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CORROSION IN THE ATMOSPHERE

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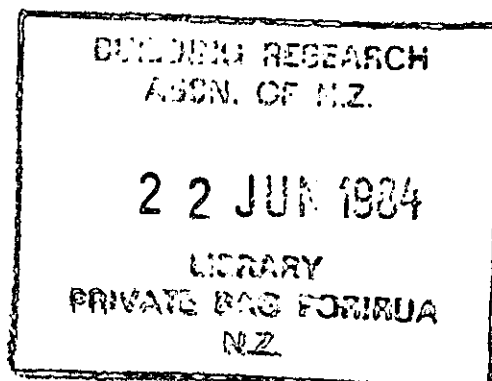
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ABSTRACT

1. THE SIGNIFICANT OF ATMOSPHERIC CORROSION IN ECONOMIC AND TECHNICAL TERMS.
2. THE IMPORTANCE OF WATER, WHETHER VAPOUR OR LIQUID, IN ALL ATMOSPHERIC CORROSION PHENOMENA. ASSESSMENT OF CLIMATES WITH RESPECT TO TIME OF WETNESS OF SURFACES.
3. MECHANISMS OF ATMOSPHERIC CORROSION OF METALS (ESPECIALLY THE DIFFERENCE BETWEEN FERROUS AND NON-FERROUS METALS). THE EFFECTS OF CORROSION PRODUCTS ON ATMOSPHERIC CORROSION PROCESSES.
4. THE STIMULATION OF ATMOSPHERIC CORROSION BY SULPHATE OR CHLORIDE IONS. ASSESSMENT OF CLIMATES WITH RESPECT TO THESE CORROSION STIMULATORS.
5. MICROCLIMATIC INFLUENCES ON ATMOSPHERIC CORROSION - ESPECIALLY THE EFFECTS OF
 - (A) SURFACES OPEN TO THE AIR, BUT SHELTERED FROM RAIN, WITH DEPOSITED SALTS WITH CRITICAL HUMIDITIES BELOW 100% R.H.
 - (B) ORIENTATION OF SURFACE WITH RESPECT TO SUN, PREVAILING WINDS, AND POLLUTION SOURCES.



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INTRODUCTIONTHE ECONOMIC IMPACT OF ATMOSPHERIC CORROSION

It is no exaggeration to claim that corrosion in the atmosphere is the most pervasive corrosion problem faced by man. No matter what country one visits, problems are evident in corrosion of building components or agricultural implements, both of which can lead to loss of food production or loss of shelter, two of our most basic needs. The more sophisticated the country's economy, the more sophisticated the problems of atmospheric corrosion become, whether due to the additional man-made additional hazards (such as industrial pollution) or to the sophistication of the corrodible structures (such as oil rigs or chemical plants). Our engineered structures, such as buildings, bridges, production plants and railway systems, in general have the atmosphere as the major environment in which they must resist corrosion. Much of our equipment (such as tools or motor vehicles) spends a significant part of its life not in service, but always having to resist atmospheric corrosion. Thus, from the most basic community to the most sophisticated, atmospheric corrosion has the ability to influence a nation's economic health.

The corrosion world is now familiar with the assessments made of the cost of corrosion to the UK economy (Report of the Committee on Corrosion and protection, 1971) and the US economy (Bennett et al 1978, Payer et al 1978). There seem to have been no recent attempts to assess how much of this cost is attributable to corrosion in the atmosphere. Barton (1976) took the ment by Uhlig (1950) of the direct corrosion costs to the USA in 1949, and suggested that half was in expenditure on measures against atmospheric corrosion. This pays no attention to the indirect cost -the financial loss because a production line has to be closed down for unscheduled repair, for example, or because a warehouse roof has corroded through, leaked, and spoiled the stored goods.

Another approach to assessing the costs of atmospheric corrosion is that used by Daeves and Trapp who are quoted by Barton (1976) to have calculated that 2% of steel production in Germany in 1937 was being converted back to rust by atmospheric corrosion each year. It should be remembered, however, that a metallic component may be rendered totally unserviceable by the loss of a few per cent of its weight if the corrosion has attacked a section of critical dimensions or strength, or if the component is part of a safety mechanism. The costs of small amounts of corrosion can be disproportionately high.

The impact of corrosion in all its forms could be significantly lessened if existing knowledge was more widely applied, and education of those responsible for materials selection in industry is just as pressing as the need for fundamental research. In this paper, an attempt has been made to indicate some of the important work on atmospheric corrosion published over the past decade or so, and the themes which seem to be emerging as most important, to provide some signposts for those not familiar with the subject. At the same time, opportunities have been taken to indicate these areas where research still seems to have some way to go.

MECHANISMS OF ATMOSPHERIC CORROSION

It is not intended in this paper to summarise the textbooks which are available on atmospheric corrosion. Special attention should be paid to those by Rosenfeld (1972), Barton (1976) and Ailor (1982) which in turn summarise the state of the art in 1960, 1972 and 1980. However, it is essential to lay down a few guidelines to important theoretical points.

The actual physical processes in which metals are converted to metallic ions in atmospheric corrosion are reasonably well characterised. In general we can place metals into one of four categories:

- (a) Noble metals, which remain unattacked in the presence of atmospheric electrolytes. Examples are platinum and gold.
- (b) Passivating metals, on which a tenacious, thin, unreactive oxide layer is formed under normal atmospheric conditions, so that corrosion is generally slow, and localised at weak points in the oxide film. Examples are aluminium, chromium, titanium, or stainless steel. Provided dust deposits do not occur (to produce differential aeration cells) these metals are generally fairly resistant to acidic pollutants in the air, but they can be quite severely attacked by chloride ions, especially under prolonged contact conditions such as occur on unwashed surfaces.
- (c) Convertible oxide metals, which form a near-insoluble oxide/hydroxide layer which reacts with atmospheric impurities to form salts of greater solubility. Zinc, copper and lead fall into this category. The attack is general across the surface of these metals, with the rate-determining process occurring at the oxide/air interface.
- (d) In a class of its own comes the most technically important metal, iron (or mild steel). This typically corrodes 10-100 times as fast as zinc over a two-year exposure period in the atmosphere (Coburn et al, 1968). In contrast to zinc, the rate of iron corrosion is determined by the process at the rust/metal interface, and the rust is sufficiently porous for air, water and pollutants to have easy access to this rust/metal interface. This point is returned to shortly. Some important consequences arise; for example, water can be physically held in the rust when it would be lost from a zinc surface; and it is necessary when protecting iron with a surface coating to remove all of the rust, to ensure that all corrosion-stimulating salts are removed, whereas less rigorous surface preparation is needed on a zinc surface.

Low alloy steels, including "weathering steels", corrode at the same rate as mild steel for the first few months of exposure, but under the appropriate exposure conditions (i.e. wet/dry cycling, and absence of chloride ions) the low alloy steels have a rapid reduction in corrosion rate. This appears to be due to a strongly adherent layer adjacent to the steel surface (though the outer layer retains its normal loose structure), and presence of copper in the alloy seems essential for this process. This inner layer has been demonstrated using Raman spectroscopy to have delta-Fe OOH as its major component (Keiser et al 1983), as originally proposed by Misawa et al (1971) from infrared spectroscopy of the rusts. Suzuki et al (1980) did not consider the delta phase, though they identified the importance

tance of an amorphous layer of unknown identity, and found that copper addition to the alloy lowered the electrical conductivity of the rust and markedly increased the buffering capacity of the rust in an acidic environment.

The corrosion products on all metals can affect the course of corrosion in this same fashion. Grauer (1980, 1981) has summarised the available information on the phases of solid corrosion products which form under a variety of exposure conditions in the atmosphere and in immersed conditions; thus, for example, four different crystal modifications of zinc hydroxide can occur, as well as an amorphous form, and each has its particular stability with respect to reaction with other anions present in the system, so that different carbonate/hydroxide mixed salts also arise. Grauer also notes that identification of the corrosion product composition can be a powerful tool in indicating the environment in which corrosion occurred and clarifying the mechanisms of the corrosion reaction.

When corrosion-stimulating anions such as chloride or sulphate occur on iron surfaces, they tend to occupy "nests" (Barton et al 1971, Barton et al 1978, Henriksen 1969). A semipermeable membrane of iron oxide/hydroxide lets water into the nest but contains the sulphate or chloride within the nest until the osmotic pressure becomes too great and the membrane bursts. It is therefore of little value, in preparing to overcoat a rusted steel surface which has been contaminated with sulphate or chloride, to simply wash the surface. Surface ablation is virtually essential. The membrane is otherwise going to retain the anions in the nest against the metal surface. Barton et al (1978) note that this membrane may also render less effective the so-called "rust stabilisers" often applied as surface treatments, by keeping the anions in a suitable reactive environment if water is still able to permeate to the membrane and through it. As Barton and his co-workers point out, we still have much to learn about the mechanism whereby the membrane controls reactivity of the surface of this, our technologically most important metal.

THE INVOLVEMENT OF WATER

The involvement of water in providing the electrolytic path for atmospheric corrosion is essential but severe atmospheric corrosion can occur even in the absence of visible water film formation on surfaces. Rain - wetting of a vertical surface creates a film at most a few tenths of a millimetre thick, because of the hydrostatics of the film, but there can be significant corrosion in films only a few tens of micrometres thick which are deposited from humid atmospheres onto salt-contaminated surfaces. During rain, the water layer continuously renews itself, and so continuously introduces to the surface film corrosion promoting species dissolved from the atmosphere. However, the rate of exchange of the water is often so great that rain will actually wash away more salts or other surface contaminants such as corrosion products than it delivers to the surface.

When the surface builds up a visible liquid film due to exposure to fog, or in dew formation, the corrosion problems can be much more severe. The amount of water exchange in the surface film is much lower, yet the film will be saturated with any corrosion-promoting species present in the atmosphere, so that when it evaporates it may leave behind larger amounts of salts

on the surface than were originally present.

Adsorption of water onto pure metal surfaces produces layers only 25-30 monolayers thick, which are much too thin to act as an electrolyte (Skorchelletti and Tukachinski, 1953). At this thickness, the water molecules will be held in a semi-rigid configuration by their physical interactions with the metal surface (Morariu and Mills, 1972). If the surface is contaminated by salts, however, the formation of surface electrolyte films can be significant even at humidities below 100% RH. Several sources (e.g. Young 1967) have tabulated "critical" relative humidity values for relevant salts. The "critical" value is the equilibrium humidity over a saturated solution of the salt; if the humidity of the atmosphere exceeds the value the saturated salt solution takes up water until equilibrium is achieved, and conversely the salt solution gives up water to the atmosphere if the humidity is below the critical value. The values for some salts are given in Table 1, for 20°C. For some salts the effect of temperature on the critical humidity is considerable, while for others such as sodium chloride there is virtually no temperature effect. As will be seen from Table 1, the salt which takes up the water may be a corrosion product; this is particularly true of the metal chlorides which may form in a marine environment.

The salt may come as concentrated electrolyte droplets in the air, if solid particles find themselves carried into an air stream which has a higher relative humidity than the critical value for that salt. There has been a suggestion that the marked increase in deposition rate of sulphur dioxide onto steel surfaces above 80% RH (Vannerberg and Sydberger, 1972; Duncan and Spedding, 1973) is in fact due to a gas molecule cluster effect in the atmosphere, where $\text{SO}_2 \cdot n\text{H}_2\text{O}$ (with $n = 5$ to 7) is more easily deposited than the unhydrated SO_2 molecule (Strekalov and Mikhailovskii 1972, Sprott 1981) but can only form at these elevated humidities.

There are thus a number of mechanisms of formation of adequate electrolyte layers for atmospheric corrosion, but in contrast there are only two possible mechanisms of loss of water from the electrolyte layer. These are evaporation (which has to be the chief mechanism) and reaction of the water at the surface. Evaporation can occur only at relative humidities below 100%. Both the temperature of the ambient air (which determines how much moisture the air can hold at 100% RH) and any temperature differences between the surface and its surroundings are certain to have considerable effects on the evaporation rate. Thus, while the likelihood of electrolyte layer formation may be reasonably predictable from humidity and rainfall duration data, the "time of wetness" of the surface (i.e. the lifetime of the electrolyte layer which forms) is much less predictable, and has been the focus of much recent effort by atmospheric corrosion researchers.

The approach to determining the time of wetness of a surface has been dominated by the use of electrical circuit sensors, and comparison of the circuit output to data on humidity in the atmosphere. Considerable developments have been made since the initial work by Sereda (1959), and the latest-generation miniature sensors (e.g. Sereda, Cross and Slade, 1982) are undoubtedly a valuable tool in assessing the relative times of wetness, and hence different hazards of corrosion, on different surfaces of a structure. The response of the sensor is extremely sensitive to the total en-

vironmental conditions, including the deposition of salts from the atmosphere and the difference between surface temperature and ambient temperature. Unfortunately, even the latest miniaturised detectors may not be able to avoid producing different surface temperature conditions from those on the substrate. While the sensor should be very reliable at providing information about the specific surface to which it is attached, it may be of less value to use the circuit response to make detailed inferences about the expected behaviour of all surfaces in the neighbourhood. The correlation to humidity values is suspect, in that a sensor gives a different value for time of wetness depending on the heat capacity of the structure behind the surfaces (Grossman 1978). Grossman also made the point that the wind speed across the surface affects the surface/ambient temperature differential, and hence the ambient relative humidity needed for condensation. Unpublished work at Building Research Association's exposure site, where we used the miniature sensors described in Sereda *et al* (1982), has shown a surface colour effect, the thermal capacity effect mentioned by Grossman, and a difference from month to month in the correlation between times of wetness to the time a particular value of relative humidity is exceeded. The early work over the period 1959-62 by Guttman (1968) using Serada's initial sensor design suggested that a rough rule of thumb was that a zinc surface was wet for the same duration as the relative humidity exceeded 86.5% (averaged over the four years) at Birchbank, Canada, but there was markedly different times of wetness for skyward - and groundward-facing surfaces of the same panel. Using a different style of sensor, Mansfield (1979) concluded that for outdoor exposure at his laboratory in California the time of wetness correlated to the period when relative humidity exceeded 40%. Using yet another sensor design, Haegenrud (1980) collected data in southern Norway which showed time of wetness to correlate closely to the duration of precipitation, and if related to a relative humidity level corresponded to 95% (or slightly above). Some of these inconsistencies arise because of the minimum current or voltage deviation from the baseline chosen to represent "wetness" for each sensor design, but there seems little doubt that there has to be considerable increase in our understanding of how to interpret the data collected, and how to allow for the vast range of meteorological parameters beyond relative humidity which affect wetting and drying of surfaces. (This does not detract from the usefulness of these monitors in assessing the fine detail of effects on atmospheric corrosion rate of very small changes under laboratory-controlled conditions, such as the techniques which have been developed by Mansfield and his co-workers).

A much more empirical approach, which appears to recognise these difficulties in correlation of corrosion rate to meteorological parameters using simple measurements, is that which the group at the G.V. Akizov Institute for Protection of Materials in Prague have been developing over a period of many years (see e.g. Cermakova *et al*, 1974, Cermakova and Barton 1982). This technique relies on availability of extensive monitoring for substitution into mathematical expressions and as such requires a minimum of a year's data collection before the site's aggressiveness can begin to be assessed. Because this group has collected so much data in Czechoslovakia, their mathematical model is likely to be satisfactory for their own country, and perhaps those surrounding, but it may be of less use without extensive prior validation in, for example, the much warmer climates of the Arabian Gulf or in heavily marine-influenced climates. (Cermakova *et al*

(1974) acknowledge this point in their paper, and suggest that their method is not valid even for mapping corrosion aggressivity of large areas within a single country).

Thus, there is still much for the corrosion scientist to perfect in his methods of anticipating the possible effects of atmospheric moisture on corrosion rates. Perhaps, too, there has been far too little attention paid to the frequency of wetting/drying, as opposed to the duration of surface wetness. Cermakova and Barton (1982) have begun to work this factor into their classification scheme, but it is so very heavily dependent on design, microclimate and the presence of adsorbed salts that it is an extremely difficult parameter to assess. Nonetheless, it is an extremely important one. Rosenfeld (1972) provided data to show the considerably greater corrosion of a steel surface which was wetted hourly than a comparable surface wetted once a day with sodium chloride solution. More recently, Schwitter and Bohni (1980) have shown the large difference in behaviour of low alloy steels when exposed to a daily series of wet/dry cycles compared with exposure to "wet" time in a single unbroken interval each day.

STIMULATION OF ATMOSPHERIC CORROSION BY POLLUTANTS

Without doubt, the world's worst atmospheric corrosion problems are attributable to pollution by oxides of sulphur. Sulphur is present in significant quantities in many low-grade fuels, and its conversion to sulphur dioxide (and sulphur trioxide) in combustion processes, and its consequent emission into the atmosphere, is responsible for many problems. Not least of these problems is the acidification of rainfall. Rain saturated with CO_2 at its atmospheric partial pressure would have a pH of approximately 5.6.² Absorption of other atmospheric pollutants can change the pH, and Likens *et al* (1979) have noted the widespread acidification of rainfall over Northwest Europe and North America, with consequent ecological disturbance to forests, lakes and streams. The cost of desulphurisation of fuel, or scrubbing of smokestack emissions, can be high, but is increasingly being regarded as an essential premium to be paid.

Beside the political implication of these ecological effects, the enhanced danger of attack on metals or building stones often seems almost lost from sight. Hydrolysis of sulphur oxides produces highly acidic solutions. It is very common to find metal surfaces around a flue to be very much more corroded than comparable surfaces only a few tens of metres distant. Because of its importance, in attacking the equipment used in industry, atmospheric corrosion processes involving SO_2 have been intensively examined, and this gas, more than any other pollutant, routinely has its concentration measured at numerous sites where corrosion investigations are in progress. The monitoring methods available are varied; the simplest is the sulphation plate (Huey 1968), where a lead oxide surface is exposed for a period of several days to several weeks, and the amount of deposited sulphur gases determined by analysing the "plate" material. This has the advantage of simplicity of collector design, but may be rather inaccurate if the plate surface composition varies.

Torikai *et al* (1971) found rates of SO_2 adsorption onto PbO_2 to depend on oxide surface area, ambient temperature, and amount of moisture on the surface. Different lead compounds appear to take up SO_2 at different rates

(Duncan and Spedding 1974). Another SO_2 detection method, using rather more sophisticated equipment, involves entrainment of the atmosphere through a solution of hydrogen peroxide and subsequent analysis of this solution (British Standards Institution 1976), and other even more sophisticated "instant" analysis methods are available. Instantaneous values for pollution are of little value, however, unless they represent "normal" long-term conditions.

These aggressive sulphur-containing gases need not arise from human activity. Natural sources such as volcanoes or geothermal zones are common, though rarely adjacent to technological centres and so are perhaps given less attention by the corrosion fraternity. The problems posed can be extreme, however. Parts of one of New Zealand's major tourist centres, Rotorua, have 7000 microgrammes of hydrogen sulphide per cubic metre of air, and the "normal" level in the city is 15 microgrammes per cubic metre (Kennett 1978). This is fifteen times the quoted level (Barton 1976) for normal urban atmosphere", and very considerable corrosion problems arise as a result. For example, special air conditioning has been needed to keep the telephone exchange from continually failing due to corroded contact points (Burns *et al* 1972). Rainfall pH values as low as 4.0 have been measured at Kawerau, at the eastern boundary of the geothermal field, and this acidity may be attributed to the natural release of acidic gases. (A pulp and paper plant is virtually the sole industry in the town, but the rainfall pH varies so widely that the plant would seem to be exerting very little, if any, effect). Zinc surfaces corrode at approximately twice the rate found in comparably situated locations in New Zealand which are remote from geothermal areas; the acceleration rate for steel corrosion does not seem to have been quantified.

The chief natural pollutant with significant atmospheric corrosion impact is the chloride ion, and, as for sulphur dioxide, its importance for protection of technological plant has led to considerable investigation of its deposition rates and atmospheric levels. The major pioneering work on analysis of chloride movement inland from the coast to participate in atmospheric corrosion is contained in the papers by Ambler and Bain (1955) and Ambler (1960). It is impossible to do justice to these papers in a brief segment of a review such as this, and the papers deserve study by all who propose to set up atmospheric corrosion studies of their own. In the paper by Ambler and Bain, which reports work done in Nigeria, assessment was made of the effects of distance from the coast on chloride deposition and on corrosion rate. The authors also compared the relative values given by different means of chloride collection from the atmosphere, and assessed the effects of night versus day, season, orientation and airborne sulphate on corrosion rates. The subsequent comparison of values obtained in UK (Ambler 1960) suggested a similar relationship of chloride deposition to distance from the sea in both Nigeria and UK, but in contrast to Nigeria (where the amount of airborne chloride approximately controlled the corrosion rate), there was no relationship of corrosion rate to atmospheric chloride in UK. Various reasons for this were advanced by Ambler; obviously, industrial pollution sources may overshadow chloride deposition as the cause of corrosion in a more heavily industrialised economy, and this is likely to be the primary cause.

Not many other intensive studies of this type have been reported. Most of

the data collected on chloride in the atmosphere has been from rainfall analysis, and Brierly (1965) summarised much of the available data in the course of defining four zones of hazard from corrosion by sea salt. These ranged in severity from oceanic islands and coastal areas (worst) to sub humid and humid areas long distances inland (least). Arid areas generally have low severity, but can have high rates of corrosion at times because though deposition of sea salt may be minimal because of the distance from the sea, there may be relatively high chloride deposition onto surfaces due to winds off highly saline lakes or from wind-blown topsoil. Brierly categorised these areas in terms of a total salt-fall level; it should be noted that total salt-fall includes both that in rainfall and that due to dry deposition of wind-borne chloride, which can be significant (Claridge, 1970). Ambler and Bain, Brierly and Claridge all comment upon the considerably (perhaps several thousand per cent) higher rates of deposition of chloride at coastal sites during storms than are indicated by average values collected over long periods. Because the chloride levels in the air are higher, and the winds are higher, chloride may be carried in storms to places far inland in quantities which, if deposited onto surfaces not exposed to direct rainwashing, may produce unexpectedly high corrosion rates. Thus, in assessing an atmospheric environment with respect to its salinity, it is important to consider the frequency of high winds blowing from the sea onto the land as well as examining the long-term average chloride deposition rates.

In our work in New Zealand, we have combined these two latter points, and are using a sheltered-surface collector devised at Harwell (Cawse 1974) to examine the variations in chloride deposition which can occur due to topography. Because some areas of New Zealand have very frequent high-speed on-shore winds it is hoped to establish a set of collectors running inland from the appropriate coasts to establish whether a relationship of chloride deposition to distance inland similar to that established by Ambler will occur. Neutron activation for the collection surface analysis (as used by Cawse) is not available in New Zealand, and is a very expensive process, so that analysis so far has been by wet chemical methods. Collection periods are 30 days long; this has been found to be an appropriate compromise between having enough chloride present to assess and still identifying the quite considerable variability from period to period of chloride detection.

The common methods of chloride deposition rate measurement tend to be by analysis of adsorbent surfaces, and little development has occurred since the work of Ambler (1960). (See British Standards Institute (1976) for details on present methods).

Interactions between two or more pollutants can produce unexpected corrosion effects. Walton *et al* (1982) have recently discussed the interactions of sulphur dioxide and a range of active and inert particulate types in initiation of corrosion, following a series of laboratory experiments. The importance of chloride in the particulate, both in its own right in involvement in corrosion and also under some conditions in producing a low critical relative humidity for moisture uptake onto the surface, emerges from their experiments. Another important point to emerge, which may have been a surprise to those who did not have a knowledge of the environmental sciences literature, was the enhanced corrosion if the particulate contained Mn(II) and Fe(II) species. These catalyse the conversion of sulphur dioxide to

sulphate, which is therefore made much more easily available for participation in corrosion reactions. The sulphur dioxide can be adsorbed and oxidised on the particle surfaces even before the particles land on the metal surface which subsequently corrodes. These workers did not confirm on earlier report (Ericsson 1978) that a synergistic effect (i.e. the corrosion found was greater than the total corrosion which would have occurred with the single agents) occurred when sulphur dioxide and chloride ions were both present on an iron surface at humidities around 90%. The key to this may be that Ericsson used NaCl, while Walton *et al* used NH₄Cl. The ammonium ions may have altered the pH values attained at the surface, and the surface tensions of sodium and ammonium salt solutions are quite different and may also have affected the experiment.

CHARACTERISATION OF ATMOSPHERES

Cermakova and Barton (1982) gave an extremely important review of the philosophies in the field of a priori corrosiveness assessment of atmospheres. These authors have been at the forefront of this field for many years, but despite this experience and their steadily-developed models for the assessment they note that their approach can really only be applied to "a standard corroding surface, or possibly for a simple product. For more complicated cases, however, even in the usual types of atmosphere, it is necessary to have specific experience or experimental data on the behaviour of materials in the type of location where it is used."

This is, of course, a counsel of perfection and, for many workers in countries where major data-gathering networks are not available, is useful guidance but cannot be a hard and fast rule. Even in some relatively sophisticated economies, simple guidelines to assessing the possible corrosivity of the atmosphere in an unfamiliar location have been regarded as desirable. A good example is the environment classification in BS 5493 (British Standards Institution 1977). Despite the absence of direct corrosion monitoring information, New Zealand was recently categorised into four zones for steel corrosion hazard (Duncan and Whitney 1982) using zone definitions developed from AS 2312 (Standards Association of Australia 1980) which rely heavily on meteorological data. Good meteorological data is available for New Zealand, as it is for most countries. The rainfall and humidity data were combined with indirect evidence of pollutant presence, such as sodium levels in grass (which had been extensively assessed) as indicators of degree of chloride deposition. Some aluminium wire-on-bolt corrosion test results (from the method of Doyle and Godard 1966) were also available for indication of the marine corrosiveness at various sites. This categorisation of New Zealand's atmosphere will, no doubt, be improved at some later date. Its most important immediate value lies in its availability as a guideline for those needing assistance on the level of protection against atmospheric corrosion at any particular location, and as a common debating base for those involved in the corrosion field.

MICROCLIMATIC INFLUENCES

The design of structures to minimise corrosion is largely a question of ensuring that the microclimate around the metal surface is benign. The general principles involve counteracting the effects of water and pollutant deposition onto the surface, which have been discussed earlier in this paper

Indoors this can be done more easily than outdoors - in the absence of chemical processing, for instance, pollutant levels are considerably lower indoors than outdoors. In some indoor environments humidity can be controlled, which will lessen corrosion problems even if pollutants are present. (However, pollutant control is a more sure means of protection - Vernon (1935) established that, even at very high humidities, iron surfaces will remain uncorroded if protected from particulate deposition, such as by a muslin screen). The principle of pollutant exclusion has been successfully applied outdoors in protection of bridge members from corrosion (Bishop and Winnett 1981).

Outdoors, the most important method of minimising atmospheric corrosion is by minimising time of wetness. Vertical surfaces tend to corrode less than horizontal surfaces, because of better drainage. (It is good practice not to have horizontal surfaces, but instead to have them inclined so that they have some drainage). A surface facing away from the ground is likely to have a lower corrosion rate than one facing the ground, because hygroscopic salts deposited onto the lower face are not removed by rainwashing, and so can have a much longer term corrosion action. The upper surface is also more easily exposed to solar drying than the lower surface.

Rain or dew should drain easily from any surface, and not be able to be trapped in crevices between members (such crevices should be filled with a sealant) or as ponds due to angles in structural members. In this latter respect, hollow sections have some advantages over conventional L, H or U solid sections, because of the absence of corners where solid deposits and water can be trapped. Another advantage of hollow sections is that they can have a smaller surface area if surface protection is needed. However, there can be very severe problems with corrosion from the inside out of hollow sections; total exclusion of water vapour from inside the section is extremely difficult, and once inside escape of the vapour is very difficult.

The surface finish can affect the time of wetness - smooth surfaces are less likely than textured surfaces to trap deposited pollutants, and hence can have a lower time of wetness. Heating and cooling due to liquids contained in the structure can also have a major effect on the microclimate: dew formation on water tanks, leading to long times of wetness even under direct solar radiation, is a common event. On the other hand, equipment which is radiating heat can provide a protective effect for surfaces around it, by keeping it dry.

All of these measures will be recognised as being matters which decisions at the design stage will influence to a severe extent. This is an extremely important factor. With all corrosion, a little thought at the design stage (especially with respect to how the structure will be maintained) can save a lot of time and money later. The books by Barton (1976) and Pludek (1977) provide a lot of background information for designers.

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TABLE 1 : Relative humidities over saturated salt solutions at 20°C

	%		%
ZnCl ₂ ·H ₂ O	10	(NH ₄) ₂ SO ₄	81
CaCl ₂ ·6H ₂ O	32	ZnSO ₄ ·7H ₂ O	90
MgCl ₂ ·6H ₂ O	34	Na ₂ SO ₄	93
NaCl	77	K ₂ SO ₄	97
NH ₄ Cl	80		
KCl	86		

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