancies concerning the effects of NO_2 and at the same time the effects of the combined NO_2 + SO_2, might also be traced to the fact that in all experiments, except those of NAPAP, concentrations were measured and corrosion related to concentrations and not deposition rates. It is therefore inevitable that the measured effects (weight increases for instance) are different from one experiment to another even if the experimental conditions are at first identical. The NAPAP chamber experiment where the deposition rates were carefully measured could have been the experiment to resolve these discrepancies for zinc, unfortunately they were not conceived to measure corrosion losses but to gather information on the reactions between the chamber atmosphere and the corrosion products. Although experiments were performed on SO_2 and NO_2 alone, no experiment is reported for a mixture of the two pollutants.

7.3.1.3 Other pollutants

Smoke, hydrocarbons and SO_2.

SO_2 being produced in part by combustion, the combination of smoke, unburnt hydrocarbons and SO_2 represents a real life situation. As a follow-up to the first publications, Skerry et al. (1989a, b and c) studied this specific combination for its effect on iron and zinc. The detailed study on iron involving smoke, SO_2, ethane, ethylene and acetylene in various combinations shows, among others, that smoke significantly accelerates the corrosion in humid air, enhances slighly the corrosion of SO_2, but that SO_2 inhibits the smoke-induced acceleration of iron corrosion. Hydrocarbons enhance in various

degrees the effect of smoke on iron but can have different actions when SO_2 and smoke are present. A long list of mechanisms is presented : smoke increases corrosion by increasing the conductivity of water through catalytic production of H_3O^+ at specific active sites, increases the corrosivity of SO_2 by promoting the the oxidation of Fe^{++} into Fe^{+++} which then catalyses the oxydation of SO_2 to SO_4^-, etc. ..... .

On zinc, smoke promotes slighly the corrosion by SO_2 and the hydrocarbons increase marginally the corrosion in humid air. When SO_2 and smoke are present, hydrocarbons either have no effect or inhibits slighly the corrosion. Again several mechanisms are presented.

This work on smoke and other rarely studied but important pollutants is currently unique. This work uses a variety of analytical techniques, and seems to generate a lot of new ideas and mechanisms in atmospheric corrosion.

SO_2 and H_2O_2

Graedel (1988) has turned his attention to H_2O_2, another pollutant which has been almost completely ignored in the study of atmospheric corrosion of metals. He suggests the following combined action of SO_2 and H_2O_2 on steel. H_2O_2 participates in the formation of the rust layer passivating the metal. In the absence of SO_2, HSO_3^- is oxidysed by Fe^{+++} into $Fe(II)SO_4$ which is much more soluble than the Fe^{+++} compounds and which is readily removed from the metal surface therefore enhancing corrosion. When H_2O_2 is present, it replaces Fe^{+++} in oxidizing HSO_3^- resulting in a lower corrosion rate since there are less Fe^{++} produced, .. less $Fe(II)SO_4$. This mechanism is suggested by the fact that in winter $FeSO_4$ content in rust is four or five time higher than in summer, this difference being greater than the seasonal variations of SO_2. No further experimental evidence of this mechanism is currently available. This is another example of the synergistic effect of several pollutants justifying the need for more such studies.

7.3.1.4 Special studies on copper

The restoration of the Statue of Liberty provided a unique opportunity to study the atmospheric patination of copper and bronze and several other studies provided new insights into the formation of the patina (Graedel, 1987a). The first stage of its formation in all environments is the formation of cuprite (Cu_2O). In marine environments, several copper minerals with atacamite

($Cu_2Cl(OH)_3$) are formed which are bonded together with small amount of organic matter into a stable configuration. In rural and urban areas, the next stage is the formation of complex sulphates, antlerite ($Cu_3SO_4(OH)_4$) and brochantite ($Cu_4(SO_4)(OH)_6$) again bonded together by organic matter. In rural areas, these sulphate phases grow slowly and a mixture of brochantite and acatamite will finally appear. In urban areas, the acidic surface water layer favors the basic sulphates whose relative proportions is established by the pH values. Again organic binders are present, but in much higher quantities. Schematic diagrams showing the formation rates of the two basic sulphates before, during and after a rain and fog period and the evolution of the main parameters responsible for their formation (Graedel, 1987b) are given. These diagrams are unique in the field of atmospheric corrosion since they show the unique and close interaction of the same atmospheric parameters leading to different corrosion mechanisms. In this case antlerite is formed when fog is present but not when rain is present.

7.3.1.5 Is there evidence that acid rain deposition causes significant damage to metals ?

In summary of section 7.3.1, it can be said that wet and dry deposition of SO_2 contributes to substantial damage to metals. As will be seen in the following, efforts have been made to quantify this effect varying success. Contributions up to 75-80% of the total damage have been claimed.

The action of NO_x is still not very clear. Controversy exists mainly on the following :
- it is different from one metal to another
- it enhances corrosion according to certain authors and it inhibits corrosion according to others, with or without SO_2 being present.

7.3.2 Paints and coatings.

7.3.2.1 Mechanisms

As described by Edney et al. (1988a), the NAPAP incorporated the test facility at Research Triangle Park to expose test panels under the following conditions :
- dry deposition only
- dry deposition plus clean rain (deonized water, pH 5.6) (DI)
- dry deposition plus ambient wet deposition.

This facility coupled with analysis of runoff water

demonstrated that the pigment component ZnO in latex-z, $CaCO_3$ in latex-c and Al in Al-phenol paints are leached out of the coatings by deposited acids. The DI spray runoff results show that $SO4^=$ and its precursors are more readily absorbed on galvanized steel than on paints or Teflon. The test system effectively separates the impacts of dry and wet deposition on damage to materials and isolate the effects of precipitation pH. The extent of damage and the deposition of SO_2 are coupled, those materials that readily react with acids will adsorb more SO_2 than more inert surfaces.

Work at the U.S. Forest Products Labs, as part of the NAPAP, involving accelerated weathering tests, Williams et al. (1987), and Williams (1988), has shown the following : that acid deposition can increase the rate of wood weathering; weathered wood has decreased paint adhesion; sulphur compounds accumulate at the paint-wood interface of specimen exposed to sulphurous acid. Clearly these effects of acid rain on the substrate can have significant effect on paint performance. It would be expected that this may lead to the so-called "catastrophic failure" involving cracking and peeling.

Research carried out at North Carolina State University, Balik et al. (1989), involving exposure of free films of paint to relatively high levels of gaseous SO_2 and UV light, and also immersion in aqueous SO_2 at pH 2.0, showed the following results : exposure to SO_2 alone has relatively little effect, however the combination of UV and SO_2 results in rapid polymer microstructural changes. The glass transition temperature increases from approximatively 22°C for the unexposed latex to about 75-80°C for samples exposed for 48 hours to both UV and SO_2. These changes are suggestive of polymer chain scission and crosslinking.

It is important to remember that the above results involve accelerated weathering studies and no accelerating factor exists to enable the application of these results to real conditions in the environment.

7.3.2.2 Is there evidence that acid deposition causes significant damage to paint coatings ?

Early work demonstrated that certain pigments, $CaCO_3$, ZnO and Al flakes were leached from coatings and caused erosion (Edney et al. 1988a). However, only the most recent work involving accelerated weathering studies showed indication of effect on the substrate and on the polymer in the paint film (Williams et al., 1989) (Balik et al., 1989). This work is preliminary and has not yielded any quantitative data.

7.3.3 Cementitious materials : stone, brick, masonry and concrete.

In contrast to metals and even paint films, cementitious materials are physically characterized by their porosity in addition to their chemical and mineralogical properties as discussed by Sereda (1986).

7.3.3.1 Is chemical interaction of SO_2 and NO_x the main mechanism for damage ?

Laboratory chamber studies have been carried out to identify and quantify the mechanism of reactions as reported by Vale and Martin (1986) Gauri et al. (1989) and Kulshreshtha et al. (1989). These authors propose certain preferred reactions and attempt to provide the rate constants based on experimental parameters with the hope that these constants will permit the prediction of the rate of deterioration of marble in a given environment. Johansson et al. (1988) were able to show a definite synergetic (or catalytic) effect of NO_2 with SO_2 giving a deterioration rate (based on weight gain) of travertine of about five times higher in 1000 hours exposure time than is the case with either one of the pollutants at the same concentration. This represents the only definitive evidence of the NO_2 effect. In other studies the amount of NO_3^- ion found was very low, leading to the conclusion that the effect of NO_x was negligible.

In these chamber studies, the concentration of pollutants relative to highly polluted environments ranged from about 10:1 to 300:1 or even higher. Where concentrations are used that are orders of magnitude higher than in highly polluted atmospheres, the conclusions drawn must be considered with caution before applying to real situations even though Kulshreshtha et al. (1989) claim reasonable agreement between predicted and observed values of recession of marble in the case of Field Museum of Natural History in Chicago.

The NAPAP study involving marble and limestone is described by Reddy (1988) giving results based on statistical analysis of the runoff. It is considered that stone recession is directly proportional to rainfall hydrogen ion loading to the stone surface and that the influence of SO_2 deposition on stone damage is not significant. This latter conclusion is in conflict with that of Ross et al. (1989a and b) who found up to 48% of the nitrate and up to 52% of the sulphate was obtained from dry deposition for limestone and up to 68% of nitrate and up to 72% of sulphate for marble at three sites (Washington, D.C., North Carolina and New Jersey). Oxidation of SO_2 by carbon particles as

well as ozone on the wetted stone surfaces and pore spaces may be the most important source of sulphuric acid production.

Henriksen et al. (1985) carried out multiple regression analysis between deterioration of calcareous stones and environmental variables. The data were obtained from 2-year exposure of sandstone and limestone samples at 25 sites in Europe and 2 sites in U.S.A. For single correlations, the best correlation coefficients are found for the variable expressing the SO_2 flux. The best correlations with multiple regression were found for the combination of SO_2 and rain days.

7.3.4 Is acid deposition a single cause of deterioration ?

Sereda (1986) discussed this difficult question, pointing out that many different processes, of which acid rain attack is one, contribute to the deterioration of different materials. No significant advance has been made to unrevel the complexity of this problem. New techniques of monitoring deposition of pollutants and the resulting reactions from runoff analysis, both in chamber studies and field exposures, including detection of surface changes to the material, should result in better understanding of the mechanisms involved and should enable the resolution of some of the processes.

It is relevant to note that two studies (Del Monte and Sabbioni, 1986; Del Monte et al., 1987) describe evidence of biodegradation on stone on various structures in Bologna, Italy. These studies identify specific oxalates (weddelite and whewellite) due to reactions with oxalic acid produced by lichens and algae, that would be suppressed if SO_2 levels were higher than at present. Some evidence of SO_2 attack on stone is present but it is not clear at what level of SO_2 one process would cease at the expense of the other. It is clear that in very high levels of pollution, deterioration of stone is due to dry deposition of SO_2 and H^+ ions in acid rain. The fact that very old stone structures such as the Orvieto Cathedral (Camuffo and Bernardi, 1988), which is 700 years old, remain well preserved because they are located in an area with low pollution level, testifies to the fact that other processes of deterioration are relatively slow acting.

7.4 Predictability of effects of acid deposition on materials in structures

The ultimate objective of all testing and evaluation of materials is the prediction of their performance in service.

7.4.1 Damage functions

Most authors use the expressions "damage function" and "dose response relationships" interchangeably. A damage function, as defined by Lipfert (1989c), is a mathematical relationship between rates of material deterioration and either concentration of air pollutants or rates of deposition from the atmosphere.

During the course of NAPAP, due to the fact that the concept of deposition rate became more and more important, and the fact that a corresponding term will have to be included in any valid damage function, several studies in the field of aerodynamics have been undertaken in order to understand the ability of the structures to modify their surrounding environment and the subsequent dispersion and deposition of pollutants (Davidson and Wu, 1989; Hosker, 1986). Dry deposition velocity on a surface is mainly dependant on three processes which can be characterized by "resistances". The "aerodynamic resistances" Ra of the first two processes represent the difficulties the pollutants have to reach the surface, these resistances are due to the atmospheric conditions (wind speed, turbulence near the surface, etc. ...). The "surface resistance" Rs characterizes the third process, the adsorption process, and represents the difficulty the pollutants have to be adsorbed by the materials. This last resistance depends on phenomena like surface reactivity, chemical affinities between the pollutants and the surface, moisture, etc. ... The deposition velocity is then :

$$V = 1 / (R_a + R_s)$$

Field studies are able to determine whether the deposition rate is controlled by Ra or Rs. If it is Ra, then the deposition rate can be described completely by the aerodynamic properties of the structures. If it is Rs, then any test sample can be used to determine the deposition rate on the structure. Wind tunnel modelling could be utilized to study the flow around specific real structures, and a catalog of typical building types could be developed to predict deposition rates (Hoydish, 1987). Such a study is currently underway on a statue (Davidson, 1989). This concept of deposition velocity has also been used as an indicator for materials damage (Lipfert, 1989a).

7.4.1.1 Metals

During the last fifty years, several authors observed that the corrosion of metals M versus time t can be represented by $M=at^b$ (the bilogarithmic law) where a and b are constants. It can

be shown that if corrosion is controlled by an ideal diffusion mechanism through the corrosion layer then b=0.5. If this mechanism is enhanced by erosion, cracking, etc. ... then b>0.5 with a limiting value of 1. If the diffusion is decreased by recrystallisation, filling up pores, etc...., then b<0.5. This b is the index of the presence of physico-chemical reactions in the corrosion layer including the reactions with environmental factors.

This very general theory and the concept of deposition rate have been used by several authors to explain recent and older data.

Older worldwide data have been analysed by Benarie and Lipfert (1986). For zinc, they give a term a which is a linear function of the sum of the deposition rate of SO_2 and Cl^-. The term b is given as linear with the average rain pH value. The function given represents within 20-50% most zinc corrosion data available in the literature. Similar expressions are given for copper and carbon steel, but the predictive accuracy is lower than for zinc. This can be explained by the fact that corrosion properties of metal as different as those reported are also different and can certainly not be represented by a unique formula representing a unique set of corrosion mechanisms. Lipfert (1987) again using the same data, derived different functions for different metals, their justification being mainly that they give good correlation factors.

The same basic concepts along with other thermodynamic and kinetic concepts of atmospheric corrosion and chemistry were also used by Haynie (1987) and Spence and Haynie (1988a and b) for galvanized steel. This function expresses various finding obtained by NAPAP namely:

- SO_2 reaching the surfaces reacts stoechiometrically with zinc during periods of wetness.
- rain acidity reacts stoechiometrically with zinc
- the corrosion film is soluble in rain water
- deposition velocity controls the rate of corrosion of galvanized steel structures by gaseous SO_2 during periods of wetness.

This function, containing a great number of terms, is currently under assessment using the NAPAP field data as data base.

This data base was also used by Cramer et al. (1988a, 1988b) in a preliminary statistical analysis for all metals tested where weight losses were mathematically related to pollutant, environmental chemistry data such as : temperature, wind speed, RH, NO_2 and SO_2 concentrations, precipitation H^+ load or pH, etc. ... and various combinations of these parameters using multiple linear regression techniques. Due to the changing

of the corrosion mechanisms with time, the importance of each of these parameters varies smoothly and monotonically with time. In most cases, dry deposition terms are more important than wet deposition terms. SO_2 is an important factor contributing to damage for steel and copper. The regression results for zinc, galvanized steel and galvalume were less well defined but SO_2 also seems important for these metals. Wind speed reduced the corrosion losses for the steels and copper, evidently due to its effects on drying. Precipitation terms are not important for the steels or copper. Results for zinc, galvanized steel and galvalume suggest that the effect of SO_2 may not be linear.

Using an earlier database, Haynie (1986) analysed the corrosion of weathering steel as being the sum of the metal remaining in the corrosion layer and the metal lost by solubilization, i.e. as being the result of two competing mechanisms : formation and dissolution of a protective corrosion layer. The variables that enhance the formation of the layer are those which increase the diffusion of the ions through it : these are temperature, fraction of time when wet and particle deposition rates. The variables influencing the dissolution are : the SO_2 deposition rate which increases the dissolution and NO_2 deposition rate which decreases the dissolution. It is interesting to note here that the inhibiting effect of NO_2 mentionned earlier from laboratory work, seems to have been assessed here in real conditions.

7.4.1.2 Paints and organics

At this stage of the research in paints, the data are inadequate to formulate any damage function. It is obvious that the effect of acid deposition on paint film is coupled with other deterioration factors of UV and moisture. Because of this it is likely that it will be very difficult to determine the contribution of acid deposition on paint failure. Catastrophic paint failure can occur without the influence of pollution.

7.4.1.3 Stone and masonry

Lipfert (1989c) states that "It is important to realize that the available data on stone loss represents only the quasi-steady state mechanisms of loss, and that it is not possible to recommend any one statistically based damage function for general use in predicting rates of stone deterioration". Despite the above, Lipfert (1989c) compiled 16 data sets from published papers and provided recession damage function for each. Most of these equations use either the concentration of SO_2 or deposition rate of SO_2. A number of the equations also include a

term for H^+ ion deposition. There is no similarity between these equations. He also derived a damage function using theoretical relationships to apply to generic calcite and for precipitation pH in the range of 3 to 5 :

$$\text{loss } (\mu m) \text{ / metre of rain} = 18.8+0.016(H^+)+0.18(V_d)(SO_2)/R$$

where Vd = deposition velocity in cm/s and R = rainfall in metres.

Using the above equation and existing conditions (typical of the Northeast U.S. : (SO_2) = 40 $\mu g/m^3$ and pH = 4.2), the annual stone loss rate would be 22 $\mu m/y$, of this amount 5% is due to acid rain, 10% is due to SO_2 and the balance 85% is due to clean rain effect. It is stated that when the SO_2 level was an order of magnitude higher then 50% of the loss of stone would have been due to SO_2. There in no evidence, because of lack of any measurements on actual buildings, that would indicate what confidence can be placed on above estimates.

It is evident that the most important parameter to be measured is the rate or flux of pollutant deposition on surfaces of materials and how it is influenced by the weathering and the changes occuring with time on the surface. To this end the NAPAP includes chamber studies but these studies have not been completed. The application of such data will be limited unless more measurements are made on structures.

7.4.2 Real structures monitoring

7.4.2.1 Dry deposition of atmospheric acids at Gettysburg (Davidson 1989)

The General G.G. Meade equestrian bronze statue was chosen to investigate the different steps of the deposition processes because it provides a variety of shapes with different aerodynamic characteristics. Overall transport from the atmosphere to the statue has been assessed by use of deposition surfaces composed of various materials (nylon, mylar, etc....) attached to the statue and with aerodynamically designed surrogate surfaces with well-defined boundary layer characteristics. The first results have shown that :

- the total dry deposition of nitrate onto all surfaces used generally exceeds that of sulphate by a factor of 1.5 to 4 (the deposition on the statue directly has not been measured).
- the dry deposition rate of sulphate and nitrate changes by a factor of 10 over these surfaces.
- Greater fluxes correspond to the locations where corrosion

seems the most important.

7.4.2.2 Corrosion monitoring on a building in Montreal

Although efforts have been made to study metals with shapes different from those imposed by standards in atmospheric corrosion testing, only one experiment on a real building is reported in the literature (Hechler et al., 1989a). During seven months at 44 locations on the walls of the Ecole Polytechnique in Montréal, the corrosion rates of copper and mild steel, the time-of-wetness, and the deposition rate of sulphur oxides have been measured. During the same time, on the roof, the same measurements were made on an ASTM rack which was used as a well-characterized reference for the other locations on the building. The time-of-wetness was determined using the Sereda sensors (ASTM G-84) with a specially designed measuring system. The sulphur oxides deposition rates were measured using the sulphation plate technique (adsorbing surfaces containing PbO_2) .

The corrosion corresponding to a vertical position can be very different from one point to another leading to very different corrosion rates within short distances over the building for a given metallic material. The same conditions on one location lead to very different corrosion behaviour for two different metallic materials : copper corrodes less in autumn than in winter while steel corrodes more. During the period of testing the corrosion rates varied by a factor of 5 for copper and by a factor of 3 for steel over the building.

For the chosen locations, the time-of-wetness changed by more than two orders of magnitude and the dry sulphur deposition by a factor of almost 3. At every location, the corrosion rates, the time-of-wetness and the dry sulphur deposition are lower than the rates measured on the ASTM rack showing that the roof is, in the case of this building, the most corrosive location. The corrosivity of each location can be more or less related to the general climatic environment, namely wind direction in the case of a free-standing building. No simple correlation has been obtained between corrosion rates and parameters like time-of-wetness and SO_2 deposition showing the complex interactions of all environmental parameters. The large variation of the corrosion rates shows that extrapolation of the results from standard atmospheric testing to real structures appears difficult. More testing incorporating aerodynamic studies are necessary in order to adapt damage functions obtained through standard testing and laboratory testing to real structures.

7.4.2.3 Microclimates studies on a historic building in Philadelphia (Dolske,1987)

Within the NAPAP, another very relevant and essential experiment is currently being done at the Philadelphia Merchants' Exchange and is not yet fully reported. The purpose of this project is to monitor the correlation between the diurnal timing of the wetting/drying cycles and the temporally-varying airborne concentrations in the local environment for several different parts of the exterior of this building. Parameters like air pollutant concentrations, temperature, relative humidity, stone surface temperature, stone surface wetness, wind velocity and solar radiation intensity are measured. Soluble surface deposits are also sampled at those locations. The results of this monitoring and the study of the weathered marble will enhance considerably the understanding of materials performance in real life situations. This experiment will also provide valuable information on the range of conditions that exist on actual buildings.

7.4.3 What records exist of pollution data that can be used to evaluate potential damage to materials ?

Data presented by Sereda (1986) is valid as a general guide. Since NRC has discontinued monitoring sulphation rate at the exposure sites, there remains only the NAPS (currently CAPMoN) monitoring program. Tables compiled by Sereda (1986) from NAPS have not been updated for this report because the data are not considered very relevant and because many concentrations are at a level below detection limits.

The two-year study in S.E. England at 25 sites by Jaynes and Cooke (1987) provides a guide for collecting background data on pollution and weather factors and the corresponding stone deterioration. This study did show a correlation between weight loss of stone and SO_2 level, confirming that SO_2 is a dominant factor in stone deterioration. They concluded that sulphation was responsible for 39% of Portland stone loss and 44% of Monk's Park stone. This is in contrast with Lipfert' (1989c) conclusion from the NAPAP data that sulphation was responsible for 10% loss. However, these data would have provided better correlation if the SO_2 deposition rate or flux had been maesured. Mirwald et al. (1988) obtained good correlation between SO_2 deposition on different stones of the Cologne Cathedral and the flux as measured by the IRMA method.

Brimblecombe and Rodhe (1988) present data on historic trends in SO_2 pollution levels for London, derived from the equation (based on a model) :

$$C = 0.135\ F\ Q\ d^{(-1.68)}$$

where C is the annual mean concentration of SO_2 ($\mu g/m^3$), F is the amount of pollutant emitted per unit weight of fuel, Q is the annual amount of fuel burnt (tonne per annum) and d is the city diameter (km.). This calculation assumes a mean wind speed of 5 m/s. This model also assumes that all SO_2 is locally produced. The levels of SO_2 derived by this equation show an increasing trend reaching a peak of 603 $\mu g/m^3$ in 1900 and decreasing to 386 $\mu g/m^3$ by 1925. Jaynes and Cooke (1987) give a value of 74 $\mu g/m^3$ obtained in the mid 1980s. Thus levels of SO_2 have probably decreased by an order of magnitude in London in the past 100 years. Mirwald et al. (1988) give levels of SO_2 as measured in different locations in Cologne during the period 1965 to 1980. The region where the Cathedral is located experienced a decrease of SO_2 from 80 to 70 $\mu g/m^3$. The question remains, what is the "safe" level to slow the deterioration to a rate that would allow the preservation of stone for centuries.

Such historic research, based on indirect evidence, should be pursued and should include records of maintenance and restoration on key historic buildings to provide the bases for estimating the risk to historic structures due to pollution.

7.5 RECORDED EVIDENCE OF MATERIALS CORROSION AND DETERIORATION ON EXISTING STRUCTURES

7.5.1 Metals

Little evidence of materials corrosion on structures is recorded in the literature. Baboian and Cliver (1986), having been involved in the restoration of the Statue of Liberty, cite some effects related to acid deposition. Sherwood et al. (1987) have started to study the degradation of some bronze statues located in the Northeastern U.S., especially the 52 replicas of the "Hiker" where general corrosion and pitting could be attributed to acid deposition, the more corroded statues being located in the more polluted environment. Eiselstein and Caligiuri (1987) did a thorough analysis of the corrosion of the suspension cables of the Williamburg Bridge in New York City. They attributed some important pitting and localized corrosion,

resulting in a loss of load-bearing capacity, to the low pH of the rain in conjunction with the chloride deposition coming from the nearby coast. Fishman et al (1987) did a detailed study of the atmospheric corrosion of architectural copper and its alloys at Yale University. The presence of contaminants, combustion products in power plant and incinerators effluents, accelerates greatly the rate of corrosion of panels located downwind from the pollution sources. Since at least some of these contaminants are acids, their influence is therefore shown here. Judging from some lectures given at the 1989 Conference of the Association for Preservation Technology, some cases of degradation, followed by restoration through private firms, could have been caused by acid deposition, but the cause of deterioration has seldom been thoroughly investigated and almost never reported in the open literature due to lack of time and money. Other cases were explicitely attributed to acid rain (Weaver, 1989) based on materials analysis having revealed high concentrations of sulphate (on copper flashings, for instance).

7.5.2 Protective coatings

No reported case studies have been found of paint weathering that might be identified with acid rain deposition. The NAPAP, although extensive, did not include any studies of paint performance on structures. Smith et al. (1987) point out the importance of surveying the situation in the field to assess the importance of various modes of failure and various strategies and motivations for repainting.

7.5.3 Stone and masonry

A number of case studies of stone deterioration on cathedrals and monuments have been carried out in recent years, as has been documented in section 7.2, but only a few are specific enough to show the relationships between material characteristics, deterioration progress, including analysis of products and the measured levels of pollution (Brocco et al., 1988; Mirwald et al., 1988; Anderson, 1988; Haber et al., 1988). These type of studies are very productive to allow the comparisons between different climates and different levels of pollutants.

The study of the 700 years old Orvieto Cathedral by Camuffo and Bernardi (1988) may point the way to determine what are the "safe" levels of pollutants in the environment. The stone

on this cathedral shows no significant sulphation although some biodegradation is taking place due to lichen growth. The authors state that the pollution levels are very low but have not measured it. This should be done at Orvieto and other similar locations where there is no evidence of sulphation on old stone structures. Such case studies will enable the separation of the effect of pollution from deterioration caused by physical and chemical processes other than due to pollution.

7.6 DAMAGE ASSESSMENT OF MAJOR ECONOMIC MATERIALS EXPOSED TO THE ENVIRONMENT AND THOSE AT RISK

To establish the economic loss due to corrosion and deterioration involves the following : the development of damage functions for each class of materials, applicable to those materials when exposed on buildings and structures in the various environment ; an inventory of such materials on the stock of buildings and structures and a unit maintenance/replacement cost. Because of the lack of any measurements of corrosion and deterioration on actual buildings and structures nor any measurements of the distribution on buildings of environmental parameters such as time-of-wetness and SO_2 flux levels, the NAPAP can not provide cost data applicable directly to existing or future stock of buildings and structures. Various studies cited in this report aim to quantify the extent of damage caused by various levels of atmospheric pollution, but none yield the required specific data.

7.6.1 Is forecasting the cost of material damage possible?

Despite the general limitations of existing data, as stated above, Lipfert (1987), based on NAPAP data, developed a number of materials damage functions for paint, zinc, copper, steel, aluminium, stone and mortar. The author made a case study of the annual materials damage costs for New Haven, CT for comparison purpose. The unit cost factors used in this comparison were : repointing \$1/ft^2 (\$10.76/m^2) but only 15% of the total area is affected; repainting mortar \$3/ft^2 (\$32.27/m^2); replacing galvanized steel \$4/ft^2 (\$43.03/m^2); replacing stone facing \$22/ft^2 (\$273/m^2). Annual material damage cost was estimated at : paint \$3.95 million, galvanized steel \$2.2 million, mortar \$1.24 million, stone \$0.6 million for a total of \$8 million/year or about \$20 per capita/year.

Horst et al. (1987) collected and analysed information to provide estimate of damage within selected urban areas in terms of materials/use combinations and building types. Four materials (paint, zinc (galvanized steel), mortar and stone), seven uses (walls, roofs, chimneys, gutters, downspouts, fencing and window-trim), and four building types (single and multiple family residences, commercial and industrial buildings and tax exempt buildings) were examined. The estimate of annual paint damage in New England is $107.1 million (62%) out of a total (for all four materials) of $162.8 million. The estimate for 17 states amounted to a total of $2.25 billion and for paint alone $1.179 billion. The authors concede that the uncertainty in these estimates span at least an order of magnitude.

It has been accepted for many years that paint or protective coatings represent the class of materials that is at the highest risk from environmental damage. As such it represents the highest potential damage cost due to pollution, at least 50% of material cost, but it has not received the high priority it deserves in studies involving atmospheric pollution. Only towards the end of the NAPAP, a concerted effort was made to provide supplement data on paint, but only preliminary results are available at present. Smith et al. (1987) criticized the values of damage to paint generated by the NAPAP, as having an uncertainty factor of about 100, because it did not consider "catastrophic" failure related to chipping, cracking, peeling or discoloration, which are the most likely modes of failure. These modes of failure may or may not be related to levels of pollution.

Hollander and Lanting (1986) present estimates of total costs from damage to metals and painted metals due to air pollution. The estimates around 1970 vary by a factor of 3 to 4 with an overall average value of $6 (1980) per capita per annum. Studies around 1980 indicate a damage of roughly $2 (1980) per capita per annum. This apparent decrease in damage costs is due partly to a reduction of ambient SO_2 level and to a more critical use of damage functions for paint. The authors concede that the damage estimate for painted surfaces and stone are highly unreliable, because the effects of acid deposition cannot be separated from natural phenomena.

Passaglia (1986) discussed various estimates of economic loss due to corrosion of metals that can be attributed to air pollution based on NBS and EPA studies and concluded that the extra corrosion costs of metals associated with air pollution are about 0.15% of the GNP, or 4% of the total corrosion loss.

Theoretical considerations of economic assessment as carried out by Lipfert and Wyzga (1986) and assessment based on damage functions derived from the NAPAP as carried out by Lareau

et al. (1986), concluded that these estimates have a high degree of uncertainty and require checking against actual deterioration rates of real buildings.

It can be concluded that an accurate estimate of the cost that can be attributed to different levels of pollution is far from being realized. The best that can be said is that the cost is significant and may be in the range of $1 to $40 per capita per annum (assuming an uncertainty factor of 2 applied to low and high values given by different workers).

7.6.2 Inventory of materials exposed to the environment

Lipfert (1989b) prepared an extensive internal report for EPA, in which he presents resumés of surveys compiling data on : types of paints used, their cost, the amount used, modes of failure and life cycle. These surveys showed that residential buildings are the most economically important subset of painted structures in the U.S. for painting costs. In August 1981, a survey showed that 70% of the sample (80% of the respondents) had homes which required exterior painting. The average time since the last painting was about three years. 65% of these homeowners did their own painting, 27% used professional painters, 65% used latex and 28% used oil-based paints. 64% were satisfied with their paint job, and 36% reported some peeling. Peeling was the most frequently mentioned problem.

In 1987 the in-place value of architectural coatings in the U.S. was $ 24.1 billion of which about 18% was maintenance expenditure. Whereas such surveys give some idea of the value of materials used, there is no indication of the cost due to pollution. Some of the data from surveys indicated that peeling at higher pollution levels has a shorter induction period than at lower air pollution levels.

Crouch and Catalano (1988) prepared an internal report for EPA on the study of the distribution of galvanized steel in the U.S.A. This study included the following applications : roofing, siding, gutters, fencing, pole line hardware, guard rails and storage facilities. This study found 1,076 km^2 of bare galvanized steel in place nationwide extrapolated to 1990, with a high estimate of 1,461 km^2 and a low estimate of 261 km^2, most of which is fencing. Bare sheet material range from 124 km^2 to 481 km^2.

7.7 METHODS USED FOR MONITORING POLLUTION

Most pollution data currently available, give values of concentration of SO_2, NO_x and ozone in ppb, pphm or $\mu g/m^3$. However, what is important to the analysis of the effect on materials is the rate of deposition (flux or dose) on the surface of a given material. The flux is derived from the product of concentration and deposition velocity. The deposition velocity is dependent on the nature of the material, relative humidity in the air (or, more correctly, the surface wetness), rougness of the surface, wind velocity, etc...

7.7.1 Dry deposition-wet deposition

The NAPAP involved much effort to measure the dry and wet deposition of various constituents of atmospheric pollution. This was possible by collecting and analizing the runoff from samples exposed to total (wet and dry) deposition and from samples exposed only to dry deposition (Edney et al., 1988a). This exposure system combined with collection of runoff, is a very helpful technique to determine the deposition rates of pollution species as well as the rates of reactions occuring under dry and wet deposition. However, the standard exposure of small samples 30 to the horizontal does not represent any surface on real structures. Chamber studies as part of the NAPAP have been started to measure the velocity of deposition on different surfaces under a variety of simulated atmospheric conditions.

Graedel (1987c) presented data from analysis of precipitation occuring in the form of fog, rain, dew and snow. His data show pH in fog deposited moisture as low as 2.3, and dew pH of 3.5. Fog provides very high concentration of all constituents of pollution : e.g. $NH4^+$ = 370-10500 micromoles/liter as compared to 0.1 to 39 in rain. This paper shows that SO_2 in the U.S., during the period 1975 to 1983, decreased from 15 ppb to 10 ppb, while NO_x concentration at 177 sites was at a mean of 28 ppb. Data in this paper suggests that total wet deposition from rain water may not reflect the influence of various ions correctly.

7.7.1.1 What method can be used to monitor dose (flux) directly?

The discussion of this question by Sereda (1986) is essentially valid. Noël et al. (1989a, 1989b) report on the performance of sulphation plates (containing lead peroxide) and

nitration plates (containing triethanolamine) (passive monitors). This work concludes that sulphation plates are excellent for monitoring the deposition of SO_2 in a real environment for periods of at least three months whereas nitration plates are unsuitable and should not be used for atmospheric corrosion studies. Hechler et al. (1989a) using sulphation plates, time-of-wetness sensors and steel and copper specimens, exposed at 44 locations on a building, monitored successfully the variations in the conditions of the microenvironment. This type of monitoring is vital to enable data collected at exposure sites to be applied to materials on buildings.

7.7.2 Monitoring environmental parameters : time-of-wetness (TOW)

It has been documented extensively that TOW is one of the most important parameters in corrosion and deterioration of materials. Despite the fact that an ASTM standard G-84 exists for TOW sensors, monitoring of this parameter has not been general. Hechler et al. (1989b) have shown that the sensors give precise values of the rain TOW, and that reliable values of condensed humidity can be obtained if proper selection of the sensors is made. Hechler and al. (1989a) showed how monitoring of TOW on large number of location on a building using TOW sensors is viable and provides important information.

See et al. (1988) report on the development of a variety of new sensors for measuring the TOW. Much field testing will be needed to prove their reliability.

It should be noted that the extensive NAPAP did not include monitoring of the TOW at the five exposure sites. This is considered a serious omission.

In the NAPAP, as in many other past and current corrosion exposure programs, relative humidity (RH) of the air is monitored and TOW is determined from duration of RH in excess of 80 or 90%. This method is unsuitable to monitor the TOW on a building.

Benarie and Lipfert (1986) developed an equation to obtain TOW from number of days per year with precipitation and average temperature higher than 0 C. This gave values of TOW surprisingly close in agreement with experimental values. However, no details are given of how the experimental values were obtained.

7.8 RESEARCH NEEDS.

Although significant advances have been made in the understanding of the various processes of corrosion and deterioration since 1986, brought about because of more sophisticated approaches to the measurement of material changes, analyses from runoff from the surfaces, chamber studies and analyses of new data, nevertheless, the state-of-the-art does not provide an answer to the main question : what part of the observed corrosion and deterioration in the Canadian environment can be attributed to the effects of acid deposition. This is particularly true of the class of materials called protective coatings or paint and yet this class represents over 50% of the total economic loss (based on surveys and estimates of damage).

7.8.1 What testing is required ?

As stated by Sereda (1986), a network of suitable buildings, located in all the major cities across Canada, should be selected to serve as sites for monitoring levels of pollution and microclimates factors. Such a monitoring program must be coordinated with characterization and monitoring of material damage. Laboratory and field testing coordinated with building studies are a necessity.

7.8.1.1 Recommendation for monitoring the distribution of the time-of-wetness

Time-of-wetness is a very important microclimate factor that must be quantified if damage to materials is to be accounted. Suitable sensors and methodology has been developed and should be used for monitoring the distribution of the time-of-wetness on buildings.

7.8.1.2 Recommendation for monitoring the distribution of pollutants deposition flux.

Although SO_2, NO_x, ozone and particulate matter are identified as the precursors that can contribute to materials damage, the most important one of these is SO_2. It is the only one for which a satisfactory passive monitor in the form of sulphation plate, is available and should be used in monitoring the distribution of SO_2 deposition on buildings. Research must continue to find suitable passive monitors for NO_x, ozone and particulate matter.

7.8.1.3 Recommendation for monitoring the distribution of chloride deposition.

Chloride deposition is a special case representing both the man-made source and a natural source. In coastal areas, in close proximity to the sea, chloride deposition must be monitored because its contribution can mask that of acid deposition. The man-made source of deicing salts can be particularly damaging to steel reinforcing in concrete on bridges and parking garages and should be properly identified and not confused with effects of acid deposition.

7.8.2 Materials at risk

As discussed by Sereda (1986), materials on structures experience different degrees of risk.

7.8.2.1 What is the state of materials on buildings ?

Surveys should be undertaken to establish a ranking for the degree of risk that various materials experience. Such a data base would establish the priority for future research and ensure maximum cost benefit.

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