

Climate Change VIS-VIS-Air Pollution

R.H.Pazare, N.S.Raman

Abstract— There are potential adverse effects of air pollutants on buildings, museum collections, artwork and ancient monuments. The study focuses on the various impacts of air pollution on these historic buildings. Sulphur dioxide, nitrogen dioxide, acidic rain, ozone, and fine particulates are the greatest culprits. Various precautionary measures for mitigating the damage are also highlighted.

Index Terms— Air pollution, damage, heritage.

I. INTRODUCTION

The first recorded outcry against air pollution was in Great Britain in 1306 A.D. when King Edward I banned the unrestricted burning of "sea" coal during parliamentary sessions in London. In 1307, a violator to this prohibition was executed for filling the air with a "pestilential odour through the use of coal". The burning of this low quality coal had caused high concentrations of sulfur dioxide and black smoke particles in the air resulting in serious health impacts and blackening roof tops. England, thus had the first smoke abatement law in recorded history. By 1661, a pamphlet entitled the "Fumifugium" was published by the orders of King Charles V. "Furnifugium or the Inconvenience of the Aer and smoke of London Dissipated together with some Remedies Humbly Proposed" was an essay written by John Evelyn, advocating the use of clean fuels and good sanitary urban planning 1. In spite of all these measures, the use of coal persisted and was worsened by the Industrial Revolution, which produced point sources of larger emissions from various industrial processes involving the burning of coal for energy production with the concomitant large scale emission of sulphur dioxide and black smoke in the atmosphere. Generally this was allowed to continue in small and large sources well into the twentieth century without too much abatement except for elevated stacks. With the passage of time, large emissions of sulphur dioxide and smoke particles overloaded the atmosphere and during temperature inversions in stable pressure situations and stagnant air, notorious air pollution episodes occurred 2'3. The 1952 London episode was the worst in history resulting to over 4000 deaths in just five days. This prompted the enactment of more stringent Air Pollution Acts in England and other countries thereby beginning the modern history of air quality management. Though the components of air pollution have changed over the years, and industrial sources now include toxic gases and metals; yet burning of coal remains a very important source of air pollution. Vehicular traffic sources have so expanded rapidly over the past decades that traffic activity in most industrialized western urban cities has increased over ten-fold. In the developing nations, the rate is even more.

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Other classical air pollution incidents include the photochemical smog in Los Angeles and Mexico City, the Bhopal gas leakage in Bhopal, India, and the Chernobyl nuclear episode in Ukraine, in the former USSR.

Table 1: Air Pollution Episodes

Locations	Date	Pollutants	Deaths
London, England	Dec 9-11, 1873	SO2	650
London, England	Jan 20-29, 1880	SO2	1,176
Meuse Valley, Belgium	Dec 1-5, 1930	SO2, SPM (smog)	63
Donora, PA, USA	Oct 26-31, 1948	SO2	20
London, England	Nov 26-30, 1948	SO2, (Smog)	700
Poza Rica, Mexico	Nov 24, 1950	H2S	22
London, England	Dec 5-9, 1952	SO2, SPM (Smog)	4,000
London, England	June 3-6, 1955	SO2, SPM (Smog)	1,000
London, England	Jan, 1956	SO2, SPM (Smog)	180-200
London, England	Dec, 1957	SO2, SPM (Smog)	180-200
London, England	Dec, 1962	SO2, SPM (Smog)	700
New York, USA	Nov 24-30, 1966	SO2, SPM (Smog)	168
Seveso, Italy	July, 1976	Pesticide Explosion	>200 Affected
Bhopal, India	Dec 3, 1984	Pesticide leakage	>10,0000
Chernobyl, Ukraine	April28, 1986	Nuclear Leakage	>2,000
Mississippi, USA (many states around)	August, 1969	Episode-104 (Air pollution haze)	Hundreds affected by cardiovascular diseases

Air Pollution has dangerous consequences on humans, animals, plants and vegetation generally, on the physical properties of the atmosphere with the resultant corroding effects on metals, rubber cracking, soiling and eroding of building surfaces and the deterioration of monuments and other works of art. These effects have long been recognised by mankind 4. In this review, discussions will be concentrated on the effects of air pollution on all forms of material heritage-marble stones, building materials, works of art in or outside museums and monumental edifices-an area that has suffered from literary neglect.

There are many mechanisms through which air pollutants attack their targets. These include abrasion from high velocity particulate matter, deposition on Interfaces of the targets and the subsequent attempts to remove these deposits from the interface of these materials, direct as well as indirect chemical attacks of some of the air pollutants which react irreversibly with the surfaces or materials of the works of art, and electrochemical corrosion.

These mechanisms are accelerated by the moisture in the atmosphere since most of these movements are wholly or

partially exposed, temperature and sunlight which accelerate the chemical changes and air movement.

II. BUILDING STONE DECAY :

Vales⁵ made short-term exposures of limestone samples in an urban environment. After two months significant amounts of gypsum were found on stone samples which had been sheltered from rainfall, but the samples exposed to rainfall had negligible gypsum development, but showed considerable micro scale evidence of dissolution. Cobourn et al⁶ measured the sulfur dioxide deposition velocity of marble and dolomite stone surfaces in humid atmosphere. For both types of stones, the deposition velocity increased significantly when condensed moisture was observed on the stone surface. Chemical analysis of the stone samples indicated that the sulfur dioxide deposited reacted with the stone material to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) on the marble surfaces but formed both gypsum and epsomite [$\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$] on the dolomite surfaces.

To evaluate the effects of the environment on the weathering of historic buildings in the Mediterranean Basin, Torfs and van Grieken⁷ carried out an elaborate study on four monuments, with specific interest directed on the action of air pollen and marine salts. The composition of the atmosphere around the monuments was investigated by monitoring the aerosols and the total deposition. They combined these results with the stone decay phenomenon to interpret the deterioration at the respective monuments. In Eleusis, Greece, a highly industrialized area, high concentrations of heavy metals and sulphate were found in the aerosol and deposition and in the decay layers of the stone, while the marine influence was obscured, in spite of its location close to the sea. In Malta and in Cadiz (Spain), the influence of the sea dominated in the stone weathering process, whereas in Bari (Italy), next to the effects of the marine aerosol on the stone decay inside and outside the building, high concentrations of sulphate were observed on the outside stones. Thus, the aerosols and depositions reflected a relatively small influence of anthropogenic-derived elements thus pointing out the action of gaseous sulphur dioxide on the stones. Because dry deposition of gases plays an important role for the deterioration of stone materials, and a better understanding of the process involved would improve our ability to maintain stone monuments and building, Henriksen⁸, as a part of EU-project, carried out an investigation with four calcereous stone types. He exposed them outdoors at two sites in Norway for two years. The exposure had been carried out in sheltered position and the amount of reaction products and the penetration depths of sulphur dioxide into the stones were determined as soluble sulphate after half a year, one year and two years. Even if most of the sulphate was found in the upper 0.3 mm of the stone, there was an increase in the sulphate content in stone, even down to the centre of the stone sample. In laboratory tests with sulphur dioxide, nitrogen dioxide and changing relative humidity, the synergistic effect of NO_2 and the importance of the relative humidity were investigated.

To investigate the response of porous carbonate building stones to acid deposition during a short time exposure period and the characteristics that influence their reactivity and/or durability, Grossi et al⁹ exposed several carbonate porous stones used in Spanish and English monuments to English urban and suburban environments. In each location, they were

both exposed to and sheltered from rainfall. Monthly analyses were carried out in order to investigate any possible sign of reaction. In addition, some physical properties of the stones relating to transfer of moisture were determined. Results indicated that the reactivity of these stones was relatively high, and significant signs of reaction were detected within only a few months of exposure. Under the same environmental conditions, the response and reactivity of porous carbonate stones were determined with their petro-chemical characteristics.

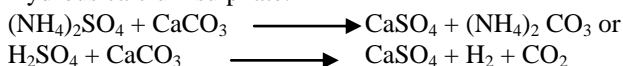
Nord and Tronner¹⁰ reported on the effects of acid rain on sandstone of the Royal Palace and the Riddarholm Church, Stockholm. They investigated the deterioration of the two kinds of sandstone for the two 18th-century buildings in central Stockholm: the Royal Palace and the Royal Carolean Burial Chapel (KarolinskaGrankoref) annexed to the medieval Riddarholm Church. They observed signs of serious decay such as gypsum formation, pulverised surface exfoliation, discolouration and salt efflorescence. The sides, which are built of the more resistant quartzitic Roslagen displayed some discolouration, cracks and slight exfoliation. On the whole they analysed some 300 samples and found that the surface concentrations of sulphur was highest at the ground level and at rain-sheltered positions. Chemical and sulphur isotope data indicated that the stone decay to a large part might be attributed to anthropogenic sources like acid deposition and vehicular traffic.

Despande et al¹¹ studied the status of marble erosion rates due to air pollution in major Indian urban cities. They confirmed that the processes of deterioration, corrosion and degradation of any material was a complex phenomenon governed by many factors such as chemical or electro chemical reaction between a material and its environment and that the degree of corrosion exposed to the atmosphere depended primarily on the moisture content and temperature as well as pollutants in the air such as SO_2 , NO_2 , SPM, O_3 and other gases. They further noted that the mechanism of atmospheric corrosion was dependent on the material involved, atmospheric meteorological conditions and pollutants present in the atmosphere. The local topography of the site, temperature, rainfall, wind speed etc. are also important factors in addition to the physical characteristics of the exposed material. They finally noted that weathering and deterioration of building stones had accelerated in the 20th century owing to air pollution which is the result of modern urbanisation and industrialisation.

III. BUILDING MATERIALS :

Seiz-Jimenez¹² of Institute de Recursos Naturales y Agrobiologia de Sevilla, Spain, in his studies on the deposition of the organic pollutants on historic buildings, noted that the black crusts coating the surfaces of building materials located in polluted urban environments, combined all kinds of organic compounds present in aerosols and particulate matter. Wet and dry deposition processes, combined with gypsum crystal growth, resulted in dirty, grey-to-black crust formation, in which aerosols, spores, pollen, dust and every class of particulate matter were entrapped in the mineral matrix. Analysis of the mineral compounds, extracted from the black crusts demonstrated them to be mainly composed of molecular markers that are characteristic of petroleum derivatives. The composition of each crust was governed by

the composition of the particulate air borne pollutant in the area. The two mechanisms for transferring pollutants to material surfaces are defined as Dry and Wet Deposition. Dry Deposition proceeds without the aid of precipitation and denotes the direct transfer of gases and particulates to the earth's surface. Dry deposition is a local phenomenon and consists of accumulation on the stone surface of air borne secondary pollutants from the atmosphere transported by wind and turbulence. Dry deposition of pollutants can cause significant deterioration of exposed surface. It is a continuous process and is accelerated in the presence of moisture, for then, the particles have a greater chance of adhering to the surface it also depends on the porosity of the stone material and its chemical nature. Its mechanism of reaction involves the sulphate, in the form of ammonium sulphate or sulphuric acid, reacting with the calcium carbonate of the stone to form anhydrous calcium sulphate.



The calcium sulphate in the presence of moisture dissolves and penetrates the matrix of the stone. After many years of crystallization, the accumulation of the pressure produced becomes large enough to break the stone.

Wet Deposition :

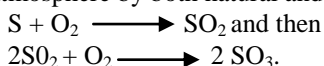
Wet deposition on the other hand encompasses all processes by which air borne pollutants are transferred to the earth's surface in an aqueous form i.e. rain, snow or fog. In this case, pollutants can become incorporated by two different mechanisms: in-cloud scavenging (rain-out) which is the main route for wet deposition and occurs when pollutants are included in the droplets developing within a cloud; and below-cloud scavenging (wash out), which involves the take-up of pollution by precipitation as it falls from the cloud. This is a much less efficient removal process than in-cloud scavenging¹³. Nevertheless, wet deposition is considered as an important pathway for the removal of pollutants from the atmosphere and also responsible for building material weathering. Corrosion due to wet deposition is a long-distance transportation.

ACID RAIN :

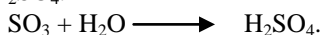
This is another name for wet and dry deposition. Acid rain, snow, dew, fog, frost and mist, represent the wet form of deposition, while dust particles containing sulphates and nitrates settled on earth is called dry deposition. However, the wet rain is much more common.

How Acid Rain is Formed :

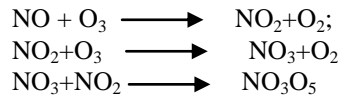
Every source of energy that we use be it coal, fuel wood or petroleum products has sulphur and nitrogen. These two elements, when burnt in the atmospheric oxygen are converted into their oxides (SO_2 and NO_x) which are highly soluble in water. Oxides of sulphur and nitrogen enter the atmosphere by both natural and anthropogenic sources.



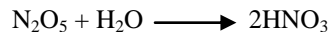
Sulphur (v1) oxide in humid atmosphere, forms droplets of H_2SO_4 .



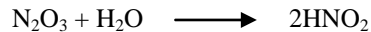
The reaction is known to be catalyzed by transition metals (Fe, Cu, Mn) and soot particles. In the case of nitrogen, the following reactions are evolved:



Under humid conditions, N_2O_5 reacts with water vapour to form HNO_3 .



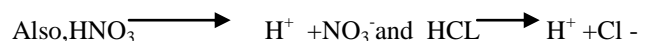
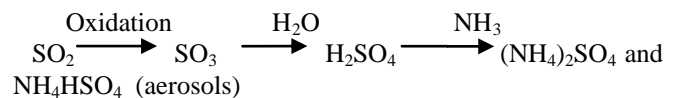
, a strong acid with high deposition rate. It is of principal interest for corrosion. Some HNO_2 is also formed.



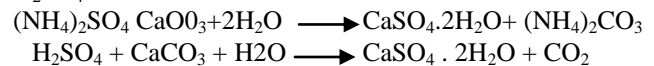
Sulphuric acid and nitric acid thus formed combine with HCl (emitted from natural and man-made sources to generate precipitation, which is commonly referred to as Acid Rain. Normally, unpolluted rain is weakly acidic and has a pH of 5.6 because CO_2 from the air reacts with water to form carbonic acid (H_2CO_3), as well as acid from volcanoes, swamps and planktons in the oceans. But acidity in rain has increased very sharply over the past 200 years as a result of industrial processes.

Acid Rain And Deterioration Of Materials

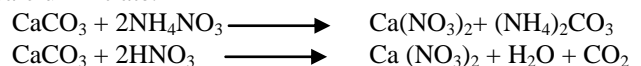
Sulphuric acid, Nitric acid and Hydrochloric acid in acid rain contribute to the generation of sulphate, nitrate and chloride ions.



Thus, sulphate in the particulate matter reacts with calcium carbonate of the stone in the form of ammonium sulphate or H_2SO_4



This calcium sulphate in presence of moisture dissolves and penetrates the matrix of the stone. During dry period, water evaporates and salt crystallizes in the pore spaces. Successive cycles of wetting and drying results in the accumulation of salts in the interior of the stone. After many years, the crystallization pressure produced as result of this accumulation becomes large enough to break the matrix of the stone. Continual growth of salts broadens the cracks and weakens the stone. The nitrate particles and nitric acid aerosol are formed by gas phase oxidation of NO_x , in the presence of O_3 and water droplets. Prolonged exposure of nitrate particulates and nitric acid weaken the building material by converting calcium carbonate of limestone to water soluble calcium nitrate.



During wet spells, this calcium nitrate is removed by rainwater thus exposing fresh surface for further interaction. The role of chloride particulates in deterioration of stone is not clear. However according to Junge and Eriksson¹⁴, in a marine environment where aerosol particles are also rich in magnesium chloride, deposition can take place on surfaces at 80% of relative humidity. Generally in nature, sodium chloride and magnesium chloride are associated with dry deposition and latter being highly hygroscopic readily goes into dissolution with atmospheric moisture and finds its way into the micro-crevices enhancing the damage of the stone. Also in dry weather, chlorides deposited on the particles, cause efflorescence. The stresses developed due to

crystallization, dissolution and re crystallization, deteriorate the articles. Chlorides also cause electro-chemical corrosion of metal objects. Formation of copper (I) oxide, than copper (II) oxide and finally hydrochloric acid, bring about a damaging cycle.

Hamilton and Alansfield¹⁵ reviewed the rate of soiling of exposed surfaces due to the deposition and accumulation of particulate matter from the atmosphere. Samples of white painted wood were exposed for 110 days in the ambient atmosphere. Separate samples were sheltered and unsheltered from rainfall, and reflectance was measured on a daily basis. They compared their results with published studies in the ambient atmosphere in the USA and in a road tunnel in the U.K. and found that existing models were satisfactory for predicting soiling in a tunnel, but underestimated soiling in an ambient situation, for which a revised formula was proposed. They concluded that rainfall generally produced a cleaning effect, but redistribution of washed-off material could produce enhanced soiling.

In 1986, the National Materials Exposure Programme (NMEP) was set up within the United Kingdom to investigate the effects of acid deposition on buildings and building materials. In response to this, Butlin et al^{16,17} had chosen thirty sites which represented a range of geographical and pollution climates. Each of these sites met a minimum metrological and pollution monitoring regime (including SO₂ and NO₂). After four years, other sites were included with less frequent data collection and some sites removed. At each site, samples of three types of stone, mild steel, painted steel, Cu, Al and galvanized steel were exposed with some of the stone sheltered from direct precipitation. Samples were removed periodically for analysis and dose-response relations derived for different materials in the form of: Decay rate = a [SO₂] + b [H⁺] + C [Rainfall] + d, thereby confirming the rate of deterioration is a direct function of the concentration of sulphur dioxide, the acidity generated and moisture available as well as other damaging factors. These dose-response relations were used to develop critical load maps for materials for the United Kingdom. Data has been collected for up to 8 years, some for the United Nations Economic Commission for Europe (UNECE) task force Programme. The researchers undertook laboratory tests using an atmospheric flow chamber and were able to include additional materials like mortar on some other sites. A further set of 8 sites was used to assess the effects of ozone on a range of organic materials — polyvinyl chloride, polycarbonate and sealants. They confirmed the dominance of dry deposition of sulphur dioxide as the main decay process for sensitive material in areas of significant pollution.

Haagenrud et al¹⁸ carried out an assessment study of air quality and metallic material degradation in the Sarpsborg / Fredrikstad regions in 1982-1983. They found out that most of the dose-response functions and mapping for UNECE on materials, for unsheltered exposures, have the same form as for zinc

HL = a + b TOW [SO₂] [O₃] + c rain [H⁺], where
 ML = Mass loss after 4 years exposure in g/m²
 TOW = Time of wetness (RH>80%, T>0°C) as time fraction of a year (8760 hrs)
 [SO₂] = Concentration, µg/m³
 (O₃) = Concentration, µg/m³
 Rain = Amount of precipitation, m/year and

(H⁺) = Concentration, mg/L

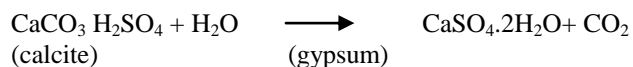
For zinc, which is used as an example here, the function is
 ML = 14.5 + 0.043 TOW (SO₂) (O₃) + 80 Rain (H⁺)

Issues pertaining to the environmental potential in decreasing the damage due to atmospheric corrosion and the evaluation of atmospheric corrosivity on the territory of the former USSR and Russia were considered by Mikhailov et al 19. They also discussed the most significant results obtained under the United Nations Economic Commission for Europe programme on the Effects on materials including Historic and Cultural Monuments. They concluded that the multiplicative to the creation of damage functions for materials and the developed conception of acceptable levels were good bases for mapping of the European part of USSR. The problems of mapping for the Asian part of USSR are not solved for extremely cold regions with low TOW. As for zinc, they determined the mass loss (ML) for sandstone as ML = 29.2 + 6.24 TOW (SO₂) + 480 Rain (H⁺). This still rests the damage to sandstone squarely on the direct concentration of sulphur dioxide accelerated by moisture and the associated acidity.

Sawangikar, Thakre and Aggarwal²⁰, in their studies on the effects of Air Pollution on building materials: Exposure studies on Indian marbles, observed that calcareous stone by their very nature would be more affected by the presence of acid air pollutants, mainly sulphur dioxide. According to them, the severe effects of sulphur dioxide appeared to be concentrated near the source of the effluents as revealed by the presence of gypsum (CaSO₄.2H₂O) on nearby ancient historical buildings and monuments even when exposed for a low concentration over time. Sulphur dioxide, now pervasive in the industrial world has further increased deterioration of marble. Acidic air pollutants like SO₂ when they come in contact with water form acids. The surface of marbles exposed to this acidic rain gets eroded slowly so that any carvings and surface details would get lost.

Associated Reactions

As stones are porous, water penetrates and reacts with crystal grains (calcite) to form gypsum (CaSO₄.2H₂O). A stone composed of smaller grains deteriorates faster than one with larger grains. The reaction is accelerated by the presence of impurities and defects in crystal lattice.



The gypsum formed dissolves readily in rain and penetrates inside where it crystallizes. In wet and dry seasons, the process of deposition and dissolution repeats and significant amount of salt is formed around the crystal boundaries. This exerts pressure large enough to break the stone. Continual growth of salt broadens the crack and further weakens the stone.

IV. MODES OF MARBLE DETERIORATION IN NATURAL ENVIRONMENTS :

Marble deterioration occurs in two modes, generally. In the first mode weathering take place where the marble is sheltered under domes and cornices and protected from direct impact of rain. Here a crust is found which after many years exfoliates due to mechanical stresses. But in the case of marble exposed to rain gradual reduction occurs, because the reaction product

is washed away by rainfall and fresh marbles is exposed to renewed action. The crusts are formed primarily due to sulphur dioxide, but the cumulative effect of all pollutants is more damaging. It is also observed that trace metals present in flyash e.g. Mn (II), Fe (III), and V (V) act as catalysts for the oxidation of SO₂ and in turn enhance the degradation of calcite into gypsum.

V. ART WORKS, MONUMENTS AND MUSEUM COLLECTIONS :

Meakiu et al²¹, under the United States National Acid precipitation Assessment programme, made a metallurgical and corrosion study of the fifty bronze replicas of the Hikar Statue cast by the Gorham Foundry, Providence, Rhode Island, between 1906 and 1966. To study corrosion damage on a microscopic scale, they developed a technique to take moulds of selected features on the statue. The moulds were examined by optical and scanning electron microscopy and surface profilometry. The overall approach had been the potential for quantitatively monitoring the local corrosion at selected sites over a period of years and also characterizing the impact of conservation procedures. In a parallel research programme, runoff samples were taken from selected Brigade Markers in a series of bronze tablets in the Gettysburg National Military Park. Parallel rainwater samples were also collected. Analysis of pH, metal content and various ion species in the runoff, yielded information on the total rate of corrosion as a function of dry and wet precipitation.

Ozone at the concentration found in the indoor atmosphere of many museums poses a fading hazard to the pigments used in the works of art. The ozone-control problem faced by museum personnel is unusual because indoor ozone exposure must be reduced to very low levels in order to protect the collections from accumulated damage over periods of 100 years or more. Cass et al²² in their studies, evaluated methods that can be used to protect museum collections from ozone damage. They examined control measures such as pollutant removal through ventilation system redesign, construction of display cases to protect the works, framing of painting, prints and water colours behind glass, selection of ozone-resistant pigments and application of binders and coating that will protect ozone-sensitive pigments.

Objects of Southern California Museums may become perceptibly soiled within periods as short as one year due to the deposition of airborne particles onto their surfaces. Methods of reducing their soiling rates include reducing the building ventilation rates, increasing the effectiveness of particles filtration, reducing the particle deposition velocity onto the surfaces concerned, placing objects within display cases or glass frames, managing the sites to achieve low outdoor aerosol concentrations and eliminating indoor particle sources. Nazaroff and Cass²³ accordingly combined a mathematical model of indoor aerosol dynamics and experimental data collected at an historical museum in South California to illustrate the potential effectiveness of their control techniques. According to the model results, soiling rates could be reduced by at least two orders of magnitudes through practical application of these control measures. They concluded that combining improved filtration with either a reduced ventilation rate for the entire building or low-air-exchange display cases is a very effective approach to reducing the soiling hazard in museums.

Lammel and Metzger²⁴ determined the dry and wet deposition of ionic trace substances and total carbon to the walls of a historical monuments (Salem Abbey, Germany) based on periodical collection of rain water samples and washing solutions from cumulative collectors (at 3 m above ground). They estimated that only a small fraction of about 1.5 - 3% of the precipitation 10% of the pollutants deposition (to a horizontal receptor area) reached the vertical collectors (at 3m above ground). With only 1/4 of the pollutants wet deposited, they concluded that dry deposition was more important. Hereby the building was a source of particulate material itself (sodium salts, CaCO₃). While the fluxes of dry deposited pollutants to the individual facades differed only very little from each other (with a preference to the East), the wet deposited fractions differ widely due to pronounced preference of precipitation from the west. Large fluxes of total carbon (C/S =9) were obviously not primarily related to carbonate stone weathering, but to airborne carbonaceous material. Thus, they finally concluded that the building was susceptible by stone decay in the forms of granular disintegration, dark encrustation and others resulting from both 20 physical factors (humid environment, the building's orientation towards the sun and prevailing weather) and chemical factors (dry and wet depositional fluxes of pollutants, albeit, at moderate concentrations).

Damage caused to materials exposed to the atmosphere constitutes one of the most important direct effects of acidifying air pollutants. Systematic field and laboratory investigations performed in the recent decade in many countries have contributed to a considerable increase in the knowledge of the mechanisms of the effects of pollutants, on the quantification of damage and in the assessment of the cost of damage. Besides the very important role of sulphur dioxide for general materials, Kucera and Fitz²⁵ also carried out studies of the direct or synergistic effect of NO₂ and O₃, which have contributed to the understanding of the complex pollution effects. Even if there are still considerable gaps of knowledge, it seems that NO₂ and O₃ may contribute in an important way to the deterioration of several materials in indoor environments which are important for, inter alia, electronic equipment, storage conditions and museums. Important knowledge has been gained from the International Cooperation Project (ICP) within UNECE, which is an extensive field exposure on 39 test sites. They obtained dose-response relations after 4-year-exposure showing the effect of dry and wet deposition on corrosion of several material groups. They also subjected to systematic studies, the effects of micro- and mesoclimate on corrosion of building materials like plaster and bricks in different positions on buildings and locations within an urban area. Results from their studies are used La. for assessment of so-called acceptable corrosion levels and for mapping areas where the levels are exceeded at different pollution scenarios, as well as for calculation of economic damage. Based on world studies for some city areas, tentative calculations of damage cost have been performed for the European regions. The indirect effects consist of increased corrosion due to water and soil acidification which are of importance in geologically active areas. Structures, which are in contact with water and soil, represent a very great capital investment and are of vital importance to the community.

Corrosion of bronze in soil is a well-known phenomenon. In particular, archaeological artifacts, which may remain in the

soil for thousands of years, are subject to severe corrosion. However, bronze objects excavated 50-100 years ago, seem to be less corroded than those found today. Therefore, recent pollution of the soil is suspected to accelerate the corrosion. In view of this, Tronner et al²⁶, started an interdisciplinary project in Sweden to search for correlations between the degree of bronze corrosion, corrosion products, general archaeological and environmental conditions and parameters, characterizing the soil chemically. They investigated three archaeological sites in Stockholm (Brika, Fresta and Valsta) from which they studied 33 bronze artifacts and related samples of soil. They analysed all the bronze products and the metal core by SEM/EDs and XRD, and identified metal oxides, carbonates, sulphates, chlorides and phosphates. They also classified each soil sample geologically and undertook a number of chemical analysis-including pH in water and KCl, resistivity, loss on ignition, exchangeable acidity, chloride, phosphate, sulphur contents, acid-soluble cations extracted in two different ways, etc. About 8000 data have been compiled in an EXCEL database. A statistical evaluation including multivariate modeling and analysis utilizing the SIMCA-S system was also undertaken. Though the results so far obtained were only tentative, but suggest that high accumulation of soot, sulphur and phosphate in the soil may have accelerated the corrosion of the investigated bronze objects, but they were not very clear about the influence of low pH-values (acidity) on the corroded materials.

Creighton et al²⁷, described the influences of particle size and rainfall on the deposition and soiling of surfaces with different surface glosses, orientations and exposures. According to them, the gradual and progressive soiling of structures exposed to the atmosphere is commonplace. Wooden homes require painting every few years for aesthetic purposes as well as for preservation, while public buildings, houses of worship and statuary require occasional exterior cleaning because of gradual soiling. Material soiling results from the deposition of aerosols, and both wet and dry deposition occur. Dry deposition mechanisms include gravitational settling, impaction, interception, diffusion, thermophoresis and electrophoresis. The particle size and orientation, exposure and roughness of the surface determine the dominant deposition mechanism. Wet deposition is not an important cause of surface soiling as precipitation removes particles from surface²⁸. Aged atmospheric particles are characterized by a bimodal size distribution of coarse and fine particles. Coarse particles tend to be inactive chemically and are removed by washout and run-off²⁸. A primary cause of building soiling in urban areas has been attributed to the fine particle mode²⁹. When fine particles contain carbon, they tend to be black and adhere more tenaciously to surfaces than do coarse particles. For example, particulate elemental carbon is adhesive, hydrophobic and tenacious²⁸. Lanting also observed that elemental carbon is usually 10-20% of the urban fine aerosol mass and that vehicular emission, particularly, diesel emission, are the major sources of urban black smoke²⁸.

Yocum and Kawecki³⁰, on their own part, observed that the soiling of buildings occurs over the years from fine particle deposition and is associated with low atmospheric concentrations.

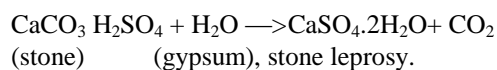
In their own contributions, Sharma et al³¹ observed that India has the largest number of archaeological sites of historical value in the world and that they are proud of this

vast and valuable treasure of sculptures, architectural pieces and monuments, which represented the golden era of art and culture. Preserving these monuments has posed a great challenge to modern day scientists³². While damage to these architectural pieces due to air pollution has been recognized for over three centuries all over the world³³, awareness of environmental problems in India, came about in the last two to three decades.

Gawalpanchi et al³⁴ reviewed the protection of museum displays from indoor pollution as a function of outdoor concentrations. They noted that besides the effects of pollutants on concrete structures, building materials, human and animal health due to outdoor pollutants, the pollutants that penetrate indoors equally deteriorate indoor materials, sophisticated equipment, films, paintings, drawings, books, fabrics antique costumes and other irreplaceable works of art. All creation follows the irreversible and inevitable course of decay, they noted. Damage to monuments of antiquity, and sculptures show the vivid evidence of the insidious effects of polluted atmosphere. As a result, specialists have removed these articles from the exterior to the indoors thinking that they would be safe inside.

VI. DAMAGE FUNCTIONS OF MUSEUM DISPLAYS AND OTHER INDOOR ARTICLES:

Air pollutants are unwanted by-products of the industrial age considered the main villain. Organic and inorganic material objects e.g., stones, metals, glass, ceramics, paper, wood, textiles, ivory, leather, etc., are generally displayed inside the museums. These articles undergo oxidation, reduction, hydrolysis, sulphonation, chlorination, etc. These reactions occur very slowly and as a result, the strength of the materials reduces thereby damaging them permanently. Sulphur dioxide is a most damaging pollutant. It gets converted into sulphuric acid and damages the articles made of stone, paper, wood and textiles. Formation of ammonium sulphate blooms the varnish layers, which react faster in the presence of light. The polymer structure of the paper-made article decomposes and deteriorates by hydrolysis and becomes yellowish, brittle and weak. The textiles made of cellulose also lose strength. The chemical composition of the stone changes due to sulphate resulting to damage. This is euphemically called 'Stone Leprosy'.



The leather goods become brittle and powdery due to the disintegration of collagen chain by sulphuric acid. The stone, plaster, siliceous articles, marble and wall paintings are converted to sulphate by the sulphuric acid, expanding its volume and cracking the articles. Metals, in the presence of moisture and sulphur dioxide, go into electrochemical corrosion. Even, very low concentrations of hydrogen sulphide, attack silver and copper articles. The silver is tarnished by the formation of sulphide, which changes and blankets the shiny appearance of the articles. Chlorides deposited on articles in dry weather causes efflorescence. The stresses developed due to crystallization, dissolution and recrystallization, deteriorates the articles. Chlorides also cause electrochemical corrosion of metal objects and damages textiles and papers. Formation of cuprous chloride rather than

cuprous oxide and then hydrochloric acid, brings about a damaging cycle. Besides these, chlorides also damage wood, ivory, ceramics and glass. Ammonia neutralizes free acidity at low concentrations and causes hydrolysis at higher concentrations. Cellulose in cotton and textiles is hydrolyzed and oxidized due to ammonia, while painted surfaces are damaged due to the formation of ammonium sulphate.

Ozone has very specific action on organic materials. All organic materials are sensitive to photo-oxidation and attack by ozone at room temperature causes depolymerization of resins. It also damages varnishes, which are used as coatings in ancient paintings, and attack cellulose causing fading of dyes in textiles and wooden fabrics. Hydrogen fluoride attacks ceramics and glass through their activity to react with silicon compounds and make the glass opaque.

VII. CASE STUDIES :

(1) TajMahal

The TajMahal, the glory of Agra, the pride of India, is well known, not only in the country, but also, throughout the whole world. It was built in 1649 A.D. as a mausoleum for the wife of one of the Muslim kings and is one of the seven wonders of the ancient world. The beauty of the TajMahal cannot be captured in words. Holy and profane men, poetsproers and the common masses, all write about the Taj in the same strain: 'too pure, too splendid a work of human hands! A poem in marble, the sigh of a broken heart". This edifice built in marble stonesis now threatened by acidic pollutants from Mathura Refinery-some 40 kilometers away from Agra, the home of the monument 31, 35' 36. Mathura refinery has a power plant, which utilizes coal for its generation. Furthermore, there are other point, line and area sources of the damaging pollutants from the two 10 MW thermal power stations, railways, and the so many industries located around it; traffic layouts with an ever-busy vehicular movement; and a fairly large population. Once the noxious gases (SO₂, NO₂, CO₂, particulates, etc.) are airborne, they attack the TajMahal by dry and wet deposition as seen above. There is need, therefore to keep it in a cautious and continuous maintenance and repair if it is to be retained in the World Heritage List.

2) Victoria Memorial Hall

A monument built for the glorious memories of Queen Victoria of Great Britain, the foundation stone was laid in 1906 and formally opened to the public in 1921. It is a marvelous structure and situates in the heart of Calcutta. It is also one of the privileged historical and cultural heritages of modern architectural monuments in India. Calcutta, the Eastern Gateway of India, with a projected population of over 14 million people in the 2001 census, is one of the mega cities of the world. It also has a large industrial base for different types of industries, contributing to point sources of atmospheric pollution. This is coupled with over 0.5 million slow moving, poorly maintained old vehicles plying the streets which aggravate the pollution load of the atmosphere^{37 3839}. No wonder, The National Environmental Engineering Research Institute (NEERI) National Air Quality Monitoring Programme (NAQMP) projected Calcutta as one of the most polluted cities of India⁴⁰. The main sources contributing towards the pollution build-up at the Victoria Memorial Hall are emissions from vehicular traffic on nearby roads, neighboring residential and commercial areas and industrial

point sources primarily located within 5-10 kilometers. Here again, marble/stone deterioration takes place by dry and wet deposition of the acid pollutants at certain spots/locations and if not checked, could lead to worse situations in future. The Monument Protection Plan suggested by NEERI should be adhered to.

3) Red Fort

The Indraprastha thermal power plant has been emitting sulphur dioxide and particulate matter, which has badly corroded the marble and stone stones used in its construction. According to reports, the marble stones have blackened due to SO₂³⁶

(4) Mathura Sculptures

Sandstones were used for these sculptures. Protection and conservation of the sculptures have become problematic nowadays because of pollution. One can now see the layers of the smooth surfaces separating and clipping off in small pieces. In some cases, the surfaces have become powdery and are disintegrating, while in other cases, the slabs are separating into two or more layers⁴¹.

VIII. CONCLUSION :

Air pollution starts from an emission source-fuel burning, mines, metabolic processes, industries, vehicular movements, etc.-and may manifest itself through acid rain, acid snow, acid fog and air-borne particulate matter. Oxides of sulphur (SO_x), nitrogen (NO_x), and carbon (CO_x) are the major air pollutants, which have either direct or indirect effect on the durability of heritage. Truly, the effects of air pollutants on heritage is a very slow process; and may only be perceptible over many years, decades or even centuries. The severity of attack may increase if measures to check air pollution are not taken on a war footing.

Since there is no agreed permissible limits for air pollutants vis-a-vis their attack on heritage, either on a short or long term basis, the present national international standards for ambient air quality based on human health and vegetation considerations, may be the starting point for evolution of a practical standard. This is necessary keeping in mind the damages already done to historic monuments like the TajMahal, Victoria Memorial Hall, Red Fort to mention but a few. In doing this, we should also not overlook the economic implications, which cart away millions of dollars, to clean, replace (dutchman) or maintain. In addition to other measures, creation of a Green Belt around the heritage should be a must, in order to serve, not only as a pollution regulator, but also for aesthetic purposes.

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