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Effects on Materials and Structures

I. EFFECTS ON METALS

The principal effects of air pollutants on metals are corrosion of the surface, with eventual loss of material from the surface, and alteration in the electrical properties of the metals. Metals are divided into two categories: ferrous and nonferrous. Ferrous metals contain iron and include various types of steel. Nonferrous metals, such as zinc, aluminum, copper, and silver, do not contain iron.

Three factors influence the rate of corrosion of metals: moisture, type of pollutant, and temperature. A study by Hudson [1] confirms these three factors. Steel samples were exposed for 1 year at 20 locations throughout the world. Samples at dry or cold locations had the lowest rate of corrosion, samples in the tropics and marine environments were intermediate, and samples in polluted industrial locations had the highest rate of corrosion. Corrosion values at an industrial site in England were 100 times higher than those found in an arid African location.

The role of moisture in corrosion of metals and other surfaces is twofold: surface wetness acts as a solvent for containments and for metals is a medium for electrolysis. The presence of sulfate and chloride ions accelerates the corrosion of metals. Metal surfaces can by wetted repeatedly over a period of time as the humidity fluctuates.

Several studies have been conducted in urban areas to relate air pollution exposure and metal corrosion. In Tulsa, Oklahoma, wrought iron disks were exposed in various locations [2]. Using weight change as a measure of air pollution corrosion, the results indicated higher corrosion rates near industrial sectors containing an oil refinery and fertilizer and sulfuric acid manufacturing facilities. Upham [3] conducted a metal corrosion investigation in Chicago. Steel plates were exposed at 20 locations, and SO_2 concentrations were also measured. Figure 13.1 shows the relationship between weight loss during 3-, 6-, and 12-month exposure periods and the mean SO_2 concentration. Corrosion was also found to be higher in downtown locations than in suburban areas. Nonferrous metals are also subject to corrosion, but to a lesser degree than ferrous metals. Table 13.1 compares the weight loss of several nonferrous metals over a 20-year period [4]. The results vary depending on the type of exposure present.

Zinc is often used as a protective coating over iron to form galvanized iron. In industrial settings exposed to SO_2 and humidity, this zinc coating is subject to sufficient corrosion to destroy its protective capacity. Haynie and Upham [5] used their results from a zinc corrosion study to predict the useful life of a zinc-coated galvanized sheet in different environmental settings. Table 13.2 shows the predicted useful life as a function of SO_2 concentration.

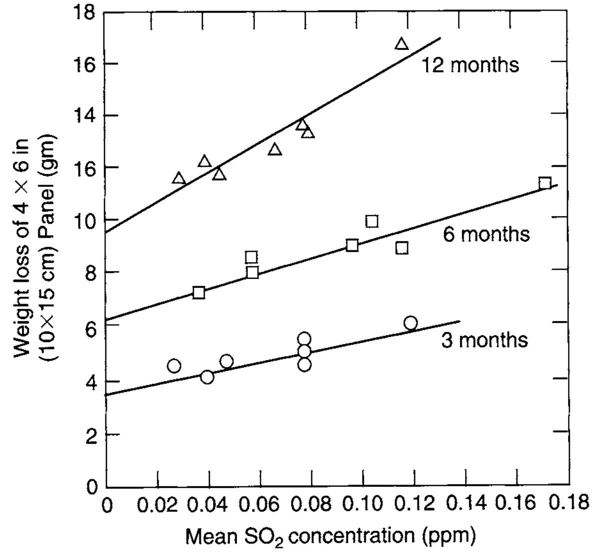

Fig. 13.1. Relationship between corrosion of mild steel and corresponding mean sulfur dioxide concentration at seven Chicago, Illinois sites. *Source*: Upham, J. B., *J. Air Pollut. Control Assoc.* 17, 400 (1967).

TABLE 13.1

Weight Loss of Metal Panels[a] After 20 Years' Exposure in Various Atmospheres (*ca.* 1930–1954)[b]

		Average loss in weight (%)					
City	Exposure classification	Commercial copper (99.9% + Cu)	Commercial aluminum (99% + Al)	Brass (85% Cu, 15% Zn)	Nickel (99% + Ni)	Commercial lead (99.92% Pb, 0.06% Cu)	Commercial zinc (99% Zn, 0.85% Pb)
Altoona, PA	Industrial	6.1	–	8.5	25.2	1.8	30.7
New York, NY	Industrial	6.4	3.4	8.7	16.6	–	25.1
La Jolla, CA	Seacoast	5.4	2.6	1.3	0.6	2.1	6.9
Key West, FL	Seacoast	2.4	–	2.5	0.5	–	2.9
State College, PA	Rural	1.9	0.4	2.0	1.0	1.4	5.0
Phoenix, AZ	Rural	0.6	0.3	0.5	0.2	0.4	0.8

[a] Panels: 9 × 12 × 0.035 in. (22.86 × 30.48 × 0.089 cm).

[b] Data from H. R. Copson, Report of ASTM Subcommittee VI, of Committee B-3 on Atmospheric Corrosion, *Am. Soc. Test Mater.*, Special Technical Publication No. 175, 1955. Used by permission of the American Society for Testing and Materials, Philadelphia.

Source: Yocom, J. E., and Upham, J. B., Effects on economic materials and structures, in *Air Pollution*, 3rd ed., Vol. I (Stern, A. C., ed.), p. 80. Academic Press, New York, 1977.

TABLE 13.2

Predicted Useful Life of Galvanized Sheet Steel with a 53-μm Coating at an Average Relative Humidity of 65%[a]

SO_2 concentration ($\mu g\,m^{-2}$)	Type of environment	Useful life (years) Predicted best estimate	Predicted range	Observed range
13	Rural	244	41.0	30–35
130	Urban	24	16.0–49.0	
260	Semi-industrial	12	10.0–16.0	15–20
520	Industrial	6	5.5–7.0	
1040	Heavy industrial	3	2.9–3.5	3–5

[a] *Source*: Yocom, J. E., and Upham, J. B., Effects of economic materials and structures, in *Air Pollution*, 3rd ed., Vol. I (Stern, A. C., ed.), p. 80. Academic Press, New York, 1977.

Aluminum appears to be resistant to corrosion from SO_2 at ambient air concentrations. Aluminum alloys tend to form a protective surface film that limits further corrosion upon exposure to SO_2. Laboratory studies at higher concentrations (280 ppm) show corrosion of aluminum at higher humidities (>70%), with the formation of a white powder of aluminum sulfate.

Copper and silver are used extensively in the electronics industry because of their excellent electrical conductivity. These metals tend to form a protective surface coating which inhibits further corrosion. When exposed to H_2S, a sulfide coating forms, increasing the resistance across contacts on electrical switches [6].

II. EFFECTS ON STONE

The primary concern in regard to air pollution is the soiling and deterioration of limestone, which is widely used as a building material and for marble statuary.[1] Figure 13.2 shows the long-term effects of urban air pollution on the appearance of stone masonry. Many buildings in older cities have been exposed to urban smoke, SO_2, and CO_2 for decades. The surfaces have become soiled and are subjected to chemical attack by acid gases. Exterior building surfaces are also subjected to a wet–dry cycle from rain and elevated humidity. SO_2 and moisture react with limestone ($CaCO_3$) to form calcium sulfate ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$). These two sulfates are fairly soluble in water, causing deterioration in blocks and in the mortar used to hold the blocks together. The soluble calcium sulfates can penetrate into the pores of the limestone and recrystallize and expand, causing further deterioration of the stone. CO_2 in the presence of moisture forms carbonic acid. This acid converts the limestone into bicarbonate, which is also water

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[1] Marble is metamorphosed limestone.

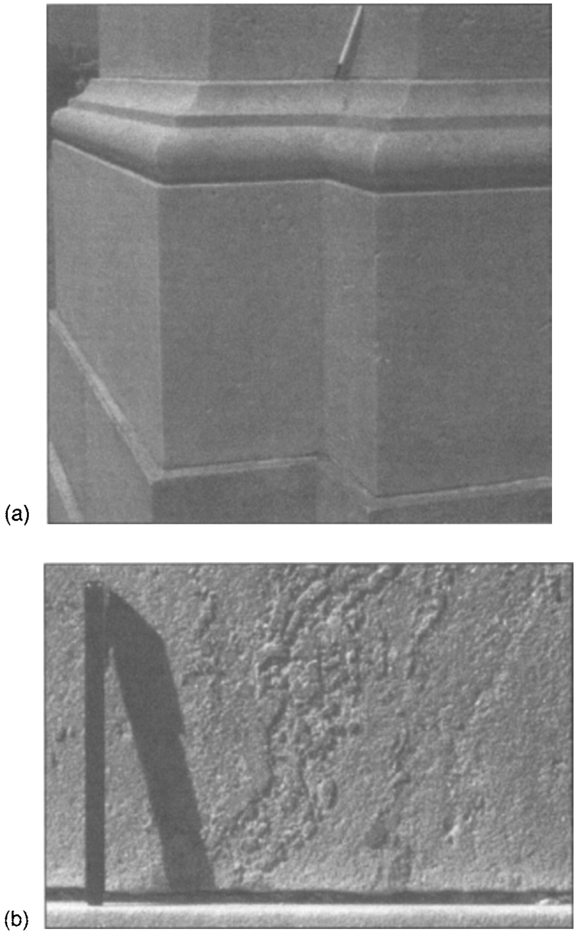


Fig. 13.2. Effects of urban air pollution on materials. (a) Pock marks in marble column on the south side of the U.S. Capitol building. Silicate mineral inclusions in the marble loosen and fall out when the calcite around them is dissolved by precipitation with pH that has been lowered (i.e. higher acidity) by urban air pollution. (b) Marble block that forms the northeast corner of the Capitol balustrade shows preferential erosion of the calcite around a silicate mineral inclusion. *Photos:* U.S. Geological Survey, http://pubs.usgs.gov/gip/acidrain/site1.html; accessed on June 30, 2007.

soluble and can be leached away by rain. This type of mechanism is present in the deterioration of marble statues.

III. EFFECTS ON FABRICS AND DYES

The major effects of air pollution on fabrics are soiling and loss of tensile strength. Sulfur oxides are considered to cause the greatest loss of tensile strength. The most widely publicized example of this type of problem has been damage to hosiery by air pollution, described in newspaper accounts. The mechanism is not understood, but it is postulated that fine droplets of sulfuric acid aerosol deposit on the very thin nylon fibers, causing them to fail under tension. Cellulose fibers are also weakened by sulfur dioxide. Cotton, linen, hemp, and rayon are subject to damage from SO_2 exposure.

Brysson and co-workers [7] conducted a study in St. Louis, Missouri, on the effects of urban air pollution on the tensile strength of cotton duck material. Samples were exposed at seven locations for up to 1 year. Figure 13.3 shows the relationship between tensile strength and pollutant exposure. For two levels of ambient air exposure, the materials exhibited less than one-half their initial tensile strength when exposed to air pollution for 1 year.

Particulate matter contributes to the soiling of fabrics. The increased frequency of washing to remove dirt results in more wear on the fabric, causing it to deteriorate in the cleaning process.

In addition to air pollution damage to fabrics, the dyes used to color fabrics have been subject to fading caused by exposure to air pollutants. Since the early 1900s, fading of textile dyes has been a continuing problem. The composition of dyes has been altered several times to meet demands of new fabrics and to "solve" the fading problem. Before World War I, dyes used on wool contained free or substituted amino acid groups, which were found to be susceptible to exposure to nitrogen dioxide.

When cellulose acetate rayon was introduced in the mid-1920s, old dye technology was replaced with new chemicals called dispersive dyes. Not

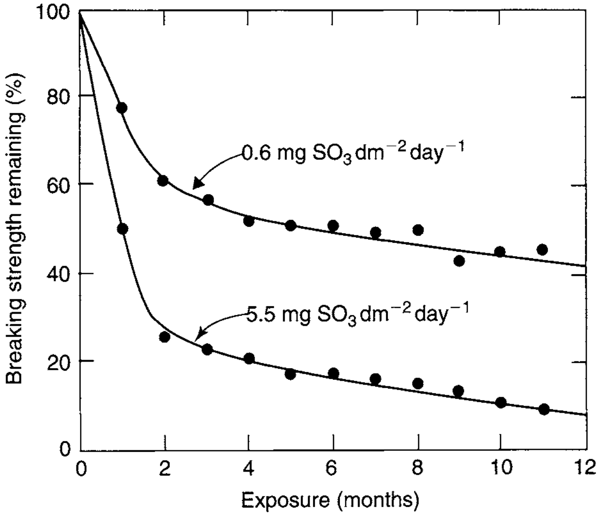


Fig. 13.3. Effects of sulfation and time on tensile strength of cotton duck. *Source*: Brysson, R. J., Trask, B. J., Upham, J. B., and Booras, S. A., *J. Air Pollut. Control Assoc.* **17**, 294 (1967).

long after their initial use, fading of blue, green, and violet shades began to be observed in material exposed to nitrogen oxides. The fabric was marked by a reddening discoloration. Laboratory studies duplicating ambient air levels of nitrogen dioxide and humidity reproduced these effects [8].

Ozone has also been found to cause fading of material. This was discovered when white fabrics developed a yellow discoloration [9, 10], leading researchers to investigate the effects of ozone on other chemicals added to the material, including optical brighteners, antistatic and soil-release finishes, and softeners. A very complex process was occurring where the dyes were migrating to the permanent-press-finish materials (e.g. softeners). Softeners have been found to be good absorbers of gases. Fading results from the combination of dye and absorbed nitrogen dioxide and ozone. This combination with high relative humidities has caused color fading in numerous types of material and dye combinations. However, dyes and pigments have improved in recent decades, so that fading from airborne pollutants has become less of a problem.

IV. EFFECTS ON LEATHER, PAPER, PAINT, AND GLASS

Sulfur dioxide affects the composition of leather and paper, causing significant deterioration. The major concern is the destruction of leatherbound books in the libraries of the world. SO_2 is absorbed by leather and converted to sulfuric acid, which attacks the structure of the leather. Initially, the edges of the exposed back of the book begin to crack at the hinges. As the cracks expand, more leather is exposed and the cracks widen, with the back eventually falling off the book. Preventive measures now include storage in sulfur dioxide free air.

The cellulose fiber in paper is attacked and weakened by sulfur dioxide. Paper made before about 1750 is not significantly affected by sulfur dioxide [11]. At about that time, the manufacture of paper changed to a chemical treatment process that broke down the wood fiber more rapidly. It is thought that this process introduces trace quantities of metals, which catalyze the conversion of sulfur dioxide to sulfuric acid. Sulfuric acid causes the paper to become brittle and more subject to cracking and tearing. New papers have become available to minimize the interaction with SO_2.

Paints are designed to decorate and protect surfaces. During normal wear, paint chalks moderately to clean the surface continuously. A hardened paint surface resists sorption by gases, although the presence of relatively high concentrations of $2620\text{–}5240\,\mu g\,m^{-3}$ SO_2 (1–2 ppm) increases the drying time of newly painted surfaces. Hydrogen sulfide reacts with lead base pigments:

$$Pb^{2+} + H_2S \rightarrow PbS + 2H^+ \tag{13.1}$$

to blacken white and light-tinted paints. Although most paints no longer contain Pb-based pigments, the reaction would expected to be similar for other metal pigments:

$$Me^{2+} + H_2Me \rightarrow MeS + 2H^+ \quad (13.2)$$

Wohlers and Feldstein [12] concluded that lead base paints could discolor surfaces in several hours at a concentration of $70\,\mu g\,m^{-3}$ H_2S (0.05 ppm). In time the black lead sulfide oxidizes to the original color. However, paints pigmented with titanium or zinc do not form a black precipitate. Alkyd or vinyl vehicles and pigments contain no heavy metal salts for reaction with H_2S. Painted surfaces are also dirtied by particulate matter. Contaminating dirt can readily become attached to wet or tacky paint, where it is held tenaciously and forms focal points for gaseous sorption for further attack. Dirt that collects on roofs or in gutters, blinds, screens, windowsills, or other protuberances is eventually washed over external surfaces to mar decorative effects.

Paints and coatings for automobiles have not been immune to damage by air pollution. Wolff and co-workers [13] found that damage to automobile finishes was the result of scarring by calcium sulfate crystals formed when sulfuric acid in rain or dew reacted with dry deposited calcium.

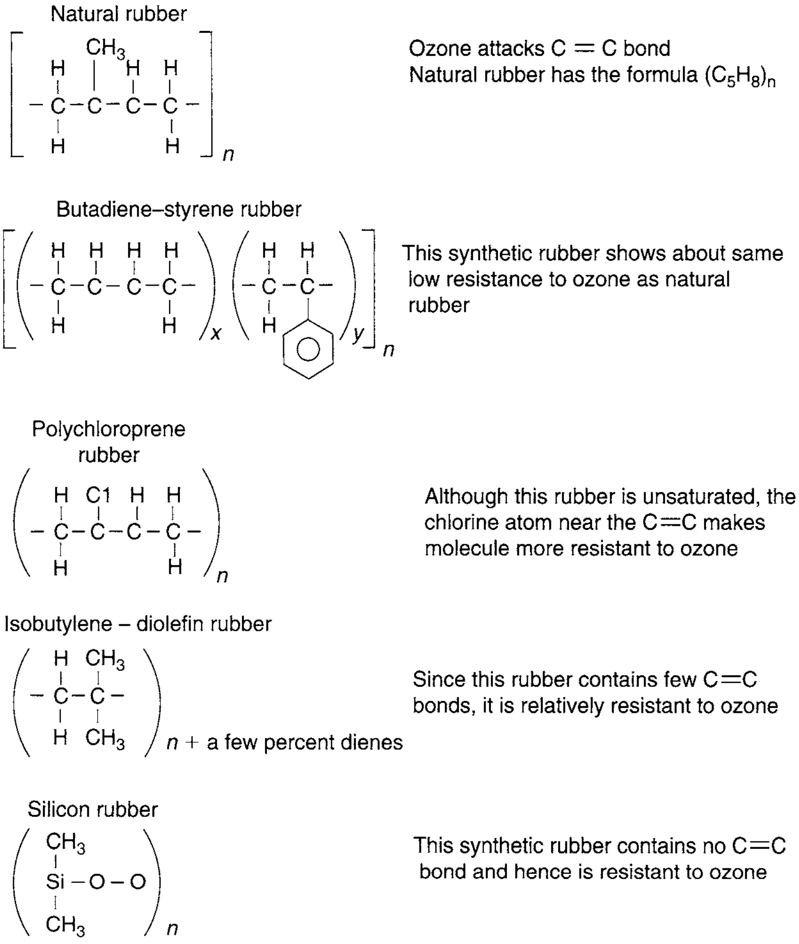
Glass is normally considered a very stable material. However, there is growing evidence that SO_2 air pollution may be accelerating the deterioration of medieval glass. A corrosion surface forms on these glass surfaces and the sulfate present helps prolonged surface wetness. This condition is conducive to further attack and degradation of the glass surface [14].

V. EFFECTS ON RUBBER

Although it was known for some time that ozone cracks rubber products under tension, the problem was not related to air pollution. During the early 1940s, it was discovered that rubber tires stored in warehouses in Los Angeles, California, developed serious cracks. Intensified research soon identified the causative agent as ozone that resulted from atmospheric reaction between sunlight (3000–4600 Å), oxides of nitrogen, and specific types of organic compounds, i.e., photochemical air pollution.

Natural rubber is composed of polymerized isoprene units. When rubber is under tension, ozone attacks the carbon–carbon double bond, breaking the bond. The broken bond leaves adjacent C=C bonds under additional stress, eventually breaking and placing still more stress on surrounding C=C bonds. This "domino" effect can be discerned from the structural formulas in Fig. 13.4. The number of cracks and the depth of the cracks in rubber under tension are related to ambient concentrations of ozone.

Rubber products may be protected against ozone attack by the use of a highly saturated rubber molecule, the use of a wax inhibitor which will "bloom" to the surface, and the use of paper or plastic wrappings to protect the surface. Despite these efforts, rubber products generally still crack more on the West Coast than on the East Coast of the United States.



Ozone attacks C = C bond
Natural rubber has the formula $(C_5H_8)_n$

This synthetic rubber shows about same low resistance to ozone as natural rubber

Although this rubber is unsaturated, the chlorine atom near the C=C makes molecule more resistant to ozone

Since this rubber contains few C=C bonds, it is relatively resistant to ozone

This synthetic rubber contains no C=C bond and hence is resistant to ozone

Fig. 13.4. Susceptibility of natural and synthetic rubbers to attack by ozone.

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SUGGESTED READING

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QUESTIONS

1. Assuming that a relationship exists among corrosion, population, and sulfur dioxide, why might one expect this interdependence?
2. Compare the solubilities in water of calcium carbonate, calcium sulfite, calcium sulfate, magnesium sulfate, and dolomite.
3. Describe possible mechanisms for the deterioration of marble statuary.
4. Explain why soiling and corrosion are hidden costs of air pollution.
5. Describe possible preventive actions to limit deterioration of books and other print material in libraries.
6. Explain the role of moisture in corrosion of materials.
7. In your location, determine whether sulfur dioxide, ozone, or particulate matter contributes to soiling or corrosion problems.
8. Describe why some types of synthetic rubber are less susceptible to ozone attack than natural rubber.
9. Many people prefer cotton to synthetic fibers. What processes are available to increase cotton fabrics' resistance to the effects of air pollutants?