

CHAPTER 6

The Effect of Acidification on Corrosion of Structures and Cultural Property

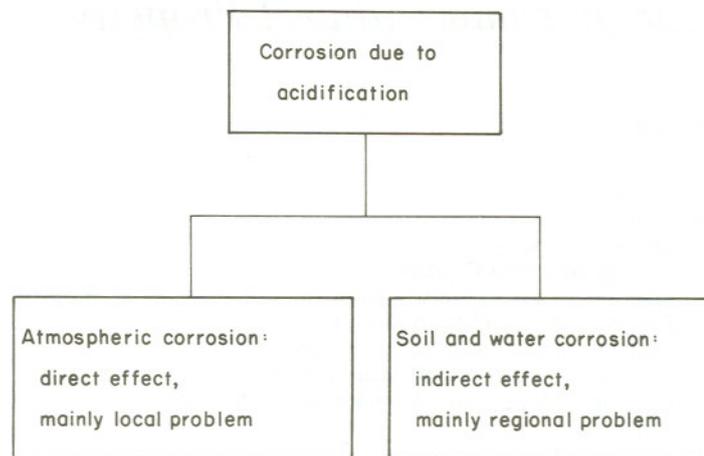
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6.1 INTRODUCTION

Acidification is one of the most serious environmental problems. Among the effects of acid deposition, corrosion of constructions exposed to the atmosphere, mainly by sulfur pollutants, is a well-known problem. The effects of SO₂ on different materials have been subject to many laboratory and field investigations, and the corrosive effects of polluted atmospheres on historic and cultural monuments of sandstone or limestone are obvious. Current knowledge of the effects of acidic air pollutants on atmospheric corrosion is summarized in several reports (Swedish Ministry of Agriculture, 1982; United Nations, 1984; Feenstra, 1984, Lanting and Moree, 1984).

Given the ongoing acidification of lakes, rivers, and soil, buried and immersed installations, including water pipes, might also be affected. The following subdivision may thus be used (Kucera, 1986a,b):



This chapter briefly reviews the effects of acidification on corrosion in the atmosphere, water and soil based on results published in the literature and on practical experience.

6.2 ATMOSPHERIC CORROSION

6.2.1 Factors Affecting Corrosion

Among the parameters determining corrosion rate are the presence of a moisture film on the surface and the pollutant content of this film. Relative humidity, rain, dew, and temperature are determinants of the so-called time of wetness, often defined as time with relative humidity $>80\%$ at temperatures $>0\text{ }^{\circ}\text{C}$. If mean values for time of wetness and temperature vary only moderately, which is usually the case in the temperate climatic zone, then the levels of air pollutants influence the corrosion rate decisively. In very cold or dry regions, however, the time of wetness becomes a significant parameter. The influence of high relative humidity and temperature, as found in the tropics, is treated in a separate chapter.

The major pollutants, in urban and industrial areas are SO_2 and NO_x ; chlorides are usually the dominant pollutant in marine regions.

6.2.2 Changes in Air Chemistry from Acidification

Most of the sulfur from burning fossil fuels is emitted as SO_2 . During its transport in the atmosphere SO_2 is oxidized to sulfuric acid in water droplets or on moist particles. The sulfuric acid can then be partly neutralized by ammonia to different forms of acid ammonium sulfates such as NH_4HSO_4 and $(\text{NH}_4)_3\text{H}(\text{SO}_4)_2$.

Dry deposition near emission sources in urban and industrial areas consists largely of adsorption of SO_2 on surfaces, with the deposited amount proportional to the content in air. The deposition rate is high at elevated humidities, especially on some metals; e.g., steel and zinc (Sydberger and Vannerberg, 1972).

The deposition rate of particulate sulfate seems to be one order of magnitude less than for SO_2 , and the content of sulfates in polluted areas near emission sources is usually much lower than the SO_2 content (Kucera, 1976). The dominant nitrogen pollutant from fossil fuel combustion is NO . The oxidation of NO to NO_2 is a comparatively fast process, but further oxidation of NO_2 to HNO_3 occurs at a low rate. Thus nitrate levels are low in the vicinity of emission sources. NO_x is the main nitrogen pollutant. The dry deposition rate of nitrogen oxides seems to be low.

Both gaseous and particulate pollutants are washed out of the air by precipitation, thus lowering rain pH. In Norway pH values as low as 3.7 and 2.9 on a monthly and daily basis respectively have been found (Haagenrud and Ottar, 1975). In California fog droplets had pH ranging from 2.2 to 4.0 (Waldman *et al.*, 1982).

6.2.3 Effects of Air Acidification on Corrosion

The effects of sulfur pollutants on various materials have been shown in extensive field tests, which in Sweden began in the 1930s (Kucera, 1976; Swedish Ministry of Agriculture, 1972). Results concerning some important materials are given in Table 6.1.

For some materials, such as carbon steel and zinc, dose-response relationships have been established. In the equations SO_2 is the most important parameter (Haagenrud *et al.*, 1983; Knotkova *et al.*, 1984; Lipfert *et al.*, 1985) (Figure 6.1). Materials comprising parts of our cultural heritage are sensitive to acid deposition. Sandstone and limestone, often used in buildings, sculptures, and monuments of great cultural value, are highly resistant in natural environments.

Increasing industrialization, however, has led to air pollution levels that accelerate deterioration of stones. The Acropolis in Athens is an example, and similar problems may arise in rapidly developing countries. The discussion concerning the Taj Mahal in India might be a warning (Lal Guari and Holdren, 1981).

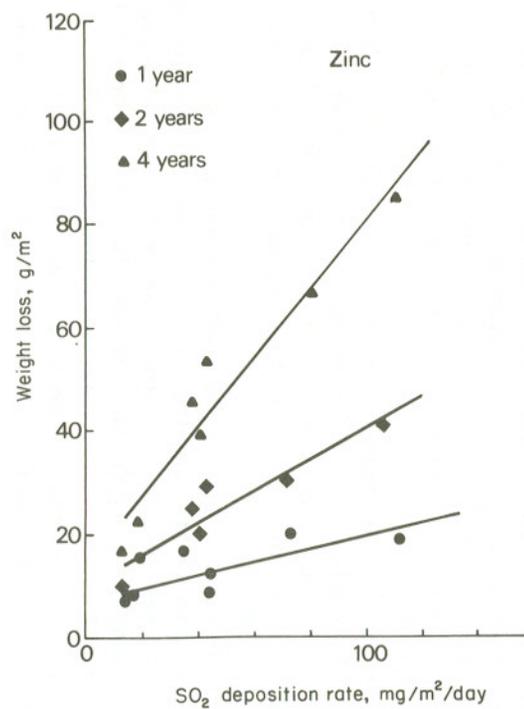
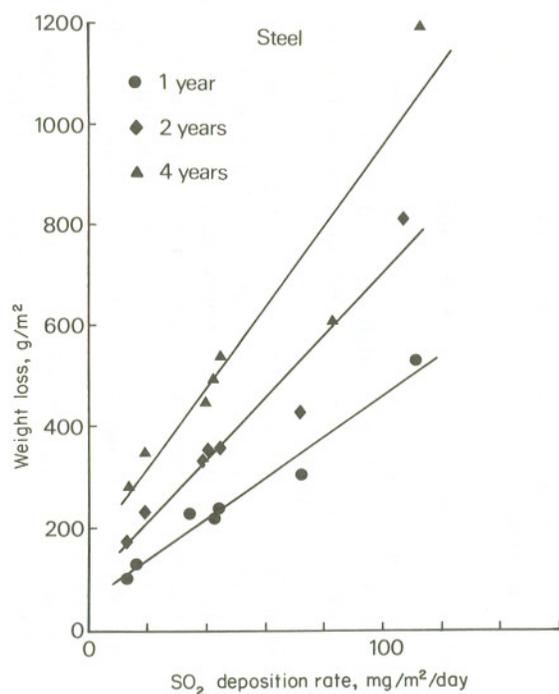


Figure 6.1 Weight loss of steel and zinc after 1, 2, and 4 years of exposure as a function of SO₂ deposition rate at seven test sites in the temperate zone (Knotkova *et al.*, 1984)

Table 6.1 Corrosion rate and service life of various materials exposed at Swedish field stations (Swedish Ministry of Agriculture, 1972)

Material	Corrosion rate or service life		Exposure period
	Rural atmosphere	Urban atmosphere	
Carbon steel	8 $\mu\text{m}/\text{year}$	30 $\mu\text{m}/\text{year}$	1958-1966
Galvanized steel	0.8 $\mu\text{m}/\text{year}$	5 $\mu\text{m}/\text{year}$	1958-1966
Copper	0.6 $\mu\text{m}/\text{year}$	1.0 $\mu\text{m}/\text{year}$	1958-1966
Nickel-plated steel (35 μm Ni/Cr)	3.5 years	1.9 years	1958-1970
Anti-rust painted steel (40 μm primer + 40 μm topcoat of alkyd type)	10 years	8 years	1958-1967

Quantitative data concerning acidification effects on sandstone and limestone published in West Germany show a clear correlation between the weight loss of freely exposed stone specimens and the SO_2 content in the air (Luckat, 1981) (Figure 6.2). Stained glass windows (Fitz, 1986), paper, leather (Feenstra, 1984) and certain types of plastics are adversely affected by deposition of acidic air pollutants.

The influence of NO_x on atmospheric corrosion, especially outdoors, has been investigated on a limited scale. Results show no or very slight effect if NO_2 is the only pollutant (Haynie *et al.*, 1978). Recent laboratory studies,

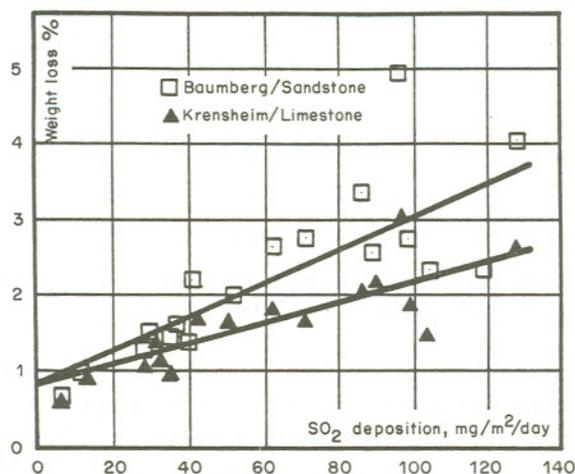


Figure 6.2 Relationship between SO_2 deposition rate and weight loss of freely exposed specimens of two sensitive stones (based on data from Luckat, 1981)

however, show that NO_2 may increase the corrosion rate of carbon steel at low relative humidities if present with SO_2 , whereas either gas alone caused only insignificant corrosion at 50% RH (Figure 6.3). This effect was not obtained at 90% RH (Johansson, 1984). The synergistic effect is explained by the formation of hygroscopic corrosion products containing nitrates. The influence of a mixture of NO_2 and SO_2 could be of practical importance at indoor storage sites with polluted atmospheres, for example.

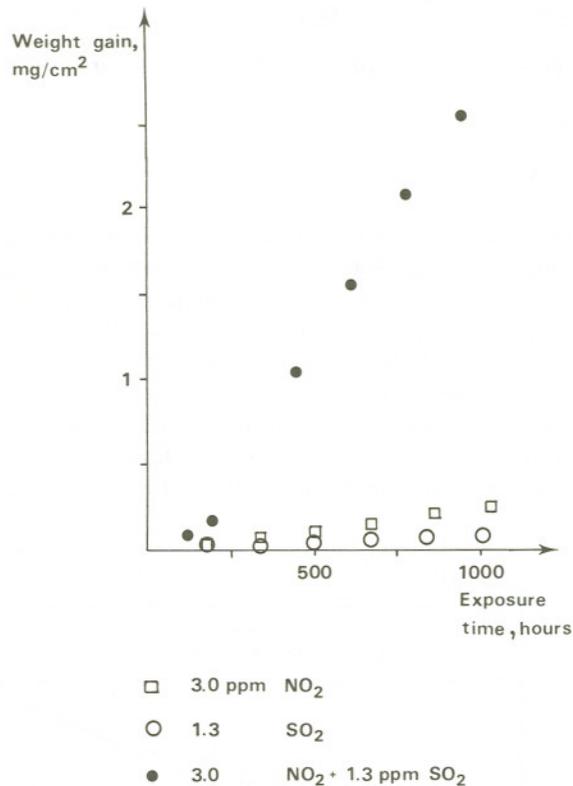


Figure 6.3 The corrosion of carbon steel in air containing different amounts of NO_2 and SO_2 at 50% relative humidity (Johansson, 1984)

One of the most important technical problems regarding indoor atmospheres is the corrosion of electrical and electronic equipment (Svedung and Johansson, 1983). Indoor climates contain in principle the same gaseous—and even most of the particulate—pollutants as outside climates, as shown by systematic investigations in the United States (Rice *et al.*, 1980). The influence of NO_x on electric contact materials appears to result from syn-

ergistic effects with other pollutants. Gold and copper contacts exposed to an atmosphere of NO₂ show no corrosion effect, but the synergistic effect of SO₂ and NO₂ is very pronounced. A possible explanation is that NO₂ oxidizes SO₂ to sulfuric acid according to the following reaction:



This reaction may proceed in humid conditions when SO₂ is not otherwise deposited and oxidized on surfaces.

Outdoors, the synergistic effect may be important for corrosion of copper materials and lead to increased corrosion of bronze statues, bells, and carillons (Johansson, 1986). Laboratory studies show that the mixture of SO₂ and NO₂ has a corrosive effect on calcareous stone materials (Johansson *et al.*, 1988).

The total corrosive effect of acid rain cannot be determined unequivocally since it has both corrosive and washing effects. Thus in heavily polluted industrial air the corrosion rate on the upper side of steel panels was only 37% of the total corrosion. In less polluted air the corrosive effect of rain was predominant and the upper sides of the test panels corroded faster than the undersides (Kucera, 1976). The atmospheric corrosion of steel proceeds in local cells, where sulfate nests act as anodes. The washing effect of rain might prevail in polluted atmospheres, because rainwater may wash sulfates away from the nests.

Precipitation pH seems to be significant for metals whose corrosion resistance is due to a protective layer of basic carbonates or sulfates such as zinc or copper. If rainwater pH falls to values of 4 or lower, protective coatings might dissolve.

6.2.4 Features of Corrosion in the Tropics

Climatic conditions within the tropics vary considerably. This overview concerns mainly areas in which high relative humidity, temperature, and precipitation prevail.

The influence of temperature on atmospheric corrosion is complex. An increase in temperature stimulates corrosion by enhancing the rate of chemical and electrochemical processes; but it also leads to more rapid evaporation of surface moisture films after rain or dew. Consequently, the time of wetness is shortened and the corrosion rate decreases, as shown by data from Cuba (Perez, 1984). Generally, temperature is not a critical determinant of corrosion during long-term exposure in open air.

Rain has a corrosive effect since it produces a moisture film on the surface and adds corrosion stimulators as hydrogen ions or sulfates. On the other hand, it washes away pollutants deposited on the surface during the

preceding dry period. In the tropics, with frequent heavy, short rains, the washing effect can dominate. This is illustrated by the corrosion of carbon steel at the marine site in Digha, India, where the corrosion rate reached a maximum in the month before the rain period starts (Rao and Lahiri, 1972). When rain commences, the corrosion rate decreases appreciably. A similar effect has been shown in systematic studies in Vietnam (Strekalov *et al.*, 1983) and Cuba (Perez, 1984).

Several studies describe corrosion in the tropics, but few of them are based on long-term exposure of test specimens. Some sources are based on field observations rather than on systematic exposure (Compton, 1947). This may be why opinions on corrosivity in the tropics differ widely. Some paint coatings, for example, deteriorate much faster in the tropics than in the temperate zone (Alexander *et al.*, 1958). After the coating breaks down, corrosion of the underlying steel suggests the presence of a highly corrosive environment (Southwell and Bultman, 1982). Corrosion in the tropics can be subdivided into two categories: corrosion under shipment and storage, and corrosion when placed in service. In the tropics shipping and storage conditions give rise to the most serious corrosive effects. This fact might have given the tropics its reputation for having a highly corrosive atmospheric environment.

The potential for corrosion in open air in the tropics can be shown by comparing corrosion rates of some common metals in different tropical and subtropical locations with data from the temperate climatic zone (ISO DP, 1986). Data on corrosion rates of steel and zinc from Panama (Southwell and Bultman, 1982; Southwell and Alexander, 1969; Mohler, 1974), Nigeria (Clarke and Longhurst, 1961; Hudson and Stanners, 1953; Ambler and Bain, 1955), Australia (Moresby *et al.*, 1982), Philippines (Southwell and Bultman, 1982; Ailor, 1974), India (Rao and Lahiri, 1972; Mukherjee and Fukushima, 1985), Japan (Mukherjee and Fukushima, 1985), Cuba (Perez, 1982, 1984), Vietnam (Strekalov *et al.*, 1983), Egypt (Ismail *et al.* 1985; Kucera and Haagenrud, 1980), Brazil (Dutra and Vianna, 1982; Vianna *et al.*, 1984), Singapore (Hudson, 1955) and China (Xiong, 1986) are listed in Table 6.2. The sites are divided into the following types of environments (Southwell and Bultman, 1982):

- rural/tropical rainforests
- rural/tropical open inland
- urban/industrial
- marine
- surf beaches.

The corrosion rate of carbon steel at selected sites is shown in Figure 6.4. In general, the corrosion of freely exposed metals in the tropics is not more

Table 6.2 Corrosion rate of carbon steel and zinc at field exposure in different tropical/subtropical environments

Type of environment	Test site	Exposure period, (years)	Corrosion rate, $\mu\text{m}/\text{year}$	
			Steel	Zinc
Tropical rain forest	Nkpoku (Nigeria)	1	5	0.5
	Innisfall (Australia)	1	15	1.4
	Manaus, Amazonas (Brazil)	1	32	
		5	10	
Tropical open inland	Miraflores (Panama)	1	34	1.3
	Santiago de las Vegas (Cuba)	16	15	0.8
		1	38-48	
		1	23	1.7
		1	13	1.5
		1	16	
5	9			
Urban/ industrial	Jamshedpur (India)	1	30-38	0.4-0.9
	Cairo (Egypt)	1	23	
	Casa Blanca (Cuba)	1	61-80	
	Cubatao (Brazil)	1	106	
		5	61	
		1	145	
	Canoas (Brazil)	5	41	
	Port Harcourt (Nigeria)	1	48	0.5
	Hanoi (Vietnam)	5	15	0.4
	Guiyang (China)	1	165	
	Manila (Philippines)	1	40	
	Singapore, aerodrome	1	15	
Marine	Aracaju (Brazil) 350 m	1	93	93
	Cowley (Australia)	1	129	2.7
	Alexandria (Egypt)	1	135	
	Honzau (Vietnam)	5	28	
	Christobal (Panama)	1	83	5.3
		16	21	2.4
	Lagos, Lighthouse 130 m	1	56	2.8
	Beach (Nigeria) 70 m	1	378	14.5
Marine-surf beach	Lagos, Lighthouse Beach (Nigeria) 15 m	1	958	38
	Galeta Point (Panama)	1	618	13
		2	657	14.5
	Cojinur (Cuba)	1	100-510	
	Aracaju, (Brazil) 100 m	1	586	
2		594		

severe than in corresponding atmospheres in the temperate zone. The corrosion rates are low in rural tropical areas, especially in the rainforests.

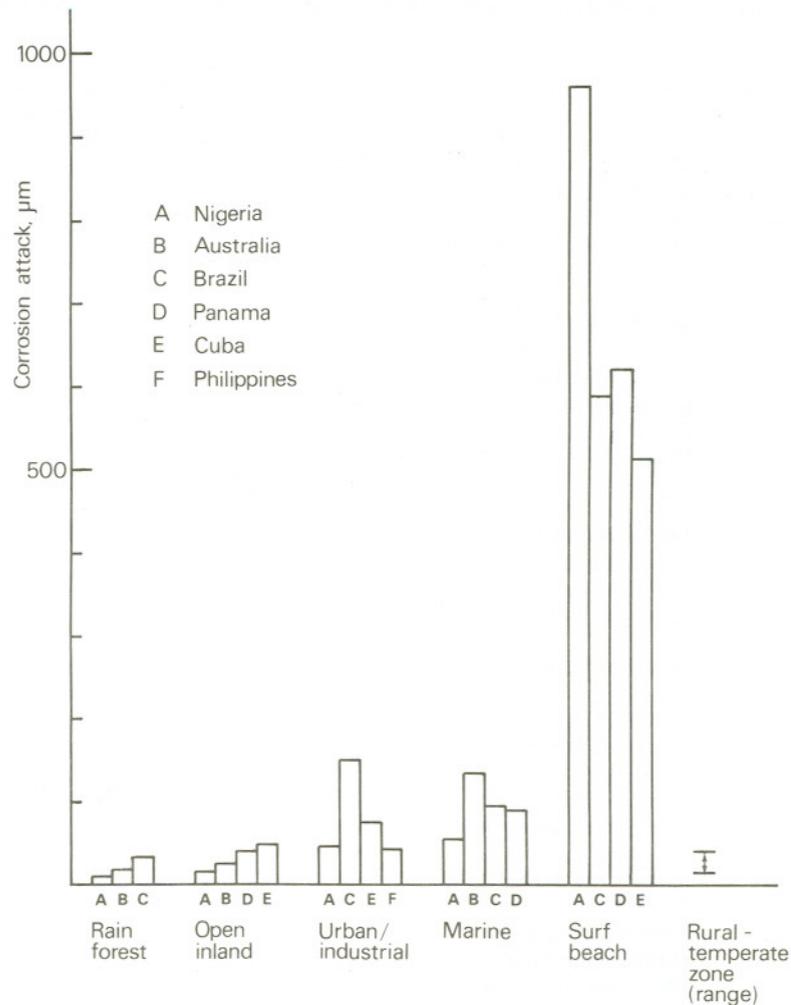


Figure 6.4 Corrosion attack on carbon steel after one year atmospheric exposure in the tropical/subtropical zone

Corrosion rates in urban/industrial areas polluted by sulfur compounds are comparable with those in Europe. High values are reported from heavily polluted areas in Brazil and China, which underscores the risk of corrosion to structures near sulfur sources in tropical and subtropical regions.

In marine regions corrosivity depends on the deposition rate of seasalt, which usually sharply decreases with distance from the shore. On tropical surf beaches with sea-spray the corrosion rates are exceptionally high. Here, long periods of wetness, a high deposition rate of chlorides and high tem-

peratures coincide. In some areas, deposition of chloride containing coral dust or sand enhances corrosion attack.

Corrosion in the tropics is illustrated by the corrosion map of India (Rao and Lahiri, 1972), which subdivides the territory into five corrosivity classes with yearly corrosion rates of carbon steel: $<5 \mu\text{m}$, $5\text{--}25 \mu\text{m}$, $25\text{--}50 \mu\text{m}$, $50\text{--}120 \mu\text{m}$ and $120\text{--}150 \mu\text{m}$. The two classes with the highest corrosivity are found almost exclusively in a narrow zone along the coast. Most of the territory, including the tropical savanna and humid subtropical regions, belongs to the corrosivity class with a corrosion rate of carbon steel between 25 and $50 \mu\text{m}/\text{year}$. In comparison, annual corrosion rates of $25\text{--}50 \mu\text{m}$ are found only in rural and slightly polluted areas of temperate regions.

Corrosion data are scarce, and most data from the tropics are based on relatively short exposure periods. The few existing values from long-term exposure of carbon steel indicate that the decrease in corrosion rate with time due to formation of a rust layer is less pronounced in the tropics than in temperate regions.

The corrosion rate of zinc during outdoor exposure in the tropics is low, except at surf beaches, where values as high as $38 \mu\text{m}/\text{year}$ have been found. Because the protective layer of zinc carbonates is sensitive to acid deposition, increased sulfur pollution in the tropics might promote more severe corrosion of zinc than of steel, as indicated by results from Nigeria. Under rain-protected conditions zinc can show very high corrosion rates. Some authors suggest that this is due to special conditions, such as high concentrations of organic compounds originating from biodeterioration. The corrosion resistance of copper and aluminum materials is considered to be very good under tropical conditions.

6.2.5 Structures, Products and Monuments that may be Affected

Acid deposition affects structures, products, and monuments both outdoors and indoors. Bridges, industrial plants, and motor vehicles are affected, some of them by the combined effect of air pollutants and de-icing salts. An important category of products includes electric and electronic equipment. The detrimental effect of acid deposition, often of a synergistic nature, can be substantial.

Monumental buildings and statues of stone, stained glass windows, paper, leather, paintings, museum textiles and archives are subject to accelerated deterioration from acid deposition.

6.2.6 Economic Aspects and Cost Reduction Schemes

From the practical and economic point of view atmospheric corrosion is closely associated with population centers. The rate of atmospheric corrosion

decreases sharply with increasing distance from the emission source. This may be illustrated by the corrosion of carbon steel as a function of distance from the stack of an SO₂-emitting industry (Figure 6.5) (Kucera, 1976). The great variation of corrosion rates within geographic areas is demonstrated by corrosion maps for cities or whole countries. The corrosion map of zinc for the UK (Shaw, 1978), the corrosion map of several metals for the Sarpsborg/Fredrikstad area in Norway (Haagenrud *et al.*, 1986), and the corrosion map of steel for Madrid (Feliu and Morcillo, 1975) are examples. The very strong local variations of atmospheric corrosion of metals indicate the major role of dry deposition.

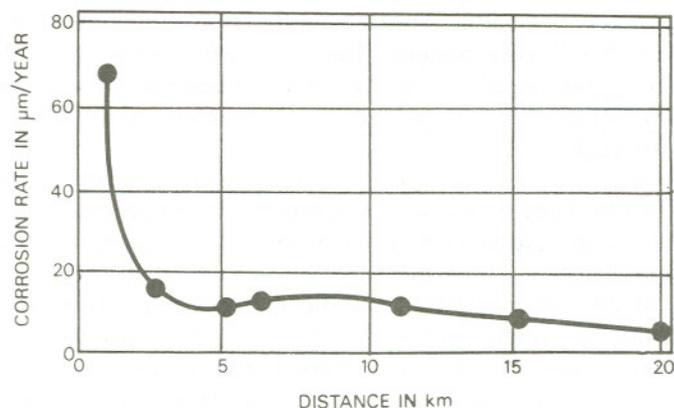


Figure 6.5 Corrosion rate of carbon steel as a function of the distance from the emission source (an industrial stack) (Kucera, 1976)

Atmospheric corrosion is thus, in most areas, a local effect caused mainly by a country's own emissions and only slightly affected by long-distance transport of pollutants. The situation may be different in densely populated areas of western or central Europe, where appreciable corrosion damage can result from transport of pollutants across national boundaries.

Estimating the cost of increased atmospheric corrosion from increased acid deposition is difficult. For some materials, such as painted surfaces, reliable damage functions are lacking. An assessment of materials at risk is now underway. Existing estimates of costs due to acid deposition are uncertain, but typical values found in the literature are often between US\$ 2 and 10 per capita/year (United Nations, 1984). The economically most important materials are painted surfaces and galvanized steel.

Any reduction of pollution levels will reduce corrosion damage. Reducing emissions is the preferable solution given the complexity of the acid rain problem. But building high stacks and discharging flue gases high up in the air may be a solution for local effects caused by acid deposition. In

Table 6.3 Corrosion rate of zinc exposed at the test site Vanadis, in Central Stockholm (Kucera, 1986)

Period	Corrosion rate ($\mu\text{m}/\text{year}$)	Period	Corrosion rate ($\mu\text{m}/\text{year}$)
1938–1953	2.0	1975–1976	2.3
1958–1959	5.0	1977–1978	2.1
1958–1963	4.3	1974–1978	2.0
1967–1968	4.0	1979–1980	1.7
1967–1970	3.0	1984	1.4
1975	2.9		

Sweden both methods are being adopted; The first in pursuance of legislation concerning a low maximum sulfur level in oil for heating, and the second by expansion of district heating systems. It has already had very positive effects, leading to a substantial decrease in the corrosion rate of zinc at points in the inner city of Stockholm, e.g. at the Vanadis test site in Stockholm (Table 6.3). Similar developments at other Swedish locations have meant important economic savings as a consequence of less corrosion.

6.3 CORROSION IN SOIL

6.3.1 Factors Affecting Corrosion

Corrosion of metals in soil is an electrochemical process in which the dissolution of metal represents the anodic reaction. In most cases the cathodic reaction consists of oxygen reduction. From the corrosion point of view, soils are very complicated systems. The corrosion rate and the type of corrosion are determined by numerous factors such as mineral composition and grain size distribution, moisture content, redox potential, electrical conductivity, pH, total acidity, chloride concentration, presence of sulfur and nitrogen compounds, and microbiological activity. In such a complicated system, assessing the effect of soil acidification on the corrosion rate is difficult.

Due to lack of comparable investigations, assessing differences in soil corrosivity between different climatic zones is difficult. Only a few systematic field investigations on soil corrosivity have been carried out. One such investigation was made in the tropical zone in Panama (Pelensky *et al.*, 1978) compared with about five in the subtropic and temperate zones: US (Romanoff, 1957), New Zealand (Penhale, 1984), Great Britain (British Iron and Steel Research Association, 1952), and Sweden (Camitz and Vinka, 1986).

A comparison of the Swedish results, which gave corrosion rates for carbon steel of about 10–40 $\mu\text{m}/\text{year}$ compared to 81 $\mu\text{m}/\text{year}$ in the Panama investigation, reveals that the corrosion rate of buried carbon steel plates is higher in Panamanian soil. However, even higher corrosion rates were

found at some soil test sites in the US and New Zealand, illustrating great local differences in soil corrosivity. Local soil characteristics might have a larger influence on the soil corrosion rate than the climatic zone.

Given a higher overall soil temperature and higher annual precipitation in the tropics, corrosivity might be higher in general in the tropical zone than in other climatic zones.

6.3.2 Changes in Soil Chemistry from Acidification

If soil is subjected to acid deposition neutralization occurs through dissolution of carbonate and silicate minerals. In this process hydrogen ions are

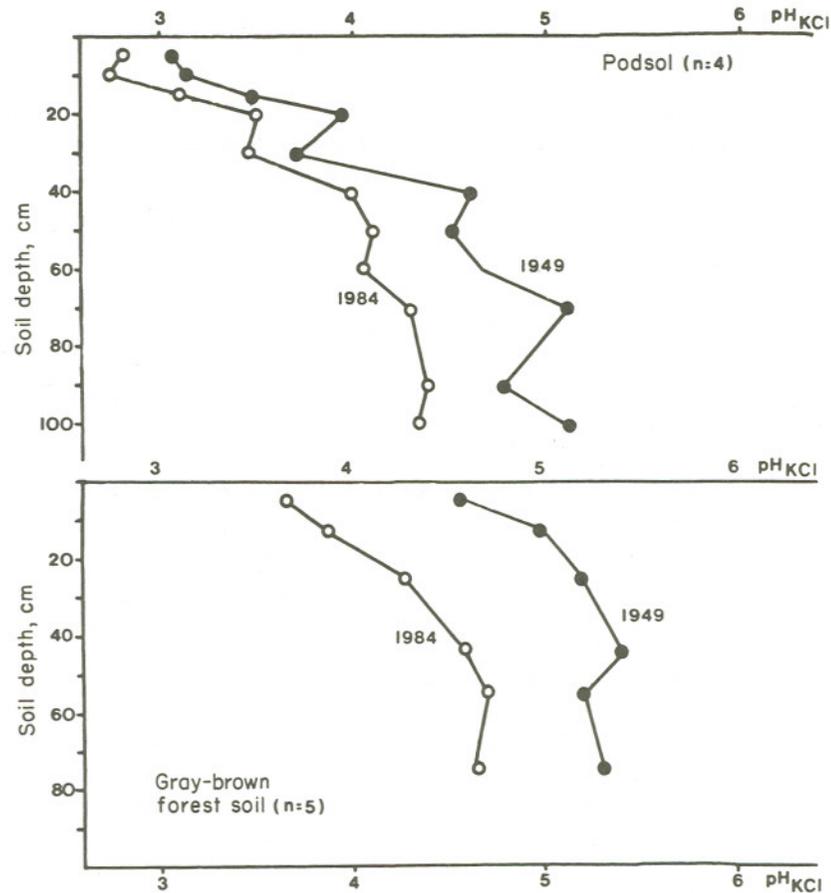


Figure 6.6 Changes in pH at different depths in forest soils in southern Sweden between 1949 and 1984 (Tyler *et al.*, 1985)

consumed and calcium, magnesium, potassium, and sodium ions are released, and the dissolution of basic minerals buffers against pH changes. If soil acidification continues, a successive pH decline in the soil and soil water will result. Different areas are affected differently, depending on the geology of the area and on the deposition load of acidifying pollutants. In a few studies the pH of soil was remeasured at the same site after several decades. These studies have shown a substantial pH decline. A recent Swedish investigation is an example (Tyler *et al.*, 1985) (Figure 6.6). The pH decreased not only in the topsoil but in the whole investigated soil profile, which may be an important fact for the corrosion of buried constructions.

6.3.3 Effects of Soil Acidification on Corrosion

A survey of the published literature reveals no systematic studies of the influence of soil pH on the corrosion rate of different metals. There are investigations where soil acidification parameters are included among other variables. Some of them can be used to make a preliminary judgement.

Carbon steel, cast iron

Opinions are divided as to how low the soil pH must be to affect the corrosion rate of steel and cast iron. It is generally agreed that the corrosion rate increases when the pH falls below about 5. Some observers, however, relying mainly on results from the analysis of several thousands of road culverts in California, consider that lowering soil pH increases corrosion at pH 6 (Figure 6.7) or even at pH 8.5 (Stratfull, 1961; AHDGA, 1982). Others consider that the corrosion rate of steel does not increase until the pH falls below about 5 (Schaschl and Marsh, 1963; Steinrath, 1965).

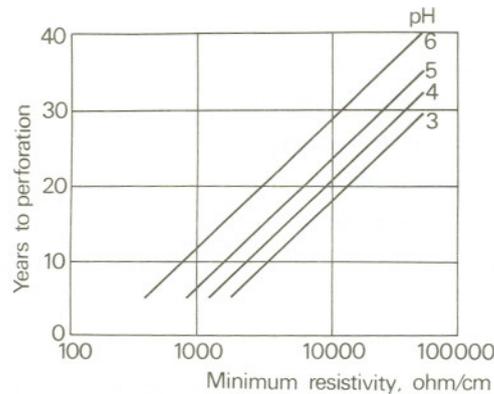


Figure 6.7 Time to perforation of a 2 mm galvanized steel culvert wall as a function of the pH value in soil (American Hot-Dip Galvanizer's Association, 1982)

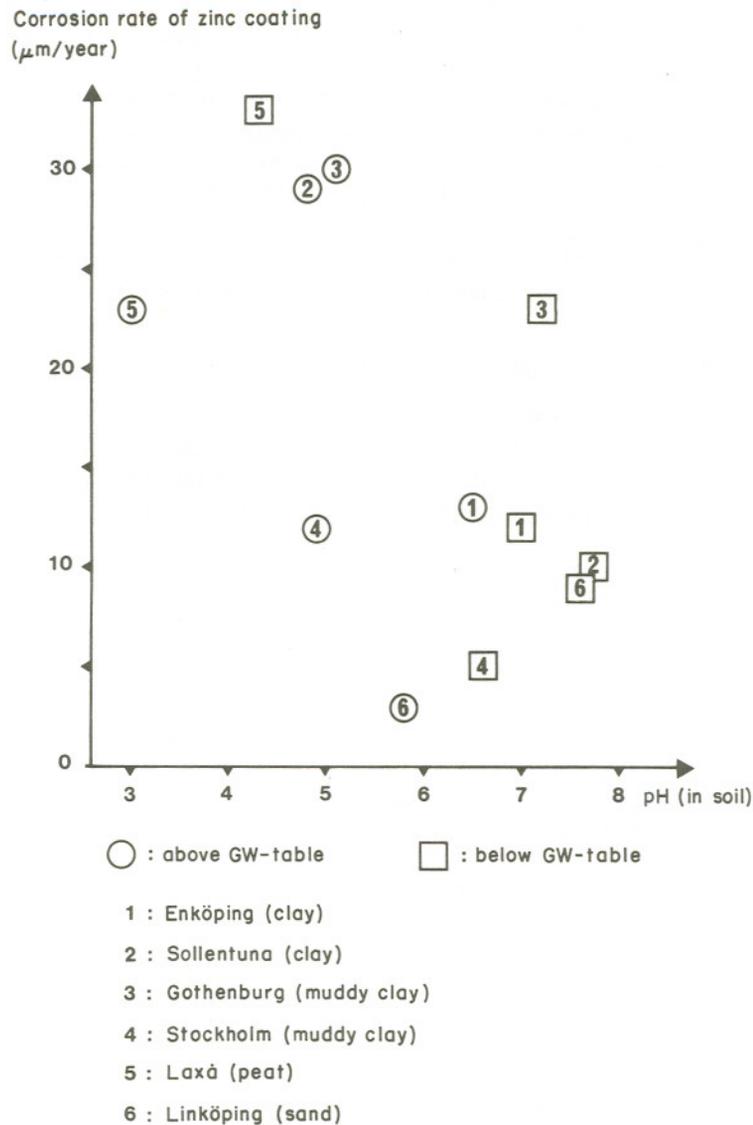


Figure 6.8 Corrosion rate of zinc coating as a function of pH in soil after one year of exposure at different test sites (Camitz and Vinka, 1986)

Zinc, galvanized steel

The corrosion rates vary widely and may be very high both in acidic and in very alkaline soils (Marcovic and Plavsic, 1961; Romanoff, 1957). Limited experimental evidence shows that the corrosion rate of zinc increases sig-

nificantly when pH falls below about 4 (Camitz and Vinka, 1986) (Figure 6.8).

Other important technical materials which may be sensitive to soil acidification are copper, lead, concrete, and impregnated wood.

6.3.4 Structures that may be Affected

Many structures important to society are buried in soil. A partial list comprises a number of technically and economically important structures that may be susceptible to soil acidification: water mains of steel and cast iron; galvanized steel, copper and lead connectors from the mains to houses; road culverts of galvanized steel and concrete; lead-sheathed telephone cables; oil and gasoline tanks; power line tower foundations, including stays; and concrete sewers.

6.4 CORROSION IN WATER

6.4.1 Factors Affecting Corrosion

Corrosion of metals in water is an electrochemical process in which the dissolution of metal is the anodic reaction and reduction of oxygen dissolved in water is the cathodic reaction. Only in extremely acid waters with $\text{pH} < 4$ can hydrogen evolution as cathodic reaction be of practical significance. Water composition is of decisive importance for the formation of protective layers on the metal surface, and these layers are often important in determining the corrosion rate. The hydrogen carbonate ion (HCO_3^-) is often the most important factor for formation of protective layers. The water composition usually determines whether certain types of local corrosion can occur at all.

Data comparing the corrosivity of fresh waters in tropical and temperate regions are scarce. An exposure series in the Panama Canal Zone revealed that although the corrosion rate of steel in fresh waters varies widely, the rate in the tropics was generally higher than in the temperate zone. This is attributable in part to the higher temperature (Southwell and Alexander, 1970; Forgeson *et al.*, 1960; Alexander *et al.*, 1957).

6.4.2 Changes in Water Chemistry from Acidification

On acidification, the HCO_3^- concentration of water drops and the SO_4^{2-} concentration and total hardness increase. This development can increase the corrosivity of water toward certain metals. When the buffering capacity of water has fallen to about 6 mg HCO_3^- /liter, the pH value becomes unstable and falls. This has been the case in several surface waters in southern

Scandinavia, in the northeastern United States and in Canada, where pH values between 4.5 and 5.5 occur.

6.4.3 Effects of Water Acidification on Corrosion

The influence of water quality on corrosion of plumbing materials is a topic of great practical interest. Knowledge of water treatment in waterworks may be used to determine the effect of water acidification on corrosion. The corrosion risks for the most important materials follow.

Carbon steel, cast iron

The corrosivity of tap water is customarily related to the ability of the water to precipitate calcium carbonate which, together with rust, can form a tight and protective layer on the steel surface. The ability of water to create protective layers is usually evaluated using so-called calcium carbonate saturation indices (Langelier, 1936; Ryznar, 1944)

Quantitative relations between saturation indices, water acidification, and the corrosion rate of steel and zinc have not been investigated systematically. Recent research in two headwater streams that supply raw water to small water systems in Pennsylvania shows adverse chemical changes during episodes of acid rain and snowmelt (Liebfried *et al.*, 1984). The pH decreased as the stream flow increased, whereas corrosivity expressed as Ryznar stability index (R_s) increased (Figure 6.9). In general, soft and acidic waters are cor-

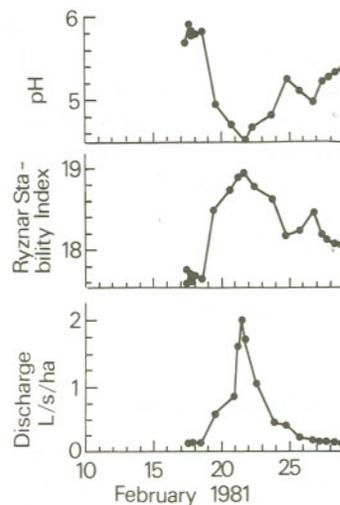


Figure 6.9 Stream flow, pH, and Ryznar stability index during an episode of acid flow in a small water stream (Liebfried *et al.*, 1984)

rosive. A soft water with low hydrogen carbonate concentration, however, produces no protective coating even if the pH is raised.

Copper and copper materials

Copper is an important plumbing material in many countries. Acidification of water that results in lower HCO_3^- content, increased SO_4^{2-} content and decline in pH can lead to different types of corrosion:

1. Dissolution of copper (cuprosolvency), or the concentration of dissolved copper salts in water, increases with falling pH below a given critical level dependent on temperature and water composition (Mattsson, 1980; Cox and Dillon, 1980) (Figure 6.10). If the copper concentration in the water becomes too high, sanitary porcelain and textiles can become stained. Small amounts of copper—up to 1–2 mg/liter—are not considered dangerous to health at least for healthy adults (Holtmeier *et al.*, 1978; BNF Metals Technology Centre, 1978). An effective countermeasure is to increase the pH of the water to 8.0–8.5.
2. Pitting corrosion/type II, occurs solely in hot-water installations if the pH is between 5.0 and 7.0, but not at $\text{pH} > 7.4$ (Mattsson and Fredriksson, 1968). The risk of type II pitting corrosion is great if the $\text{HCO}_3^-/\text{SO}_4^{2-}$

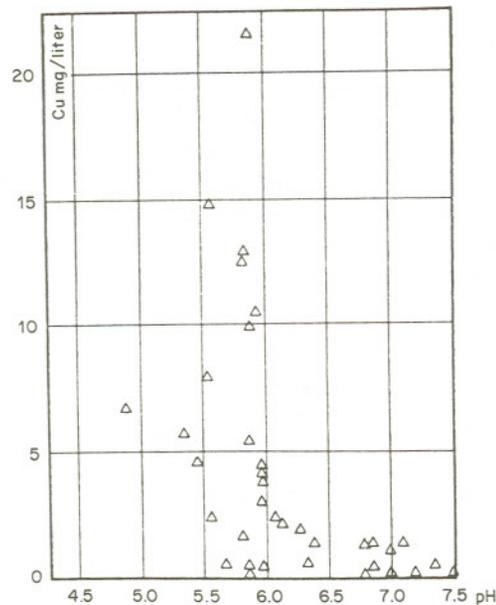


Figure 6.10 Copper concentrations in tap water that has been stagnant overnight in copper pipes as a function of pH (Swedish Ministry of Agriculture, 1982)

ratio is < 1 . Acidification of water thus increases the risk of this type of corrosion.

3. Pitting corrosion/type III occurs in cold-water pipes and is caused by the water composition. The damage arises in very soft and salt-deficient water; the pH of the treated water is high (von Frangué *et al.*, 1975; Linder and Lindman, 1983). All Swedish cases have occurred in acidified areas with extremely low concentrations of hydrogen carbonate in the raw water.
4. Erosion corrosion occurs if the water flow in the pipe is too high so that protective layers are removed by the turbulence. Such attacks have been found to be both more extensive and to occur at lower flow rates if the pH of the water is lowered, for example, from 8.0 to 6.5 (Knutsson *et al.*, 1972).

Galvanized steel

The corrosion resistance of galvanized steel water pipes depends on whether a protective layer of basic zinc carbonate (DIN, 1976; Hissel, 1979; Bächle *et al.*, 1981) or a mixture of basic zinc carbonate with calcium carbonate (Butler and Ison, 1966) can be formed. A high hydrogen carbonate concentration contributes to formation of such layers. In general soft acidic waters are corrosive, with the water pH affecting the protective properties of the layer (Figure 6.11).

Lead

Although the use of lead for water pipes is decreasing, there are areas in Europe, the US, and Canada where lead is still used in plumbing. The lower the pH and the concentration of salts, the more corrosive the water. The mean concentration in municipal water supplies in the US is about 10 $\mu\text{g}/\text{liter}$. In some areas, e.g. in Boston, lead concentrations are more than 50 $\mu\text{g}/\text{liter}$; in other areas, where the water is stored in lead-lined tanks, concentrations above 1 mg/liter have occurred (Young and Sharp, 1984; Richards and Moore, 1984).

6.4.4 Structures that may be Affected

Existing knowledge is insufficient for assessing whether acidification has had any practical significance for the corrosion rate of most structures in contact with fresh water. When increased damage has been found, the knowledge has usually not been sufficient for quantification, as is often the case with plumbing systems in buildings and with road culverts.

Water pipes

The internal corrosion of water pipes caused by acidic groundwater and

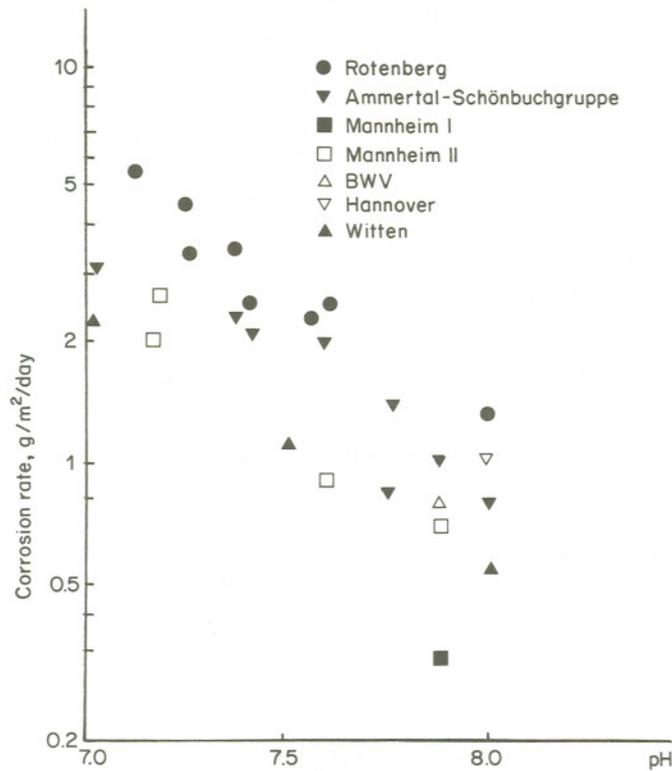


Figure 6.11 Corrosion rate of zinc in 26 different tap waters as a function of pH (Bächle *et al.* 1981)

surface water is one of the most evident corrosion problems today. The corrosion of copper, galvanized steel, and lead pipes can increase considerably by acidification of water supplies, and the concomitant drop in pH and hydrogen carbonate concentrations and rise in sulfate concentrations. This is particularly manifest if the pH falls below about 7.0.

Municipal waterworks in several countries treat water to maintain a pH between 7.0 and 9.0. In areas with acidic water supplies the hydrogen carbonate concentration as well as the pH should be raised in the treatment. Houses receiving treated municipal water probably are little affected if the initial water source has become more acidic, but the acidity will increase the costs of equipment and chemicals in the waterworks.

The corrosion risk in drinking water is related to how supplies are managed. Risks are generally greater the smaller the water supply. The greatest risk is in small privately owned supplies (Clarkson 1983).

Roof-catchment systems, which consist of a rain collector and a storage tank, give rise to corrosion problems in plumbing installations in areas with acid precipitation. These systems are common in some regions in the eastern United States where groundwater has been polluted by mining activity and public water supplies are not available. Tap water samples from such systems plumbed with Pb-soldered copper pipes showed mean standing tap water Pb concentrations above the limit of 50 $\mu\text{g/liter}$ in 22% of cases and 28% had Cu concentrations exceeding the 1,000 $\mu\text{g/liter}$ drinking water limit for copper (Richards and Moore, 1984).

In connection with water supplies, the corrosion of pump elements, such as bowls and impellers made of cast iron and bronze, in groundwater is also a factor. Water pH was found to be the closest indicator of lifetime (Kelly, 1983).

Road culverts

Acidification of lakes and watercourses may also affect the corrosion rate of structures such as sluice gates, pipelines in power stations, or in road culverts of galvanized steel and concrete. Investigations of the corrosion of galvanized steel and concrete road culverts and of the water and soil pH at those places were conducted in Sweden and in the United States. They reveal that corrosion effects are considerably greater in water with lower pH (Arrhenius, 1966; Hurd, 1984) (Figure 6.12).

6.5 CONCLUSIONS

1. The atmospheric corrosion of metals caused by acid deposition is mainly a local problem restricted to areas close to pollution sources.
2. The main corrosive effect is caused by dry deposition of air pollutants. The influence of acid precipitation may differ for different materials and depends on the pollution level.
3. The effects of S-pollutants, especially SO_2 , are of greatest importance.
4. According to existing knowledge, NO_x has a limited influence on the corrosion of steel and zinc in outdoor atmospheres. There are indications that NO_x in combination with SO_2 can promote corrosion of, for example, copper and calcareous stone materials.
5. Indoors, NO_2 in combination with SO_2 has a synergistic corrosive effect on electrical contact materials like gold plating and copper, and may also be important for other materials (e.g. carbon steel) at storage in industrial atmospheres.
6. Important technical materials and materials used in historical monuments and buildings are seriously damaged by increased atmospheric corrosion from acid deposition.

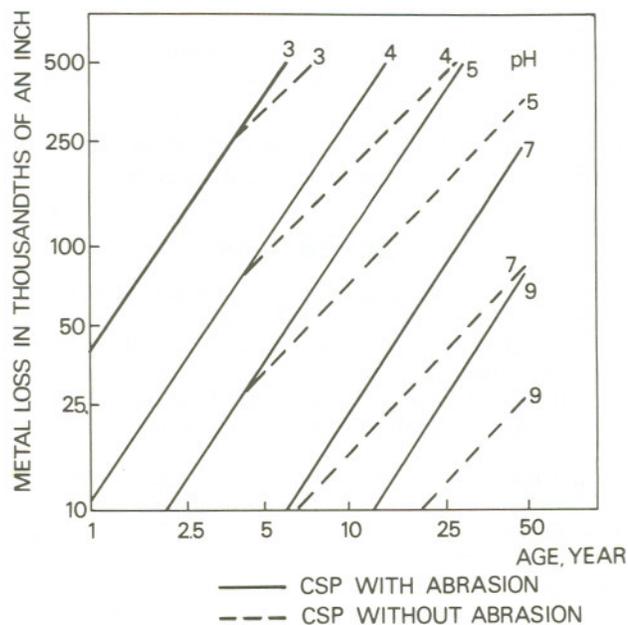


Figure 6.12 Predicted metal loss for corrugated steel pipe culverts as a function of water pH (Hurd, 1984)

7. Corrosion due to acidification of water and soil is principally a regional problem and thus is affected by long-range transport of air pollutants to susceptible areas.
8. Corrosion in soil is a complicated process and dose-response relations between the corrosion rate and pH or acidity are lacking. Indications that soil acidification may increase the risk of corrosion of important technical materials and constructions exist.
9. Decreased alkalinity and pH and increased sulfates from acidification increase the corrosivity of water to important engineering materials, such as steel and cast iron, galvanized steel, copper, lead, and concrete. Criteria of occurrence are known for some of the related corrosion phenomena. Dose-response relations are lacking.
10. Increased internal corrosion of copper, lead, and galvanized steel water pipes in buildings is a great technical problem in areas sensitive to acidification. Where lead pipes or lead-containing solder are used, elevated lead content in tap water creates a potential health hazard. Increased corrosion of road culverts in these areas can also be expected.
11. Distribution mains and house connections; certain types of foundations for power line towers, including stays; lead-sheathed telephone cables

and underground tanks are among the buried structures identified as potentially susceptible to soil acidification.

12. Assessing the risk of increased corrosion damage by acidification in the tropics does not seem possible. However, due to higher temperature and higher humidity, structures in the atmosphere, water, and soil could be subject to stronger corrosive influences from acidification than in the temperate zone. More research is urgently needed.

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