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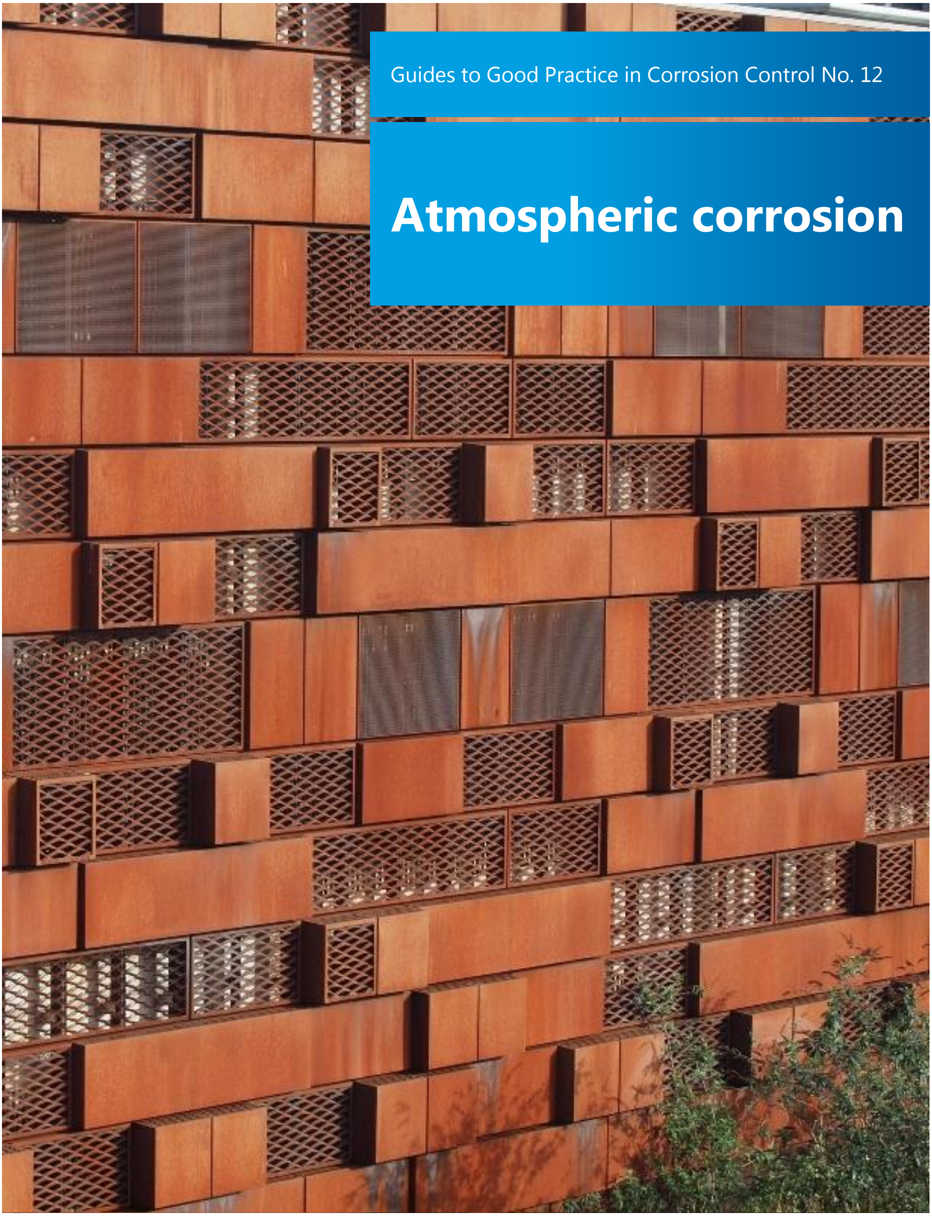

Guides to Good Practice in Corrosion Control No. 12

Atmospheric corrosion

NPL
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Corrosion Research and Testing

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1. The atmospheric environment

1.1 Composition of the atmosphere

The atmosphere, along with the sea, is one of the most common natural environments in which materials are exposed. However, unlike most other types of corrosion environment, the atmosphere does not provide a constant exposure condition.

As an example, in order tocheck the corrosion rate of a sample of steel it might be tested in the laboratory in 3.5% sodium chloride solution at 20°C under conditions of defined mass transfer (i.e. a constant stirring rate). Under these conditions, the corrosion rate might be expected to be generally reproducible. However, a steel sample exposed in the atmosphere does not experience a constant environment at all and, hence, the measured corrosion rates are much less reproducible.

The main components of the atmosphere have an effectively constant composition; however, the minor components affecting corrosion can vary by large amounts.

AVERAGE COMPOSITION OF THE NATURAL ATMOSPHERE	
Substance	Concentration by volume: %, parts per million (ppm) or parts per billion (ppb)
Nitrogen (N_2)	78.1%
Oxygen (O_2)	20.9%
Argon (Ar)	0.93%
Water vapour (H_2O)	variable
Carbon dioxide (CO_2)	405 ppm (2019 value)
Other rare gases (Ne, He, etc.)	24 ppm
Hydrocarbons (mainly CH_4)	2 ppm
Hydrogen (H_2)	0.5 ppm
Nitrous oxide (N_2O)	300 ppb
Carbon monoxide	120 ppb
Ammonia (NH_3)	100 ppb
Oxides of nitrogen (NO_x)	1 ppb
Sulphur dioxide (SO_2)	0.2 ppb
Hydrogen sulphide (H_2S)	0.2 ppb

The last 4 minor atmospheric components are those that can affect corrosion reactions significantly and also have substantial man-made contributions. Carbon dioxide also affects the formation of protective corrosion products (patinas) on some materials (e.g. zinc) and can also react with alkaline building materials (e.g. concrete). It is present in much larger, and rising, quantities. The atmospheric concentration of CO_2 has been measured over the last few thousand years by analysis of gases trapped in ice at the poles. The pre-industrial concentration of CO_2 was about 270 ppm but by 2019 had increased to over 400 ppm on a rising trend of about 1 ppm per year.

The only species whose concentration varies naturally within large limits is water vapour. Thus, on a hot, humid day there may be several percent H_2O vapour in the air while this would drop to close to zero on a cold, dry day.

1.2 Natural air pollution

There are 3 main primary sources of natural air gas pollution: volcanic action, vegetation, and animal wastes. In addition, there are 2 primary sources of natural particulate pollution: sea-spray and dust from the earth. In addition, secondary sources of pollution arise from transformations in the atmosphere; for example, ozone and other photochemical action.

Note that pollution is generally classified into “primary” species that remain unchanged in the atmosphere after emission, and “secondary” species that have been transformed (changed) from some other primary species. Also, note that pollutants can be classified as either gaseous, particulate (e.g. dust from the ground), or aqueous (i.e. dissolved in rain).

SOURCES OF NATURAL POLLUTANTS	
Primary	Primary
Volcanic action	SO_2, H_2S, HCl, Cl_2 – gaseous Volcanic ash – particulate
Biological respiration	CO_2 – gaseous
Animal waste	NH_3, organic sulphides – gaseous
Vegetation	Hydrocarbons – gaseous
Soil microbes	N_2O – gaseous
Sea spray	Cl^-, SO_4^{2-} – particulate aerosol
Soil (earth) from the ground	Inorganic dusts – particulate
Natural fires (arising from lightning strikes)	CO_2 – gaseous Ashes and smoke – particulates
Secondary	Secondary
Oxidation of SO_2	SO_3 – gaseous SO_4^{2-} – particulate aerosol
Reaction of $NH_3 + SO_4^{2-}$	$(NH_4)_2SO_4$ – particulate aerosol
Reaction of sea-spray with SO_3	HCl – gaseous
Oxidation of N_2 during lightning	NO/NO_2 (NO_x) – gaseous
Atmospheric photochemistry	O_3 (ozone) – gaseous
Plant hydrocarbons + O_3	Hydrocarbon peroxides and radicals ("Blue mountains of Virginia") – gaseous

Those gaseous species above that are soluble may dissolve in precipitation (e.g. rain) forming the aqueous state. Also, as particulate aerosols are dried crystals of a salt, they may also dissolve in rain.

1.3 Man-made atmospheric pollution

The main sources of man-made pollution derive from burning fossil fuels and other combustible materials in processes such as power generation, transportation and waste incineration. Additional atmospheric pollution comes from chemical processing, sewage treatment and farming.

SOURCES OF MAN-MADE POLLUTION	
Primary	Primary
General combustion (all fuels)	CO, CO_2 – gaseous "Fly-ash", carbon (smoke) – particulate
Fossil fuel combustion (oil, coal, gas)	SO_2, NO_x – gaseous
Incineration (waste, plastics, coal)	HCl, Cl_2 – gaseous
Transport (vehicle exhaust)	NO_x, CO, hydrocarbons – gaseous carbon (smoke) – particulate
Chemical processing	Hydrocarbons, sulphides, NH_3 – gaseous
Sewage treatment	Sulphides, NH_3 – gaseous
Farming (domesticated animals)	CH_4, NH_3, sulphides – gaseous
Farming (growing crops)	Hydrocarbons (CH_4) – gaseous
Secondary	Secondary
Oxidation of SO_2 by O_3	SO_3 – gaseous SO_4^{2-} – particulate aerosol
Reaction of NH_3 + SO_4^{2-}	$(NH_4)_2SO_4$ – particulate aerosol H_2SO_4 – "acid rain"
Oxidation of NO_x by O_3	NO_3^- – particulate aerosol HNO_3 – "acid rain"
Hydrocarbons + O_3	Hydrocarbon peroxides and radicals ("Photochemical smog") – gaseous

1.4 Climate effects

The climate essentially corresponds to the weather at a specific location. Clearly, the weather changes from place-to-place, from country-to-country and from season-to-season. The general weather pattern for a region of a country is usually known as the macroclimate. However, significant variations can occur locally (e.g. as a function of height or distance from the sea), as a function of human activity (e.g. cities are usually slightly warmer and more humid than the countryside) and vary locally (e.g. depending on the arrangement of buildings). These smaller variations are known as the microclimate.

2. Pollutant deposition

2.1 General overview

Pollutants in the atmosphere consist of either “dry” species, such as gases, dry salt particles, dusts and smoke, or “wet” species, such as gases or ionic salts dissolved in water droplets. While suspended in the atmosphere, they contribute to general atmospheric pollution (i.e. a reduction in atmospheric quality). However, until the pollutants deposit onto a surface or the ground, they will have no influence on atmospheric corrosion or ground quality.

The deposition rate is defined as the quantity of pollutant that transports (by absorption, etc.) onto an area of a surface in a particular time. It has units of mol m^{-2} s^{-1} or mg m^{-2} s^{-1}.

2.2 Dry deposition

Gases or particulates (particles) can transport onto a surface by 3 main mechanisms: advection, which is due to the airflow (wind), convection, which is due to thermal air currents, and diffusion, which is due to a concentration gradient of the species between the surface and the atmosphere. Dry deposition mechanisms generally account for most of the pollution transported to a surface. The exact fraction in a region depends on local climate and rainfall, but dry deposition amounts to about 70% of worldwide deposition of pollutants over land.

2.3 Pollutant concentrations

Only very approximate limits for man-made atmospheric pollution can be given as they will vary widely depending on location, climate, industrialisation, etc.

CONCENTRATION RANGES FOR ATMOSPHERIC POLLUTANTS

(1 µg m^{-3} = 1 part per billion, ppb)

Pollutant	Industrial (µg m^{-3})	Urban (µg m^{-3})	Rural (µg m^{-3})
SO_2	100 – 200	30 – 80	5 – 20
NO_x	100 – 200	20 – 40	< 10
HCl	10 – 20	1 – 5	< 1
Smoke and ash	100 – 1000	20 – 50	< 20
	Inland		Coastal
Sea-salt aerosol	(air) 30 µg m^{-3} (rain) 5 mg dm^{-3}		1000 µg m^{-3} 50 mg dm^{-3}
Other dusts	0.1 – 50 µg m^{-3}		

2.4 Wet deposition

Although most atmospheric pollutants transport to surfaces in the dry state, a significant quantity dissolves in water droplets in clouds eventually to fall as precipitation (i.e. rain, snow, or fog). This generally amounts to about 30% of overall pollutant deposition. Wet deposition also plays a role in removing accumulated dry deposition by periodic washing. So, counter-intuitively, open well-washed surfaces can corrode more slowly than sheltered surfaces where washing is infrequent or non-existent.

2.5 "Acid rain"

This term describes all forms of deposition, including wet and dry, that eventually result in acidification of surface water. However, it is important to remember that, in the absence of any acidic pollutants such as SO_2, NO_x and HCl, natural rainwater will be slightly acidic due to the presence of atmospheric CO_2. The natural pH of rainwater can be easily calculated from a knowledge of the equilibrium:

$$CO_2 + H_2O \leftrightarrows H^+ + HCO_3^-$$

$$K = \frac{[H^+]\cdot[HCO_3-]}{[CO_2]} = 1 \times 10^{-7.6}$$

For every H^+ ion that is released in solution there is a corresponding HCO_3^- ion, so:

$$[H^+] = [HCO_3^-]$$

$$[H^+]^2 = 1 \times 10^{-7.6} \times [CO_2]$$

For a volume concentration of CO_2 in the atmosphere of 400 ppm (value at ~2018) then:

$$: [H^+]^2 = 1 \times 10^{-7.6} \times 400 \times 10^{-6}$$

$$[H^+]^2 \sim 10^{-11}$$

$$[H^+] = 10^{-5.5} \text{ (= pH 5.5)}$$

So, the pH of natural rainwater, in the absence of any other pollutants, is about 5.5. In fact, the presence of a natural background level of SO_2 and NO_x (from volcanic action and lightening respectively) lower this natural pH to about 5.0 ± 0.2 depending on location.

"Acid rain" is, therefore, any deposition that results in a surface pH of less than the natural level (i.e. 5 or less). The typical pH of deposition in an urban/industrial atmosphere is about 4 to 4.5 however, rain of pH = 2.8 (vinegar!) has been known to fall. The table below gives the average composition of rainwater that fell in the Greater Manchester area in 1986 ("Manchester rainwater").

MANCHESTER RAINWATER COMPOSITION (1986)	
Species	Concentration (mg dm^{-3})
H_2SO_4 (98%)	3.185
$(NH_4)_2SO_4$	4.620
Na_2SO_4	3.195
HNO_3 (70%)	1.575
$NaNO_3$	2.125
NaCl	8.483
	pH approximately 4.5

2.6 Atmospheric classifications

The international standard, ISO9223, provides a classification scheme for ranking pollution in a particular climatic location based on the deposition rates of SO_2 and Cl^-.

SULPHUR DIOXIDE			CHLORIDE	
SO_2 class	Deposition Rate mg/m²/day	Concentration mg/m³	Chloride Class	Deposition Rate mg/m²/day
P_0	<10	<12	S_0	<3
P_1	10 - 35	12 - 40	S_1	3 - 60
P_2	36 - 80	41 - 90	S_2	61 - 300
P_3	81 - 200	91 - 250	S_3	>300

2.7 Humidity and time of wetness

Atmospheric corrosion, like all other metallic corrosion, cannot occur unless there is sufficient water present to solvate the ions produced during the anodic and cathodic reactions. Thus, the atmospheric humidity is very important in determining when atmospheric corrosion can or cannot happen.

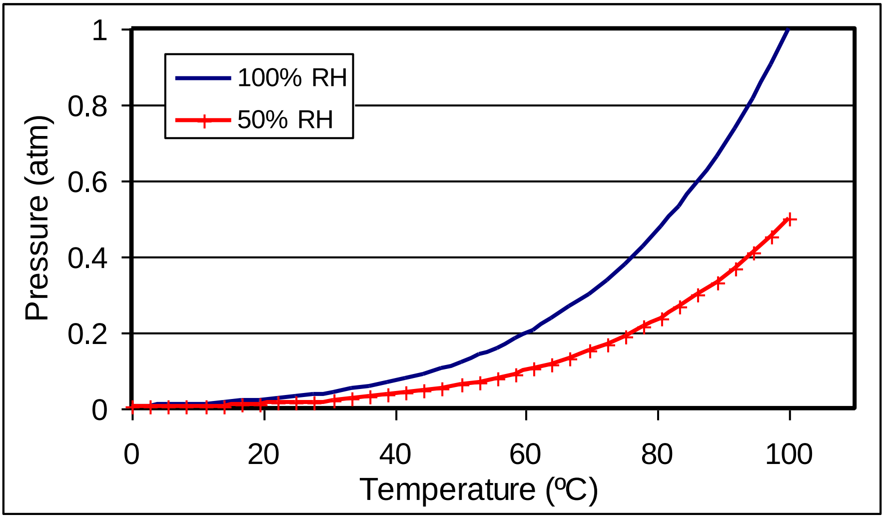
The atmospheric humidity is a measure of the amount of water vapour in the air. Humidity can be defined in two ways:

$$\text{Absolute humidity} = \text{concentration (partial pressure) of water vapour in air}$$

$$\text{Relative humidity} = \frac{\text{water vapour pressure}}{\text{saturated (maximum) water vapour pressure}}$$

Relative humidity is very useful as it defines the thermodynamic water vapour activity at any temperature. This is important when condensation of water on a surface is considered. Thus, from the definition, at RH = 100%, liquid water is a stable phase and condensation occurs. However, if RH < 100%, then water vapour is the stable phase and, normally, condensation does not occur. It is important to remember that the saturated or maximum concentration of water vapour in the air varies as a function of temperature, shown below. At 100ºC water boils so the maximum vapour pressure of water is 1 atmosphere. Below 100ºC, the water vapour pressure is less than 1 atmosphere. For a given humidity, the temperature below which water vapour will condense is known as the dewpoint. Corrosion of a metal cannot occur unless there is sufficient liquid water on its surface, the time during which the RH exceeds a critical value, can be defined as the Time-of-Wetness of the surface.

The graph below shows the variation in humidity with temperature. As an example, it can be seen that at 35ºC, 100% RH corresponds to a water vapour pressure of 0.05 atmospheres. This is a significant fraction of the total atmospheric pressure and is one of the reasons that high humidities in hot climates are more uncomfortable than in colder climates.



ISO9223 provides a classification scheme for ranking a particular climate in terms of its time-of-wetness. In this standard, the time-of-wetness (TOW) is calculated as the total time when the RH is greater than 80% at temperatures above 0°C. Note that when it is raining the RH is, by definition, equal to 100%.

WETNESS CLASS	**TIME OF WETNESS** (hours/year)	(%)	**EXAMPLE OF OCCURENCE**
T_1	<10	<0.1	Indoor
T_2	10-250	0.1 - 3	Indoor, unheated
T_3	250-2600	3 - 30	Outdoor, dry/cold climate, ventilated buildings
T_4	2600-5200	30 - 60	Outdoor temperate climate
T_5	>5200	>60	Tropical outdoor or surf

3. Atmospheric corrosion

3.1 Surface condition

In atmospheric corrosion, the electrochemical (i.e. anodic and cathodic) reactions occur in a very thin layer of water condensed onto the corroding surface. Clearly, the physical and chemical nature of that surface (e.g. roughness and contamination), as well as the amount of water that is condensed on the surface, controls the rate of corrosion. Typical thicknesses of water layers on a clean (freshly polished) metal surface are shown below:

CONDITIONS	WATER LAYER THICKNESS
Wet during rainfall	> 500 µm
Covered by dew or condensation	10 – 500 µm
100% relative humidity	1 – 10 µm
< 100% RH	< 1 µm

The presence or absence of water on an exposed surface is a dynamic equilibrium between the atmospheric and the surface condition. Several regimes of atmospheric corrosion can be identified at any time:

A. *Fully dry*: there is no liquid water present although there may be pollutants depositing and contaminating the surface – <u>no corrosion</u>.

B. *Condensing*: liquid water is condensing from the atmosphere and increasing in thickness, dry pollutants previously deposited dissolve. Often the corrosion rate is initially very high due to the concentrated surface solution and very thin water layer allowing rapid oxygen transfer – <u>corrosion starts</u>.

C1. *Wet – humid*: the water layer thickness is in equilibrium with the atmospheric RH. Corrosion continues at a steady rate usually controlled by the rate of diffusion of species to the reacting metal surface, pollutants may continue to deposit – <u>steady-state corrosion</u>.

C2. *Wet – raining:* liquid water falls on the surface, often resulting in washing of previously deposited pollutants from the surface and a reduction in the corrosion rate – <u>steady-state corrosion</u>.

D. *Evaporating:* liquid water on the surface is evaporating and decreasing in thickness, pollutants are concentrating and diffusion rates especially of oxygen are increasing because of the thinner water layer – <u>corrosion rate increases above steady-state rate, then falls to zero</u>.

In atmospheric corrosion, electrochemical (anodic and cathodic) reactions occur as normal. However, as the diffusion distance through the electrolyte (the condensed water layer) is relatively small, oxygen diffusion in the electrolyte is not a rate-limiting process. In fact, the main controlling factors on the atmospheric corrosion rate are: (a) whether the surface is sufficiently wet for electrochemical reactions (corrosion) to occur and, (b) diffusion of oxygen, water, and other species through corrosion product layers.

3.2 Factors affecting critical relative humidity

Water condensation can occur on metals at a relative humidity much less than 100% by two mechanisms. Firstly, small diameter cracks and pores on the surface, for example in a corrosion product layer, can significantly reduce the equilibrium humidity for condensation. Essentially, a long thin crack can stabilise water at its base even though the external humidity might be quite low. This process is known as capillary condensation and is the reason that a polished metal surface corrodes, at first, more slowly than a rusty surface.

The second mechanism for a reduction in the critical RH is more important and relates to chemical contamination (e.g. by pollutants) on the metal surface. A dried salt on a surface will have a tendency to dissolve in condensed water to give, initially, a saturated solution of the salt on the metal surface. The dissolved salt will lower the thermodynamic activity of the water and, hence, the equilibrium RH in the air immediately above the surface. The table below shows the RH at which water will condense on a surface, contaminated with the salt.

RH OF CONDENSATION ON A POLLUTED SURFACE AT 20 °C

Polluting salt	RH of condensation
Na_2SO_4	93%
$(NH_4)_2SO_4$	81%
NaCl	78%
$MgCl_2$	35%
Magnesium chloride is a component of sea salt.	So, a surface polluted with seasalt is wet and will corrode at RH > 35%

3.3 Atmospheric corrosion maps

The local intensity of atmospheric corrosion within a country or region can be experimentally mapped by exposing regularly spaced metal samples outdoors for a given length of time then determining the mass loss due to corrosion at that location. This was first carried out in the UK in the 1970s to determine the influence of pollution on corrosion of galvanized steel. An alternative methodology is to measure, or estimate, the local deposition of pollutants, which can then be correlated to metal corrosion rates. Atmospheric corrosion maps exist for many countries and the UK version is available on-line.

3.4 Sheltered v. open exposure outdoors

While it might be expected that sheltered materials might corrode more slowly than materials that are fully open to the environment, the reverse is usually true. This is because pollutants that are deposited on surfaces in open locations are occasionally washed/diluted by rain whereas this does not occur in sheltered locations. Sea-salt deposited by airborne transport particularly problematic as the deliquescence (wetting) humidity lies in the range around 35-40% RH. Since this value will be regularly exceeded, in practise, during much of the day and in most climates. In this way, corrosion under sheltered conditions is relatively aggressive.

3.5 Indoors corrosion and packaging

Despite an apparently benign environment, atmospheric corrosion will also occur indoors. where airborne dust and salt deposition, as well as manual handling, can give rise to significant contamination on surfaces. In addition, enclosed indoors environments may result in the concentrations of atmospheric gases that arise from animal/human occupation (e.g. sulphides, ammonia, etc.) and building materials (e.g. organic acids, etc.) to increase, which can result in severe corrosion inside farm buildings, for example.

Packaging of material/components against atmospheric corrosion during storage and transport requires significant attention to detail to avoid inadvertently creating a potentially corrosive environment inside the packaging. For example, items may be packed under working conditions of 21 °C and 50% RH (which is relatively dry) if, during shipping, the temperature falls to below 10 °C then condensation inside the packaging will occur leading to “unexpected” corrosion. Temporary protectives and dehumidification, using desiccants, within the packaging can help to prevent corrosion during storage and transit. Further information on control of corrosion in packaging can be found in the relevant NPL guide.

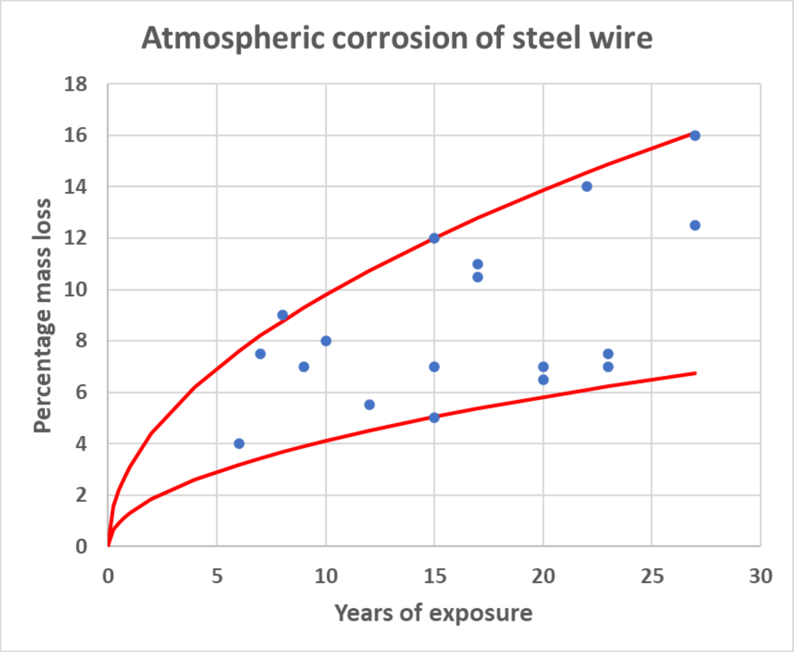
4. Atmospheric corrosion of metals and alloys

4.1 Protection against atmospheric corrosion

Most materials are protected in some way from atmospheric corrosion by metallic/inorganic or organic coatings. Corrosion protective organic coatings (i.e. paints) generally offer the best combination of performance and cost for many substrates. Corrosion protective metal coatings for carbon steel are sacrificial and are based on zinc (galvanizing) and/or aluminium (aluminizing). Alternatively, such metal coatings can be decorative in nature and are often based on a thin decorative surface (such as chromium plate) over a thicker nickel corrosion protective layer. In some cases, metallic materials may be exposed outdoors without protection. This may be for aesthetic reasons, for example architectural alloys that form an attractive patina on atmospheric exposure. Additionally, some alloyed "weathering" steels are available that corrode between one-third to one-half the rate of normal carbon steel and can be used unpainted in engineering applications.

4.2 Corrosion in atmospheric environments

Atmospheric corrosion rates over time depend on the corrosion mechanism and substrate. For carbon steel and iron, a rust layer will develop and thicken which will slow down the rate of corrosion as the reactants have further to diffuse to reach the underlying metal. On the other hand, the much thinner corrosion product layer on zinc/galvanized surfaces react by dissolving slowly so the corrosion rate does not decrease much with time. Knowledge of how such materials behave during atmospheric corrosion allow prediction of materials loss and engineering structures to be designed with realistic corrosion allowances. Importantly, there is a rather large scatter in corrosion rates (shown below for 20 years' corrosion of steel wire) such that the minimum metal loss may be one-half of the maximum rate. This variation must also be taken into account when designing structures for atmospheric exposure.

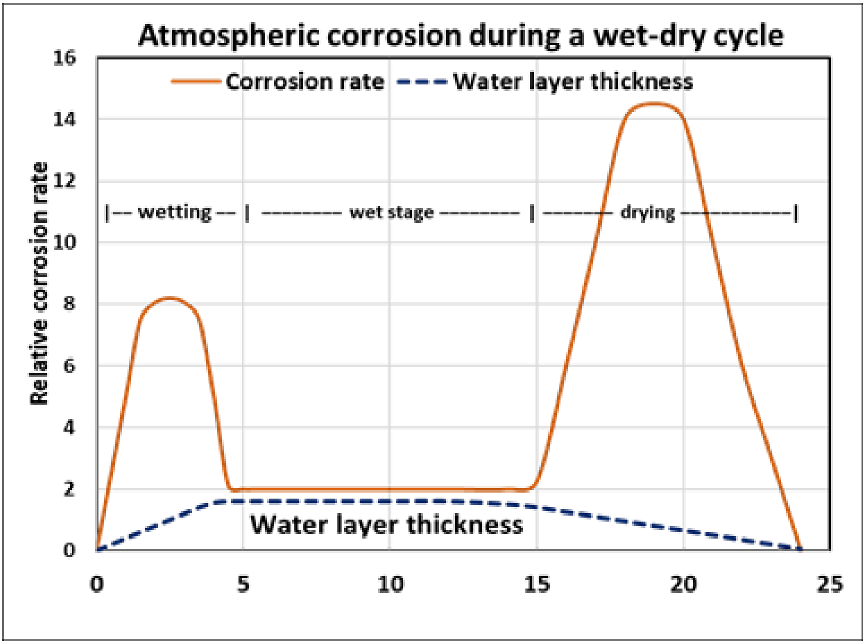


ISO9223 provides a classification scheme for the corrosivity of an environment based on the expected corrosion rates of materials exposed outdoors for 1 year. Thus, from a knowledge of the pollution classifications and the TOW (time of wetness) classification, the corrosivity classification can be derived.

CORROSIVITY CATEGORY	**CORROSION RATES OF METALS**				
	Units	Carbon steel	Zinc	Copper	Aluminimum
C_1 (very low)	g m^{-2} y^{-1} µm y^{-1}	0 - 10 0 - 1.3	0 - 0.7 0 - 0.1	0 - 0.9 0 - 0.1	negligible
C_2 (low)	g m^{-2} y^{-1} µm y^{-1}	10 - 200 1.3 - 25	0.7 - 5 0.1 -0.7	0.9 - 5 0.1 - 0.6	0 - 0.6
C_3 (medium)	g m^{-2} y^{-1} µm y^{-1}	200 - 400 25 - 50	5 - 15 0.7 - 2.1	5 - 12 0.6 - 1.3	0.6 - 2
C_4 (high)	g m^{-2} y^{-1} µm y^{-1}	400 - 650 50 - 80	15 - 30 2.1 - 4.2	12 - 25 1.3 - 2.8	2 - 5
C_5 (very high)	g m^{-2} y^{-1} µm y^{-1}	650 - 1500 80 - 200	30 - 60 4.2 - 8.4	25 - 50 2.8 - 5.6	5 - 10

4.3 Corrosion during wet-dry cycles

Atmospheric corrosion necessarily proceeds in relation to the quantity of water present on a material surface, which varies as the material surface wets and dries. A schematic diagram of the corrosion rate during a single wet/dry cycle is shown below. Initially, there is a rise in the corrosion rate as the accumulated pollutants on the surface dissolve and form a relatively corrosive electrolyte solution on the surface. As the surface wets more, this solution dilutes and becomes less corrosive giving rise to a relatively steady-state corrosion rate. Finally, as the surface dries out the corrosion rate rises again until the surface is fully dry and no further corrosion can occur. For a typical atmospheric wet-dry cycle around 60-80% of the corrosion occurs during the initial wetting and final drying phases.



4.4 Carbon steels

Plain carbon steels corrode in the atmosphere forming a porous layer of iron oxide/hydroxide (brown rust). The rust layer give some protection provided that it stays intact on the steel surface. Thus, the corrosion rate of unpainted steels tends to decrease with time following simple power law kinetics:

$$\mathrm{Rate} = \mathrm{k} \cdot \mathrm{t}^{\mathrm{n}}$$

Where k is a rate constant, t is time and n is the power relationship. For kinetics controlled by diffusion through the thickening rust layer, $n = 0.5$ (parabolic kinetics). However, as rust is porous, then the kinetics are not completely diffusion controlled and $n \approx 0.7$. This provides a way to predict, within broad limits, the likely corrosion loss over time.

The brown rust layer formed in the atmosphere generally consists of a crystalline iron oxide-hydroxide, lepidocrocite, FeO(OH). Other species that can form include magnetite, Fe_3O_4. The anodic reactions for atmospheric corrosion of iron are:

Formation of ferrous hydroxide:	$Fe + 2H_2O \rightarrow Fe(OH)_2 + 2H^+ + 2e^-$
Oxidation of $Fe(OH)_2$ to lepidocrocite:	$Fe(OH)_2 \leftrightarrows FeO(OH) + H^+ + e^-$
Oxidation of $Fe(OH)_2$ to magnetite:	$3Fe(OH)_2 \leftrightarrows Fe_3O_4 + 2H_2O + 2H^+ + 2e^-$

Note that the last two reactions are reversible and that both magnetite and lepidocrocite can be reduced back to ferrous hydroxide. For iron particularly, this reversible reaction contributes significantly to the overall corrosion process during wet/dry exposure cycles.

The effect of controlled alloying of small (< 5%) quantities of Cu, Ni, Cr and P into Fe is to slow the corrosion rate by forming a much more protective rust film. Such “weathering” steels are designed to be without any form of additional protection (e.g. painting) but their use should be restricted to atmospheres of low corrosivity (i.e. C3/C2 and below).

4.5 Zinc and galvanised steel

Although zinc is considerably more active than iron, it corrodes in the atmosphere at a rate that is about 10-20 times less. This is because the corrosion product layer that forms is highly protective. Like iron, the corrosion rate of zinc with time follows a power law relationship, but with the value of the exponent close to one; that is, zinc tends to have linear corrosion kinetics. This makes it easy to predict the lifetime of a galvanized coating on steel.

The corrosion product that initially forms on zinc is zinc hydroxide. However, this has an alkaline surface and reacts with acidic species in the atmosphere (CO_2, SO_2, NO_x, HCl, as well as sulphate and chloride ions) to form a generally more protective layer. The reaction products are crystalline salt complexes of zinc hydroxide and the corresponding zinc salt; these are known as basic zinc salts.

Initial reaction: $Zn + 2H_2O \rightarrow Zn(OH)_2 + 2H^+ + 2e^-$ (zinc hydroxide)

Reaction with CO_2: $4Zn(OH)_2 + CO_2 \leftrightarrows 3Zn(OH)_2.ZnCO_3 + H_2O$ (basic zinc carbonate)

Reaction with SO_3: $5Zn(OH)_2 + SO_3 \leftrightarrows 4Zn(OH)_2.ZnSO_4 + H_2O$ (basic zinc sulphate)

Reaction with HCl: $5Zn(OH)_2 + 2HCl \leftrightarrows 4Zn(OH)_2.ZnCl_2 + 2H_2O$ (basic zinc chloride)

So, during atmospheric corrosion of zinc, a thin, coherent, non-porous zinc hydroxide layer initially forms. This then transforms, at its interface with the atmosphere, to a basic zinc salt that is slightly soluble. Thus, the corrosion product layer thickness stays approximately constant being determined by the solubility of the basic salt. In turn, this is determined by the quantity (concentration) of pollutants in the atmosphere.

As the corrosivity of the atmosphere increases, the corrosion product layer thickness decreases (because the basic zinc salts are more soluble). Thus, the corrosion rate of zinc increases. Conversely, if the atmospheric corrosivity decreases, then the corrosion product layer increases in thickness (because the basic zinc salts are now less soluble) and the corrosion rate decreases.

4.6 Copper and lead alloys

These materials have been traditionally used for architectural purposes that includes: building cladding, roofing, ornamental statuary and door furniture/ ironmongery. The atmospheric corrosion of copper follows a similar mechanism to zinc whereby various basic copper-containing salts are formed and transform over time to an attractive blue-green appearance. Once this “patina” is established, the corrosion rate continues at a relatively low and constant rate with time. Architectural lead performs similarly although it has a dull grey appearance. Service failure of architectural lead is usually as a result of mechanical fatigue rather than any thinning due to corrosion.

4.7 Stainless steel, aluminium and titanium

Decorative architectural cladding materials using passive alloys are often considered to be "maintenance free". However, although the overall corrosion rates are low and the materials can maintain an attractive appearance for long periods, localised corrosion must still be considered a risk. This is due to continued atmospheric deposition of airborne particulates (including dusts, soils and salt aerosols) initiating localised pitting corrosion by a crevice mechanism underneath the deposit. Such surfaces need to be cleaned regularly by washing to obtain a long service life. Additional issues may occur where alloys suffer from stress corrosion cracking due to the high salt concentrations that can develop within a sea-salt droplet at a low humidity close to the salt's deliquescence point. Consequently, the use of a high-grade corrosion-resistant alloy may be needed in order to be reliably "maintenance free". Thus, titanium cladding is sufficiently resistant to localised corrosion to be used without further concern.

5. Further reading

"Corrosion of metals and alloys; Corrosivity of atmospheres - classification, determination and estimation", International Standards Organisation: ISO 9223

"Atmospheric corrosion map of the UK": https://www.galvanizing.org.uk/corrosion-map/

"Atmospheric corrosion", I.S. Cole in Chapter 2.16 of "Shreir's corrosion – 4th edition", pp. 1051-1093, pub. Elsevier (2010)

"Coatings for the protection of structural steelwork", NPL guide to good practice in corrosion control #3

"Temporary corrosion protection", NPL guide to good practice in corrosion control #7

"Atmospheric corrosion – 2nd edition", C. Leygraf, et al., pub. The Electrochemical Society (2016)

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The National Physical Laboratory

The National Physical Laboratory (NPL) is the UK's National Measurement Institute. The heart of our mission is to deliver science with impact by disseminating research and measurement best practice for economic and social benefit.

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