

EFFECTS OF ACIDIFICATION ON MATERIALS AND CULTURAL PROPERTY

N.S. BAER

Conservation Center, New York University, 14 East 78th Street
New York, New York (U.S.A.)

ABSTRACT

Historic structures, outdoor sculpture, museum and library artifacts, and the common materials of construction are all affected by acid deposition. The nature, magnitude and extent of observed damage to materials is discussed. Dose-response relationships or damage functions are reviewed with reference to their ability to predict the benefits of environmental reductions in acid deposition. The multistep process whereby dollar costs are assigned to damage associated with a given cause (e.g. SO₂, acid precipitation, particulate soiling) is outlined in the form of a flow diagram. In the discussion, the status of knowledge, unknowns, uncertainties and research needs are noted.

INTRODUCTION

Even the casual observer is confronted daily by the combined effects of air pollution and natural weathering induced materials damage. The bridges, roads, buildings, and utilities that form our urban infrastructure are joined with our cultural monuments and artifacts in vast materials maintenance and replacement projects. A U.S. Department of Commerce Report (ref. 1) estimates the total annual metallic corrosion cost in the U.S. at \$82 billion in 1975. Far greater sums will be required for the repair and replacement of damaged reinforced concrete facilities and structures. A sense of the scope of such projects is provided by the estimated time and cost for repairs to the four major East River bridges in New York, an average of 13 years and \$180,000,000 per bridge (Table 1).

Repair and refurbishment costs for cultural properties, e.g. \$40,000,000 each for the Statue of Liberty and U.S. Capitol, present proportionately large public expenditures. Less

visible and more difficult to quantify are the maintenance and replacement costs expended by private owners of small business and residential properties.

TABLE 1.

Estimated Cost of Repairs to Major Bridges in New York City.^a

<u>Bridge Name</u>	<u>Length of Repair Project (years)^b</u>	<u>Estimated Cost in 1986 Dollars (U.S.)^c</u>
Brooklyn	15	138,300,000
Manhattan	10	135,900,000
Queensboro	12	202,200,000
Williamsburg	15	231,700,000
		708,100,000 (total)

^a Data supplied by the New York State Transportation Department.

^b Projects began 1980-1981 fiscal year. Anticipated completion 1994-1995 fiscal year.

^c Estimates subject to change.

Natural Weathering vs. Acid Deposition

In the press and popular literature, damage to materials, in particular cultural properties, is with increasing frequency assigned to "acid rain" or acid precipitation. A key issue thus becomes, what is known about the effects of acid deposition on materials, what roles do other pollutants play, and what levels of damage would be observed due to natural weathering phenomena in the absence of anthropogenic pollutants. Phrased in the terminology of the policy-maker, what can be stated with confidence about the decrease in the rate of damage to materials that will result from an incremental reduction in emissions.

MATERIALS EFFECTS

In Table 2, the natural weathering phenomena, effects of other pollutants and effects of acid deposition are tabulated together with methods for quantifying damage and possible

Table 2.
Air Pollution Damage to Materials.^a

<u>Material^b</u>	<u>Type of Damage</u>	<u>Principal Air Pollutants</u>	<u>Other Environmental Factors</u>	<u>Methods of Measurement</u>	<u>Mitigation Measures</u>
Building Stone	Surface erosion, soiling, black crust formation	Sulfur oxides and other acid gases	Mechanical erosion, particulate matter, moisture, temperature fluctuations, salts, vibration, CO ₂ , microorganisms	Weight loss of sample, surface reflectivity, measurement of dimensional changes, chemical analysis	Cleaning, impregnation with resins, removal to controlled environment
Ceramic and Glass	Surface erosion, surface crust formation	Acid gases, especially fluoride-containing	Moisture	Loss in surface reflectivity and light transmission, change in thickness, chemical analysis	Protective coatings, replacement with more resistant material, removal to controlled environment
Metals	Corrosion, tarnishing	Sulfur oxides, and other acid gases, hydrogen sulfide	Moisture, air, salt, particulate matter, ozone	Weight loss after removal of corrosion products, change in surface characteristics	Surface plating or coating, replacement with corrosion-resistant material, removal to controlled environment
Paint and Organic Coatings	Discoloration, soiling, erosion	Sulfur oxides, hydrogen sulfide, alkaline aerosol	Moisture, sunlight, ozone, particulate matter, microorganisms	Surface reflectivity loss, chemical analysis	Repainting, replacement with a more resistant material
Rubber	Cracking	Ozone	Sunlight, physical wear	Loss in elasticity and strength, measurement of crack frequency and depth	Add antioxidants to formulation, replace with more resistant materials

^a Adapted from Reference [2].

^b For Leather, Magnetic Storage Media, Paper, Photographic Materials, Textiles and Textile Dyes see Table 1 of "Effects of Acidification in Archives and Museums," This volume.

mitigative strategies. With rare exceptions, damage is the result of multiple factors interacting, at times, in a synergistic manner.

Quantification of Damage

Damage may be measured by weight loss, loss of strength, soiling, erosion, chemical analysis, etc. Most frequently damage has been measured by weight loss. This reflects the usual experimental method where a weighed test specimen is exposed to the environment or in a test chamber for a given period. At the end of the exposure the corrosion layer, if any, is stripped off and the test specimen is weighed. The loss of mass is defined as the damage. Various assumptions are made to convert the weight loss to dimensional surface erosion. In many cases, e.g. aluminum (pitting), paint (delamination), sandstone (spalling), the mode of failure is not by uniform surface loss so that this conversion is inappropriate.

Exposure Methodologies

In general, three approaches are taken for the quantification of damage to materials:

1. Field exposure of prepared specimens,
2. Chamber studies in controlled environments, and
3. Retrospective studies of exposed materials.

Field exposure studies which approximate normal conditions are slow and seldom continue for realistic time periods. How relevant is a 2-year exposure study of freshly quarried polished marble to the Parthenon? Further, how well can we characterize the variations in atmospheric conditions, and indeed, the causative agents interacting with our specimen when we only intermittently examine that sample. Similarly, when evaluating the results of chamber studies, how well have we simulated the real world. In our synthetic atmosphere, have we omitted a critical ingredient, e.g. ozone or carbonyl sulfide or an aspect of natural weathering, e.g. UV radiation or freeze-thaw cycles.

While retrospective studies are clearly of great relevance,

they often present frustrating results. The evidence of damage is real, compelling, and readily characterized. What is lacking is any reliable data on the conditions to which the artifact was exposed.

Damage Functions

The role of the damage function is to describe the relationship between natural loss, soiling, etc. and such environmental variables as SO_2 , NO_x , Cl^- , precipitation pH, time-of-wetness, dustfall, and insolation. The damage function may be: entirely theoretical; based on curve-fitting using regression analysis of field or laboratory data; or a combination, fitting a body of experimental data to a model of corrosion. A great many damage functions have been generated for metal systems while relatively few are available for other materials. The most successful is that for zinc as affected by SO_2 . The literature reporting damage functions has been reviewed generally by various authors (ref. 2-6) and specifically for metals by Benarie (ref. 7) and carbonate paints by Livingston (ref. 8).

Damage Functions vs. Corrosion Mechanisms

When damage functions are developed from weight loss experiments, little insight is gained into the mechanism of damage. Yet, it is the determination of damage reaction mechanisms that is essential to the development of mitigative strategies and the assignment, with confidence, of the portions of damage attributable to wet and dry deposition, other anthropogenic factors, and natural weathering. The reaction mechanism provides a detailed and complete sequence of reactions from the initial phases of attack through conversion to corrosion products.

Some indication of the complexity of corrosion mechanisms is gained in Table 3 where the results of anion analyses for corrosion products on metals exposed both indoors and outdoors are compiled (ref. 9). In the case of copper: OH^- , $SO_4^{=}$, $S^{=}$, $CO_3^{=}$, NO_3^- and Cl^- have been observed both indoors and outdoors. Similarly, zinc exposed outdoors has OH^- , $SO_4^{=}$, $CO_3^{=}$, and Cl^- in its patinas while on exposure indoors only $SO_4^{=}$, NO_3^- and

Cl⁻ were reported. Yet most damage functions for zinc only consider SO₂ and some time-of-wetness related variable.

TABLE 3.
Anions Found in Corrosion Films on Metals^a

Metal	Location	OH ⁻	SO ₄ ⁼	S ⁼	CO ₃ ⁼	NO ₃ ⁻	Cl ⁻
Ag	Indoor	*b	-	*	*	*	*
Al	Indoor	-	*	-	-	*	*
Cd	Indoor	-	*	*	*	-	*
Co	Indoor	*	*	-	*	*	*
Cu	Indoor	*	*	*	*	*	*
Cu	Outdoor	*	*	*	*	*	*
Fe	Indoor	*	*	-	*	*	*
Ni	Indoor	*	*	-	*	*	*
Pb	Outdoor	-	*	*	-	-	*
Pd	Indoor	-	-	-	-	-	*
Sn	Outdoor	-	*	-	-	-	*
Zn	Indoor	-	*	-	-	*	*
Zn	Outdoor	*	*	-	*	-	*

^a After Franey and Graedel (ref. 9).

^b * denotes anion reported.

ECONOMIC CALCULATIONS

The goal of these studies is to identify the causes of damage, assist in the development of mitigative strategies, and ultimately to develop an economic evaluation of damage. The process illustrated in Figure 1 involves many inputs in addition to dose-response damage data. The approach shown is that used in the 1985 draft EPA Assessment, generally available but never officially released (ref. 10). It is essential to realize that each of the inputs is subject to error and bias. For example, there is no credible damage function currently available for any single stone type. Thus, the \$5 billion annual acid deposition damage loss for 17 Northeastern States as reported in the New York Times (ref. 11) and based on the draft report may well be revised downward by an order of magnitude as the data and assumptions used undergo careful

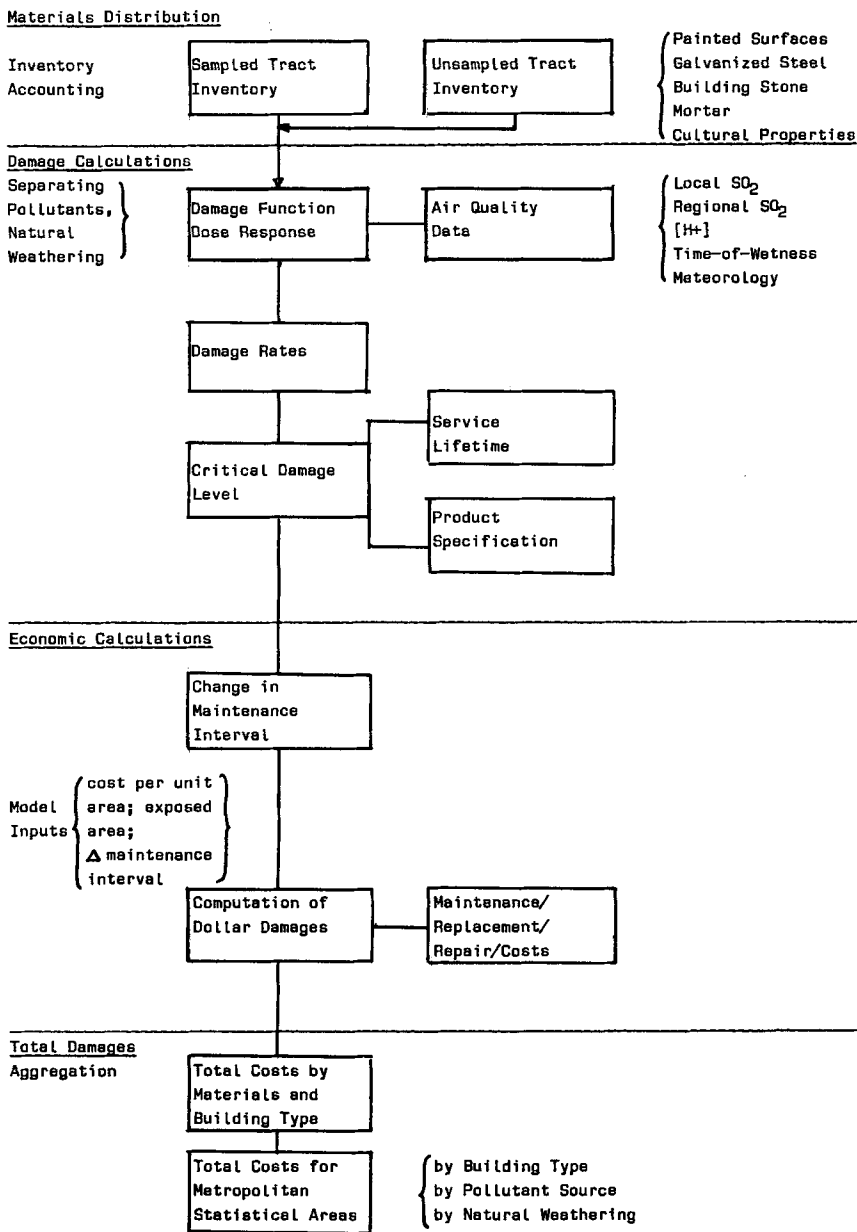


Fig. 1. Flow Diagram for Materials Effects Estimates. After Figure 3.5—27 EPA Draft Materials Effects Chapter for the 1985 Assessment [ref. 10].

analysis. It is of interest to note that the overwhelming percentage of damage was assigned to painted surfaces.

Mitigation, Replacement and Substitution

The consumer, be it individual home owner, corporate officer, or custodian of cultural property, is assumed to behave in a rational manner when confronted with materials damage. In the case of common building materials the market is considered to reflect behavior. Mitigation strategies for common building materials were listed in Table 2. Specific examples of replacement or substitution for materials where air pollution may be thought to be a cause of damage are given in Table 4. It is important to note that such replacements may introduce increased value (reduced future replacement intervals or costs; improved appearance; reduced maintenance) or may represent a loss of value (loss of options in surface treatments, increased risk of other types of damage, e.g., light, fire hazard). Economic models generally incorporate such concepts.

TABLE 4.

Illustrative Replacements or Substitutions for Pollution Impacted Materials.

Old Material

Galvanized link fence
Carbonate filled paint
Marble grave marker
Wood (painted/unpainted)
Coated carbon steel
Copper gutters and leaders
Copper flashing

Substitute Material

Vinyl coated link fence
Silicate filled paint
Granite grave marker
Aluminum siding (coated)
Weathering steel
Aluminum gutters and leaders (coated)
Stainless steel flashing

CULTURAL PROPERTY

It is the case that in the United States materials damage and in particular damage to cultural property is considered far less important than effects on agriculture, soil, water,

forests and human health. This contrasts with the Fourth Report from the Environment Committee on Acid Rain (ref. 12) where the lead area of interest was damage to buildings. The reason for this is clear if we contrast the situation with regard to stone monuments in the U.S. and Canada with that in Europe (Table 5). However, damage to cultural property cannot be evaluated in simplistic terms. The public will support substantial expenditures for the preservation of important monuments, e.g. our Declaration of Independence, sealed in helium, displayed under reduced illumination and lowered into a vault each evening or the great public support for the restoration of the Statue of Liberty and Ellis Island.

An indication of estimated costs associated with air pollution damage to cultural monuments is given in Table 6.

Further, just as a small level of material loss may lead to catastrophic failure of an electrical switch, a bridge, or an architectural element, damage to cultural property is irreversible and not readily subject to economic evaluation. What is lost is lost.

TABLE 5.
 Contrast in Distribution, Characteristics, and Air Pollution Effects on Stone
 Monuments in Europe vs. the U.S. and Canada

<u>Characteristic</u>	<u>U.S. and Canada</u>	<u>Europe</u>
Quantity	Few	Many
Age	Usually less than 100 years	Continuous from prehistoric to present
Distribution	Generally urban with exception of American Indian sites	Widely distributed
Stone types	Generally durable except for sandstones	Often poor quality stone chosen for ease of cutting and carving
Degree of Working of Stone	Limited examples, some free-standing sculpture	Statuary, sculpture, decorative carving commonly incorporated as architectural elements
Pollution Levels	With some exceptions relatively low, materials impact usually dominated by local sources	Relatively high, especially in urban and industrial areas

TABLE 6

Estimated Restoration Costs Associated with Air Pollution
 Damage to Cultural Property.^a

<u>Country or City</u>	<u>Type of Cultural Property</u>	<u>Basis for Cost Estimate</u>	<u>Period for Estimate</u>	<u>Cost (millions)</u>	<u>Year of Estimate</u>
Germany [FRG]	Medieval Stained Glass	Damage	Total	200-300 [DM]	1980
London	Houses of Parliament	Repair of Fabric	Total	5 [£]	1980
Rome	Monuments	Repair of Damage	10 year Expenditure	200 ^b [\$US]	1980
Netherlands	Monuments	Conservation	Total	120-200 [Dutch Guilder]	1984
New York	Statue of Liberty	Conservation/ Refurbishment	Total	40 ^b [\$US]	1986

^a Adapted in part from ref. 2.

^b Combined costs of repairing natural weathering and air pollution induced damage.

REFERENCES

1. L.H. Bennett, J. Kruger, E. Passaglia, C. Reimann, A.W. Ruff, and H. Yackowitz, *Economic Effects of Metallic Corrosion in the United States, Part I: A Report to the Congress by the National Bureau of Standards*. NBS Special Publication 511-1, U.S. Department of Commerce, National Bureau of Standards, Washington, D.C., 1978.
2. J.E. Yocom and N.S. Baer, in *The Acidic Deposition Phenomenon and its Effects: Critical Assessment Review Papers*, U.S. EPA, Washington, D.C. EPA-600/8-83-016BF, 1984, chapter E-7, section 7.1.
3. J.E. Yocom, N.S. Baer and E. Robinson, in A.C. Stern (Ed.), *Air Pollution, Volume VI*, Academic Press, New York, 1986, chapter 4.
4. J.E. Yocom and A.R. Stankunas, *A Review of Air Pollutant Damage to Materials, A Report to the EPA Environmental Criteria and Assessment Office*, 1980.
5. S.E. Haagenrud, R.W. Lanting and G. Santomauro, "Draft Report on Effects of Sulphur Compounds on Materials, Including Historical and Cultural Monuments, UNESCO, Interim Executive Body for Convention on Long-Range Transboundary Air Pollution, Geneva, Switzerland, 1982.
6. P. Harter, *Acidic Deposition and Damage to Materials and Human Health, Working Paper 71*, IEA Coal Research, London, 1986.
7. M. Benarie, *Metallic Corrosion as Functions of Atmospheric Pollutant Concentrations and Rain pH*, BNL 35668, Brookhaven National Laboratory, Upton, New York, 1984.
8. R.A. Livingston, *Pap. Proc. Annual Meeting, Air Pollution Control Assoc.*, 86, 85.7, 1986.
9. J.P. Franey and T.E. Graedel, *JAPCA*, 35, 1985, 644-648.
10. Environmental Protection Agency, *Draft Materials Effects Chapter for the 1985 Assessment*.
11. P. Shabecoff, *The New York Times*, 18 July 1985.
12. *Fourth Report from the Environment Committee Session 1983-1984, Acid Rain, Volume 1, Paragraph 37, p. xxii*, H.M. Stationary Office, London, 1984.