Atmospheric Corrosion

Module Nine of CCE 281 Corrosion: Impact, Principles, and Practical Solutions

Lesson Objectives

- Describe various geographical environments in terms of their atmospheric corrosivity
- Summarize the main factors causing atmospheric corrosion
- Explain how these factors are measured
- Examine how the safety introduced by the massive usage of deicing salts has modified the corrosivity of road environments
- Design a testing program to establish the corrosivity map of a given site or even a country
- Recommend a corrosion test for a proposed environment

Required Reading

This Module consists of eight Web pages of required reading. The pagination is visible at the bottom of each page with direct links to adjacent pages.

Additional information can be found in sections 9.1 to 9.7 of the reference textbook (Corrosion Engineering: Principles and Practice).

Introduction

Atmospheric corrosion is surely the most visible of all corrosion processes, e.g. rusty bridges, flag poles, buildings and outdoor monuments. The large segment of the paint industry committed to the manufacture and application of products for the protection of metals, as well as the large-scale operations of the galvanizing industry attest to the importance of controlling atmospheric corrosion. (reference)

Economic losses caused by atmospheric corrosion are tremendous and therefore account for the disappearance of a significant portion of metal produced. Consider, for instance, agricultural machinery, steel structures, fences, exposed metals on buildings, automobile mufflers or bodies, and the myriad of other metal items which are discarded when they become unusable as a result of corrosion. These constitute direct losses from corrosion.

Atmospheric corrosion has been reported to account for more failures in terms of cost and tonnage than any other type of material degradation processes. This particular type of material degradation has recently received more attention, particularly by the aircraft industry, since the Aloha incident in 1988, when a Boeing 737 lost a major portion of the upper fuselage in full flight at 7,300 m.

All of the general types of corrosion attack occur in the atmosphere. Since the corroding metal is not bathed in large
Atmospheric corrosion operates in highly localized corrosion cells, sometimes producing patterns difficult to explain as in the example of this rusting galvanized roof.

Rusting galvanized roof with regular bands of rust

Thus, calculation of the electrode potentials on the basis of ion concentration, the determination of polarization characteristics, and other electrochemical operations are not as simple in atmospheric corrosion as they are in liquid immersion corrosion. However, all of the electrochemical factors which are significant in corrosion processes do operate in the atmosphere.

Information Module

- Types of Corrosive Atmospheres
- Factors Affecting Atmospheric Corrosion
- Measurement of Atmospheric Corrosion Factors
- Deicing Salts
- Corrosivity Classification Schemes
- Atmospheric Corrosion Tests
- Corrosion Behavior and Resistance

See also CCE 513: Corrosion Engineering
Corrosion in the Atmospheres
Types of Corrosive Atmosphere

While atmospheres can be classified into four basic types, most environments are mixed and present no clear demarcation. Furthermore, the type of atmosphere may vary with the wind pattern, particularly where corrosive pollutants are present, or with local conditions such as illustrated in the following Figure.
Bird damage to a 1931 bronze statue commemorating the 21st Battalion battles in WWI.

**Industrial**

An industrial atmosphere is characterized by pollution composed mainly of sulfur compounds such as sulfur dioxide (SO₂), a precursor to acid rain, and nitrogen oxides (NOₓ), the backbone of smog in modern cities. Sulfur dioxide from burning coal or other fossil fuels is picked up by moisture on dust particles as sulfurous acid. This is oxidized by some catalytic process on the dust particles to sulfuric acid which settles in microscopic droplets and fall as acid rain on exposed surfaces. The result is that contaminants in an industrial atmosphere, plus dew or fog, produce a highly corrosive, wet, acid film on exposed surfaces.
In addition to the normal industrial atmosphere in or near chemical plants, other corrosive pollutants may be present. These are usually various forms of chloride which may be much more corrosive than the acid sulfates. The reactivity of acid chlorides with most metals is more pronounced than that of other pollutants such as phosphates and nitrates.

**Example problem 9.1**

Are industrial sites near where you live more corrosive than adjacent locations? Provide some examples.

**Marine**

A marine atmosphere is laden with fine particles of sea mist carried by the wind to settle on exposed surfaces as salt crystals. The quantity of salt deposited can vary greatly with wind velocity and it may, in extreme weather conditions, even form a very corrosive salt crust, similar to what is experienced on a regular basis by sea patrolling aircraft or helicopters as shown in the following *Figure*. 

![Figure](image-url)
Sea salt deposited on the external surface a) of a Cormorant sea and rescue helicopter radar antenna, and b) salt causing corrosion to the antenna internal components due to a broken seal. (courtesy Major S.J.R. Giguère)

The quantity of salt contamination decreases with distance from the ocean, and is greatly affected by wind currents. The marine atmosphere also includes the space above the sea surfaces where splashing and heavy sea spray are encountered. The equipment exposed to these splash zones are indeed subjected to the worst conditions of intermittent immersion with wet and dry cycling of the corrosive agent as illustrated in the following Figure.
Rural

Rural atmospheres are typically the most benign and do not contain strong chemical contaminants, that is unless one is close to a farm operation where byproducts made of various waste materials can be extremely corrosive to most construction materials.

Arid or tropical atmospheres are special variations of the rural atmosphere. In arid climates there is little or no rainfall, but there may be a high relative humidity and occasional condensation. This situation is encountered along the desert coast of northern Africa. In the Tropics, in addition to the high average temperature, the daily cycle includes a high relative humidity, intense sunlight, and long periods of condensation during the night. In sheltered areas, the wetness from condensation may persist long after sunrise. Such conditions may produce a highly corrosive environment.

Indoor

Normal indoor atmospheres are generally considered to be quite mild when ambient humidity and other corrosive components are under control. However, some combinations of conditions may actually cause relatively severe corrosion problems. While there is no typical contaminant or set of conditions associated with an indoor atmosphere, any enclosed space which is not evacuated or filled with a liquid can be considered an indoor atmosphere. If not ventilated, such an environment may contain fumes, which in the presence of condensation or high humidity could prove to be highly corrosive.
Example problem 9.2

Indoor corrosion has caused many unpleasant surprises. Find some examples close to your immediate surrounding.

Even in the absence of any other corrosive agent, the constant condensation on a cold metallic surface may cause an environment similar to constant immersion for which a component may not have been chosen or prepared for. Such systems are commonly encountered in confined areas close to ground level or, worse, below ground where high humidity may prevail. The following Figure shows the advanced corrosion of the frame and contacts in an electric junction box only four years after a building was completed. While the junction box in this example was only at the ground level, the wires coming to the box were buried without additional insulation and in constant contact with much cooler ground than ambient air in the room.
Electric junction box badly corroded only four years after a new residence was completed.
Factors Affecting Atmospheric Corrosion

The most important factor in atmospheric corrosion, overriding pollution or lack of it, is moisture, either in the form of rain, dew, condensation, or high relative humidity (RH). In the absence of moisture, most contaminants would have little or no corrosive effect.

Rain also may have a beneficial effect in washing away atmospheric pollutants that have settled on exposure surfaces. This effect has been particularly noticeable in marine atmospheres. On the other hand, if the rain collects in pockets or crevices, it may accelerate corrosion by supplying continued wetness in such areas as illustrated in the following Figure.
Factors Affecting Atmospheric Corrosion

Dew and condensation are undesirable from a corrosion standpoint if not accompanied by frequent rain washing which dilutes or eliminates contamination. A film of dew, saturated with sea salt or acid sulfates, and acid chlorides of an industrial atmosphere provides an aggressive electrolyte for the promotion of corrosion. Also, in the humid Tropics where nightly condensation appears on many surfaces, the stagnant moisture film either becomes alkaline from reaction with metal surfaces, or picks up carbon dioxide and becomes aggressive as a dilute acid.

Temperature plays an important role in atmospheric corrosion in two ways. First, there is the normal increase in corrosion activity which can theoretically double for each ten-degree increase in temperature. Secondly, a little-recognized effect is the temperature lag of metallic objects, due to their heat capacity, behind changes in the ambient temperature.

As the ambient temperature drops during the evening, metallic surfaces tend to remain warmer than the humid air surrounding them and do not begin to collect condensation until some time after the dew point has been reached. As the temperature begins to rise in the surrounding air, the lagging temperature of the metal structures will tend to make them act as condensers, maintaining a film of moisture on their surfaces.

The period of wetness is often much longer than the time the ambient air is at or below the dew point and varies with the section thickness of the metal structure, air currents, RH, and direct radiation from the sun.

Cycling temperature has produced severe corrosion on metal objects in the Tropics, in unheated warehouses, and on
metal tools or other objects stored in plastic bags. Since the dew point of an atmosphere indicates the equilibrium condition of condensation and evaporation from a surface, it is advisable to maintain the temperature some 10 to 15°C above the dew point to ensure that no corrosion will occur by condensation on a surface that could be colder than the ambient environment.

**Relative humidity (RH)**

RH is defined as the ratio of the quantity of water vapor present in the atmosphere to the saturation quantity at a given temperature, and it is expressed as %. A fundamental requirement for atmospheric corrosion processes is the presence of a thin film electrolyte that can form on metallic surfaces when exposed to a critical level of humidity. While this film is almost invisible, the corrosive contaminants it contains are known to reach relatively high concentrations, especially under conditions of alternate wetting and drying.

The critical humidity level is a variable that depends on the nature of the corroding material, the tendency of corrosion products and surface deposits to absorb moisture, and the presence of atmospheric pollutants. It has been shown that, for example, this critical humidity level is 60% for iron if the environment is free of pollutants. In the presence of thin film electrolytes, atmospheric corrosion proceeds by balanced anodic and cathodic reactions. The anodic oxidation reaction involves the corrosion attack of the metal, while the cathodic reaction is naturally the oxygen reduction reaction as shown in the following Figure.

![Schematic description of the atmospheric corrosion of iron.](image)

Marine environments typically have high percent relative humidity (%RH), as well as salt rich aerosols. Studies have found that the thickness of the adsorbed layer of water on a zinc surface increases with %RH and that corrosion rates increase with the thickness of the adsorbed layer. There also seems to be a finite thickness to the water layer that, when exceeded, can limit the corrosion reaction due to limited oxygen diffusion. However, when metallic surfaces become contaminated with hygroscopic salts their surface can be wetted at lower %RH. The presence of magnesium chloride (MgCl₂) on a metallic surface can make a surface apparently wet at 34% RH while sodium chloride (NaCl) on the same surface requires 77% RH to create the same effect.
Example problem 9.3

The depression of the critical humidity levels on a metallic surface may seriously limit the use of some materials in various applications. Propose some design solutions to limit or avoid altogether such problems.

Example problem 9.4

Calculate the dew point temperature for a RH of 45% when the ambient temperature is 22°C? ... when it is 26°C? You may have to consult the Internet or the textbook to solve this problem.

Deposition of aerosol particles

The behavior of aerosol particles in outdoor atmospheres can be explained by invoking the laws that govern their formation, movement and capture. These particles are present throughout the planetary boundary layer and their concentrations depend upon a multitude of factors including location, time of day or year, atmospheric conditions, presence of local sources, altitude and wind velocity. The highest concentrations are usually found in urban areas, reaching up to 108 and 109 particles per cm cube, with particle size ranging from around 100 µm to a few nm. Size is normally used to classify aerosol because it is the most readily measured property and other properties can be inferred from size information. The highest mass fraction of particles in an aerosol is characterized by particles having a diameter in the range of 8 µm to 80 µm. Some studies have also indicated that there is a strong correlation between wind speed and the deposition and capture of aerosols. In such a study of saline winds in Spain a very good correlation was found between chloride deposition rates and wind speeds above a threshold of 3 m s⁻¹ or 11 km h⁻¹.

Aerosols can either be produced by ejection into the atmosphere, or by physical and chemical processes within the atmosphere (called primary and secondary aerosol production respectively). Examples of primary aerosols are sea spray and wind blown dust. Secondary aerosols are often produced by atmospheric gases reacting and condensing, or by cooling vapor condensation (gas to particle conversion). Once an aerosol is suspended in the atmosphere, it can be altered, removed or destroyed. It cannot stay in the atmosphere indefinitely, and average lifetimes are of the order of a few days to a week.

The lifetime of any particular particle depends on its size and location. Studies of the migration of aerosols inland of a sea coast have shown that typically the majority of the aerosol particles are deposited close to the shoreline (typically 400 to 600 m) and consist of large particles (>10µm diameter), which have a short residence time and are controlled primarily by gravitational forces. The aerosols that form also have mass and are subject to the influence of gravity, wind resistance, droplet dry-out, and possibilities of impingement on a solid surface, as they progress inland.

Pollutants

Sulfur dioxide (SO2), which is the gaseous product of the combustion of fuels that contain sulfur such as coal, diesel fuel, gasoline and natural gas, has been identified as one of the most important air pollutants which contribute to the corrosion of metals.

Less recognized as corrosion promoters, are the nitrogen oxides (NOx), which are also products of combustion. A major source of NOx in urban areas is the exhaust fumes from vehicles. Sulfur dioxide, NOx and airborne aerosol particles can react with moisture and UV light to form new chemicals that can be transported as aerosols. A good example of this is the summertime haze over many large cities. Up to 50% of this haze is a combination of sulfuric and nitric acids.
Measurement of Atmospheric Corrosion Factors

Various methods have been developed for measuring many of the factors that influence atmospheric corrosion. The quantity and composition of pollutants in the atmosphere, the amount collected on surfaces under a variety of conditions, and the variation of these with time have been determined. Temperature, RH, wind direction and velocity, solar radiation, and amount of rainfall are easily recorded. Not so easily determined are dwelling time of wetness (TOW), and the quantity of sulfur dioxide and chloride contamination. However, methods for these determinations have been developed and are in use at various test stations. By monitoring these factors and relating them to corrosion rates, a better understanding of atmospheric corrosion can be obtained.

Time of Wetness

TOW is an estimated parameter based on the length of time when the relative humidity is greater than 80% at a temperature greater than 0ºC. It can be expressed as the hours or days per year or the annual percentage of time.

A method of measuring the TOW has been developed by Sereda and correlated with the corrosion rates encountered in the atmosphere [9]. The moisture sensing elements in this sensor are manufactured by plating and selective etching of thin films of appropriate anode (copper) and cathode (gold) materials in an interlaced pattern on a thin nonconductive substrate as shown in the following Figure. When moisture condenses on the sensor it activates the cell, producing a small voltage (0 to 100 mV) across a 107 W resistor.
Interlocking combs of gold and copper electrodes in a ‘Sereda’ humidity sensor.

Thin sensing elements are preferred in order to preclude influencing the surface temperature to any extent. Although a sensor constructed using a 1.5-mm thick glass reinforced polyester base has been found to be satisfactory on plastic surfaces, this will not be the case with the same sensing element on a metal surface with a high-thermal conductivity. For metal surfaces, the sensing element should be appreciably thinner. Commercial epoxy sensor backing products of thickness of 1.5 mm, or less, are suitable for this purpose.

**Pollutants**

Sulfur dioxide is usually measured in terms of its concentration in air in units of µg m\(^{-3}\). Precise methods are available to monitor continuously the amount of sulfur dioxide in a given volume of air. However, this is only indirectly related to the effect of sulfur dioxide on corrosion since only the actual amount of hydrated sulfur dioxide or sulfur trioxide deposited on metal surfaces is important.

Since it is the SO2 deposited on the metal surface which affects the corrosion, it is also often measured in terms of deposition rate on the surface in units of mg/m\(^2\)/day. The pollution levels can also be measured in terms of the concentration of the dissolved sulfate in rain water. The collection of sulfur dioxide by the lead peroxide cylinder method has been employed and seems to correlate with corrosion rates when combined with the TOW.

**Airborne Chlorides**

Airborne salinity refers to the content of gaseous and suspended salt in the atmosphere. It is measured by the concentration in the air in units of µg/m3. Since it is the salt that is deposited on the metal surface that affects the corrosion, it is often measured in terms of deposition rate in units of mg/m\(^2\)/day. The chloride levels can also be measured in terms of the concentration of the dissolved salt in rain water.

A number of methods have been employed for determining the contamination of the atmosphere by aerosol transported chlorides, e.g. sea salt and road deicing salts. The ‘wet candle method,’ for example, is relatively simple, but has the
disadvantage that it also collects particles of dry salt that might not be deposited otherwise. This technique uses a wet wick of a known diameter and surface area to measure aerosol deposition as shown in the following Figure.

![Schematic of a wet candle chloride apparatus.](image)

The wick is maintained wet using a reservoir of water or 40% glycol/water solution. Particles of salt or spray are trapped by the wet wick and retained. At intervals, a quantitative determination of the chloride collected by the wick is made and a new wick is exposed.
In reality, the wet candle method gives an indication of the salinity of the atmosphere rather than the contamination of exposed metal surfaces. The technique is considered to measure the total amount of chloride arriving to a vertical surface and its results may not be truly significant for corrosivity estimates.

**Atmospheric Corrosivity**

The simplest form of direct atmospheric corrosion measurement is by coupon exposures. Subsequent to their exposure, the coupons can be subjected to weight loss measurements, pit density and depth measurements and to other types of examination. Flat panels exposed on exposure racks are a common coupon-type device for atmospheric corrosivity measurements. Various other specimen configurations have been used, including stressed U-bend or C-ring specimens for stress corrosion cracking (SCC) studies. The main draw back associated with conventional coupon measurements is that extremely long exposure times are usually required to obtain meaningful data, even on a relative scale. It is not uncommon for such programs to run for **20 years or longer**.

Some variations of the basic coupon specimens can provide rapid material/corrosivity evaluations. The helical coil adopted in the **ISO 9226** methodology is a high surface area/weight ratio coupon that gives a higher sensitivity than panel coupons of the same material. The use of bimetallic specimens in which a helical wire is wrapped around a coarsely threaded bolt can provide additional sensitivity and forms the basis of the **CLIMAT coupon** for Classify Industrial and Marine Atmospheres.

An ASTM standard describes the construction of CLIMAT coupons. According to this standard CLIMAT coupons can be made from 1100 aluminum (UNS A91100) wire wrapped around threaded rods of nylon, 1010 mild steel (UNS G10100 or G10080), and CA110 copper (UNS C11000) [13]. The mass loss of aluminum wire after ninety days of exposure is considered to be an indication of atmospheric corrosivity. However, the relative corrosivity of atmospheres could be quite different for the various combinations of materials.

The aluminum wire on copper bolts has been found by many to be the most sensitive of the three proposed arrangements in the ASTM standard. While this arrangement is the most sensitive, the use of triplicate coupons on a single holder additionally provides an indication of the reproducibility of the measurements. A CLIMAT coupon with three copper rods was installed at the **NASA Kennedy Space Center (KSC) beach corrosion test site** shown the following Figure.
Aerial view of the NASA Kennedy Space Center beach corrosion test site where atmospheric corrosivity is the highest corrosivity of any test site in the continental United States.

The following Figures show the coupon shown immediately after it had been installed (a), after thirty days (b), and after sixty days (c).
Measurement of Atmospheric Corrosion Factors

a)
Measurement of Atmospheric Corrosion Factors
A CLIMAT coupon with three copper rods immediately after it was installed at the Kennedy Space Center beach corrosion test site a), after thirty days b), and after sixty days c).

KSC has the highest corrosivity of any test site in the continental United States. The mass loss recorded after a shorter exposure than usual can be very high. In the present example it was already 16% of the original aluminum wire after sixty days. The CLIMAT coupons sensitivity to atmospheric corrosivity can be used to study fluctuations on a micro-environmental scale.
Deicing Salts Corrosion

Snow fighting has a long history. However, the first use of salt for deicing roads can only be traced back to the 1930’s and it was not until the 1960’s that the use of salt in conjunction with plowing became widespread after winter maintenance personnel learned of its effectiveness. The following Figure presents the usage made of deicing salt or rock salt (mostly sodium chloride) in the U.S. between 1940 and 2005. Initially confined to the ‘snowbelt’, ice fighting has become a priority activity in the ‘sunbelt’ too.

Usage of rock salt for deicing in the U.S. in thousands of tons. (Data from the Salt Institute http://www.saltinstitute.org/)
The Benefits of Salting

There is a vast international experience in effective snow fighting and the efficient use of deicing salts. A 1972 study by Paul J. Claffey presented to the Highway Research Board (now Transportation Research Board) concluded that the roughness of road ice and slippage of wheels can result in an increase in fuel consumption around 35% in averages and as much as 50% when there is 5 cm of snow on the road. A 1976 report by the Institute for Safety Analysis (TISA) listed the following cost benefits (reported here using 1976 prices and rates) of using salt in the U.S. to deice highways:

- Reduces wages lost due to lateness to work by $7.6 billion
- Saves $3 billion in wage loss because of absenteeism
- Reduces production losses by $7 billion
- Reduces losses in goods shipment by $600 million
- Saves 1.4 to 4.5 billion liters of fuel
- Has an 18:1 benefit/cost ratio

A study published in 1993 concluded that ‘As a winter maintenance service, deicing pays for itself within the first 25 minutes after the first hour that salt is spread on two-lane highways. Then, during the first four hours after the hour of application of salt, the direct road user benefits were $6.50 for every $1.00 spent on direct maintenance costs for the operation.’ The study found that costs related to accidents, including medical expenses, emergency services, workplace costs, travel delay, property damage, and administration and legal expenses decrease by 88% after the application of deicing salt. The following Figure illustrates the results of two studies of traffic accident rates carried out in two different countries (Germany and the U.S.) before and after salt spreading,

![Graph showing traffic accident rates before and after salt spreading.]
Statistics revealing the number of accidents before and after applying deicing salts.

Use of salt, in conjunction with a good plowing program, is the fastest and most efficient means of snow and ice removal. The use of abrasives requires at least seven times more material to treat a given distance of roadway. Therefore, it takes seven loads and seven round trips to the loading point, compared to just one for salt, resulting in a greater use of fuel, increased manpower and more time to treat roads during a storm. Studies by the Salt Institute have determined that a loaded salt truck, spreading at the generally accepted rate of 140 kg per two-lane km for general storm conditions, can treat a 36 km stretch of roadway, traveling a total of 72 km. A sand truck requires seven loads, must travel a total distance of 300 km to treat the same section of road and that truck requires four times more fuel. In more ways than one, salt used in snow and ice control contributes to energy savings.

The Bad and the Ugly Corrosion

The massive spreading of salt on roads and highways unfortunately has also some serious negative effects. Besides environmental concerns, one of the major criticisms of salt use for deicing is its contribution to corrosion of metal in steel bridges, road vehicles, reinforced concrete (bridge decks, parking garages), and any other metallic objects in close proximity to roads and highways (lampposts, statues, etc.).

Although another effective but less corrosive deicing agent is commercially available (calcium magnesium acetate or CMA), its price is apparently too high for wide usage. One ton of CMA costs $300-600 as opposed to $20-70 for rock salt. The use of CMA has thus been confined to areas where corrosion could cause critically important damage such as for airport winter maintenance. It can therefore be expected that the road environment will likely remain corrosive well into the future.

Maps are powerful tools for communicating information related to geographical landscapes and corrosivity maps of various countries have thus been drawn to illustrate the corrosion severity of the regions of these countries as it varies from coastal areas to deserts and from rural to heavily industrial locations. One of the very first such maps has been produced to summarize many years of results obtained by exposing bare steel coupons attached to different vehicles in the north-eastern U.S. and Canada. This corrosivity map is shown in the following Figure in which the snowbelt region is circled. The higher level of vehicle corrosion in the snowbelt region when compared to adjacent non-marine regions can only be attributed to the use of deicing salts.
The impact of salts on protective coatings is widely recognized. Any breach or holiday in the coating will let salts reach the metallic substrate and initiate a very aggressive environment that in turn will force the coating to blister and peel off as shown in the following Figures.
Blistering and peeling of protective coating subjected to regular deicing salt application.
The effect of deicing salts extends much beyond the immediate vicinity where the salts are spread because these salts can travel as aerosol particles generated by the traffic circulation. The lifetime of any particular particle depends on its size and location. Studies of the migration of aerosols inland of a sea coast have shown that typically the majority of the aerosol particles are deposited close to the shoreline (typically 400 to 600 m) and consist of large particles (≥10µm diameter), which have a short residence time and are controlled primarily by gravitational forces. Some studies have also indicated that there is a strong correlation between wind speed and the deposition and capture of aerosols.

The following Figure summarizes the results of a study using standard corrosion coupons deployed on a pedestrian walkway across a well traveled road during the winter months of a snowbelt city (Kingston, Ontario, Canada).
Results of a study investigating the transport and effects of deicing salt laden aerosols.

These results clearly indicate that the corrosion rates (% mass loss) while being highest closer to the ground (at the bottom of the pillars) are still appreciable many meters above the traffic level. For comparison, similar measurements made in non-trafficked areas of the same city typically showed corrosion rates fifty times smaller.
Corrosivity Classification Schemes

Environmental Severity Index

An environmental corrosivity scale, based on atmospheric parameters, has been developed over the years for the maintenance management of structural aircraft systems. A corrosion damage algorithm (CDA) was proposed as a guide for anticipating the extent of corrosion damage and planning maintenance operations. This classification scheme was developed primarily for uncoated aluminum, steel, titanium and magnesium alloys exposed to the external atmosphere at ground level. The section of the CDA algorithm presented in the following Figure considers distance to salt water, leading either to the very severe AA rating for close distance to seashore or a consideration of moisture factors.
The PACER LIME algorithm for determining the corrosion severity for a given location.

Following the moisture factors, pollutant concentrations are compared with values of Working Environmental Corrosion Standards (WECS). The WECS values were adopted from the 50th percentile median of a study aimed at determining ranges of environmental parameters in the U.S. and represent “average of averages”. For example, a severe A rating would be given if any of the three pollutants considered in this scheme, i.e. sulfur dioxide, total suspended particles and ozone levels, would exceed the WECS values in combination with a high moisture factor.

The environmental corrosivity, predicted from the CDA algorithm, of six marine air bases has been compared to the actual corrosion maintenance effort expended at each base. Considering the simplicity of the algorithms and simplifying assumptions in obtaining relevant environmental and maintenance data the correlation obtained was considered to be reasonable. Further validation of the CDA algorithm approach was sought by comparison of the predicted corrosivity data to actual coupon exposure results and a good agreement was reported between the algorithm rankings and available experimental data. However, subsequent attempts to enhance the PACER LIME algorithm by using the results obtained from broad based corrosion testing programs have failed to provide enough differentiation between moderately corrosive environments and were not considered in the final classification scheme adopted.
In order to remedy some of the deficiencies in this scheme Battelle has been tasked to monitor the atmospheric corrosivity of Air Force and other sites worldwide. The database describing the relative corrosive severity levels of different locations and actual corrosion rates of a variety of metals has now grown to more than 100 sites worldwide. The metals included in that study are three aluminum alloys (A92024, A96061, and A97075), copper, silver and steel.

The data are collected for metals directly exposed to the outdoor environment in a standard sample mounting configuration and test package. A typical plastic test rack with its metallic coupons is shown in the following Figure besides a CLIMAT coupon exposed at the KSC beach corrosion test site.

Metal coupons in a plastic test rack exposed at the Kennedy Space Center beach corrosion test site besides a CLIMAT coupon. (Courtesy of Battelle Institute)

The following Figure shows a close-up view of the coupons before exposure.
Once exposed to the environment for a given period of time the corroded metal strips such as shown in the following Figure would be sent back to the laboratory for mass loss measurements following standard methods and further analysis.
ISO Classification of Corrosivity of Atmospheres

The International Organization for Standardization (ISO) has implemented a worldwide atmospheric exposure program known as ISO CORRAG. This program includes exposure of steel, copper, zinc, and aluminum for 1, 2, 4, and 8 years at sites located in 51 sites in 14 nations in order to generate the necessary data to produce a classification system for predicting atmospheric corrosivity from commonly available weather data. The standard was obviously not intended for extreme service atmospheres such as those within chemical or metallurgical processing facilities or where there is direct contact with salt spray.

The program consisted of six one-year exposures of flat panels (100 x 150 x 2 mm) and helix specimens beginning every six months for three years. Triplicate specimens were used for each exposure. The metals selected were a low carbon steel from a single supplier and commercially pure zinc, copper, and aluminum. These nonferrous metals were obtained from local sources in each of the participating nations. The program was initiated in 1986 and officially closed in 1998. At the conclusion of each exposure, the specimens were retrieved and sent to the laboratory that had done the initial weighing for cleaning and evaluation. Mass loss values were obtained and converted to corrosion thickness loss values. Based on these data, a simple classification scheme of five corrosivity classes was established for each metal.

**Details of the ISO 9223 standard**

Experience from applying the ISO classification system has shown, however, that certain observations need further
clarification. Substantial corrosion has also been measured on specimens exposed at temperatures well below 0°C, which is in direct contradiction to the ISO criterion. It is proposed on the basis of these results, that the TOW in these environments be estimated as the length of time that relative humidity exceeds 50% and the ambient temperature exceeds –10°C.

Example problem 9.5

The ISO 9223 standard indicates that there should be no corrosion at temperature below 0°C. Independent researchers have however proposed to lower the minimum temperature stated in the standard to lower values in order to account for the actual corrosion observed in Nordic climates. Provide an explanation for the observed corrosion at temperature below the freezing point.

Maps of Atmospheric Corrosivity

The north-eastern U.S. and Canada corrosivity map shown on the previous page is a simple and efficient way to communicate the general features of atmospheric corrosivity. Similar corrosivity maps have been created from data available in the literature. A list of the maps is available here.
Atmospheric Corrosion Tests

For many years, different individuals and organizations have been putting specimens out in the atmosphere in all kinds of tests and shapes. There has been an attempt to standardize some of these tests, as well as the method of reporting the results. When initiating corrosion tests in the atmosphere, these standardized procedures should be consulted and used whenever possible. There tend to be three general types of specimens:

- Panels;
- Tensile specimens; and
- Stress corrosion cracking specimens.

The panels are usually in the form of sheets 10 cm wide, 15 cm long, and about 0.2 cm thick; the tensile specimens in a machined "dumb bell" shape to fit tensile testing machines; and the stress corrosion specimens in jigs to suit the type of stress being considered.

Effect of Conditions of Exposure on Atmospheric Corrosion

In addition to the atmospheric conditions at the test site the following factors are important aspects for the design and interpretation of atmospheric corrosion tests:

- Shape of the specimen
- Direction it faces
- Amount of shelter, drip, or runoff from other specimens
- Elevation
- Shading
- Unusual contamination.

Panel specimens are usually placed in racks at a 30-degree angle to the horizontal, facing the source of corrosive elements. They are electrically insulated from the racks on which they are mounted and are arranged so that drip from neighbouring panels does not contaminate them as illustrated in the following Figure.
Cylindrical specimens are mounted horizontally, facing the same direction as the panels. They may be exposed fully to the weather or be partially sheltered, depending upon the requirements of the test. There is a great variety of test fixtures and shape of specimens used for environmental cracking tests. The following Figures show respectively a full exposure and a semi-sheltered test stations equipped with TOW galvanic sensors, temperature, and SO$_2$ level recorded with a data logger.
Outdoor exposure test station with specimen rack on top and data logger attached below at an Army Base in Northern Australia. (Courtesy of DSTO Australia)
Semi sheltered test station with test coupons, wet candle apparatus, and data logger attached at an Army Base in Northern Australia. (Courtesy of DSTO Australia)

The following Figure shows a custom built test rack designed to be mounted on a full exposure test station in order to reveal the atmospheric corrosion resistance of aluminum and magnesium alloys to crevice corrosion.
Aluminum and magnesium test specimens equipped with crevice spacers and mounted on a rack to be exposed at the previous test station. (Courtesy of DSTO Australia)

In most exposure tests, enough specimens are used so that removals may be made after periods of 1, 2, 7, and 20 years or 2, 5, 10, and 20 years. Such programs correct for materials that have changes in corrosion rate after the first one or two years. Very short-term tests usually can be misleading in that the condition of the metal surfaces during the first few days of exposure may affect the initial corrosion rate, or "average weather conditions" may not be encountered during the initial exposure period.

Some tests are continued until failure, as in SCC testing. However, in tests of protective coatings, as well as in others, periodic measurements of weight loss, pit depth, and change in tensile strength are made. All of these factors affect the duration of tests, but in most atmospheric exposures, a program covering a time span of ten years or more is often considered.

In many atmospheric corrosion tests, the specimens are observed every year for changes in appearance. At predetermined intervals, samples are removed, the weight loss is determined, tensile tests are made, and if pitting is significant, the deepest pit is measured, as well as a number of other pits, to determine average depth. In a few instances, composition of corrosion products is determined.

**Measurement of Corrosion**

Results of corrosion tests are usually reported as:

- Loss in weight or reduction in thickness per unit of time
- Change in tensile strength
- Time-to-fracture (SCC)
- Time-to-perforation
- Time-to-10%-increase-in-electrical-resistance
Atmospheric Corrosion Tests

- Time-to-initial-rust, 10% rust, or complete rust, or
- In some cases, changes in ductility

The reduction in thickness or penetration in microns per year (µm/y) or mils per year (mpy) is the most general and useful measurement of corrosion rate.

**Accelerated Tests**

So far, reference has been made to natural exposures in the atmosphere. Many workers feel that evaluations are needed in times less than those required for on-site tests, and therefore have devised accelerated methods based on a previous determination of the dominant corrosion factors. The preferred practice is to design such tests to represent the most severe conditions for the corrosion mechanism involved.

However, it is useful to consider how realistically corrosion acceleration may be achieved. Raising the temperature can be useful but may cause changes in the form and nature of hydrous gels often important in the initial stages of corrosion. Increasing the concentration or corrosive agents in the salt spray, for example, may not necessarily be appropriate during cyclic testing since even an initially dilute spray will, after a sufficient number of cycles, result in the solubility of ionic species being exceeded.

Generally, corrosion products developed by synthetic environments such as those produced in the ASTM B117 test are substantially different from those produced during natural weathering or even by wet-dry mixed salt spray tests. For example, corrosion of aluminum or zinc specimens in ASTM B117 primarily produces soluble species such as AlCl₃ or ZnCl₂ with little corrosion product remaining on their surfaces. Exposures in a wet-dry test, in contrast, cause the formation of corrosion products on those metals more representative of those formed during natural exposure. On aluminum, for example, hydrated alumina containing chloride and amorphous material are produced in both the high sulfate and high chloride cyclic salt spray tests. The reality can be even more complex as illustrated in the following Table in which it can be seen that the products found on specimens exposed to real environments often consist of corrosion products mixed with various foreign materials.

**Results of X-Ray diffraction of products found specimens exposed to real environments.**
<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Chemical or mineral name</th>
<th>Chemical formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Product formed on Magnesium during 3 month immersion in tap water</td>
<td>Nesquehonite</td>
<td>MgCO₃·3H₂O</td>
</tr>
<tr>
<td></td>
<td>Calcium fluosilicate</td>
<td>CaSiF₆</td>
</tr>
<tr>
<td></td>
<td>Beta silicon carbide</td>
<td>β-SiC</td>
</tr>
<tr>
<td></td>
<td>Sodium fluoride</td>
<td>Na₂S</td>
</tr>
<tr>
<td>Sodium fluoride</td>
<td>MgCl₂·2MgCO₃·Mg(OH)₂·6H₂O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mg₃P₂O₇</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(Na,K)AlSi₃O₈</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td></td>
</tr>
<tr>
<td></td>
<td>NaOH</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ca₃Al₆O₁₂·SO₄</td>
<td></td>
</tr>
<tr>
<td>Substance found on heat exchanger</td>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td>Substance found beneath paint on metal surface</td>
<td>Alpha quartz</td>
<td>SiO₂</td>
</tr>
<tr>
<td>Product formed on automobile bumper support during 3 year service</td>
<td>Lepidocrocite</td>
<td>γ-Fe₂O₃·H₂O</td>
</tr>
<tr>
<td></td>
<td>Goethite</td>
<td>Fe₂O₃·2H₂O</td>
</tr>
<tr>
<td>Product from conversion unit in marine Environment</td>
<td>Zinc ferrite</td>
<td>ZnO·Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>Cobalt ferrite</td>
<td>CoO·Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>Cobaltous ferrite</td>
<td>CoO·Fe₂O₃</td>
</tr>
<tr>
<td></td>
<td>Halite</td>
<td>NaCl</td>
</tr>
<tr>
<td></td>
<td>Chromic oxide</td>
<td>Cr₂O₃</td>
</tr>
<tr>
<td></td>
<td>Nickel, zinc ferrospinel</td>
<td>(Ni,Zn)O·Fe₂O₃</td>
</tr>
<tr>
<td>Sodium Fluothorate</td>
<td>Sodium Fluothorate</td>
<td>Na₃Th₂F₁₁</td>
</tr>
<tr>
<td></td>
<td>Embolite</td>
<td>Ag(CI,Br)</td>
</tr>
<tr>
<td></td>
<td>Magnesioferrite</td>
<td>MgFe₂O₄</td>
</tr>
<tr>
<td></td>
<td>Beryllium palladium</td>
<td>BePd</td>
</tr>
<tr>
<td></td>
<td>Magnetite</td>
<td>Fe₂O₄</td>
</tr>
<tr>
<td></td>
<td>Nickel titanium</td>
<td>NiTi</td>
</tr>
<tr>
<td>Product formed on copper during 3 month immersion in tap water</td>
<td>Botallackite</td>
<td>CuCl₂·3Cu(OH)₃·3H₂O</td>
</tr>
<tr>
<td></td>
<td>Ilvaite</td>
<td>Ca(Fe,Mn,Mg)₂(Fe,Al)(SiO₄)·OH</td>
</tr>
<tr>
<td>Product from Al-Cu alloy exposed to deep-sea environment</td>
<td>Ammonium copper fluoride dihydrate</td>
<td>(NH₄)₂·CuF₄·2H₂O</td>
</tr>
<tr>
<td></td>
<td>Potassium cyanide</td>
<td>KCN</td>
</tr>
<tr>
<td></td>
<td>Chi alumina</td>
<td>Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>Calcium aluminate</td>
<td>3CaO·Al₂O₃</td>
</tr>
<tr>
<td></td>
<td>Alpha cadmium iodide</td>
<td>CdI₂</td>
</tr>
<tr>
<td>Product from Al-Zn-Mg-Cu alloy exposed to deep-sea environment</td>
<td>Chi alumina</td>
<td>A1₃O₃</td>
</tr>
<tr>
<td></td>
<td>Alpha cadmium iodide</td>
<td>CdI₂</td>
</tr>
<tr>
<td>Product from Al-Mn alloy exposed to deep-sea environment</td>
<td>Ammonium copper fluoride dihydrate</td>
<td>(NH₄)₂·CuF₄·2H₂O</td>
</tr>
<tr>
<td></td>
<td>Nobletie</td>
<td>CaB₆O₁₀·4H₂O</td>
</tr>
</tbody>
</table>

*Substances shown in italics are not corrosion products of the primary metals or alloys involved in the system.
Corrosion Resistance to Atmospheric Corrosion

The following sections contain some specific information on the atmospheric corrosion performance of the most popular systems used in normal atmospheric conditions.

**Iron and Steel**

Iron, in its various forms, is exposed to all kinds of environments. It tends to be highly reactive with most of them because of its natural tendency to form iron oxide. When it does resist corrosion it is due to the formation of a thin film of protective iron oxide on its surface by reaction with oxygen of the air. This film can prevent rusting in air at 99% RH, but a contaminant such as acid rain may destroy the effectiveness of the film and permit continued corrosion. Thicker films of iron oxide may act as protective coatings, and after the first year or so, could reduce the corrosion rate significantly as shown in the following Figure.

![Graph showing corrosion rate over time for carbon steel, copper steel, and Cor-ten steel](image-url)
Time-corrosion curves of three steels in industrial atmosphere, Kearny, NJ: (1) ordinary steel; (2) Copper steel; and (3) Cor-ten.

While the corrosion rate of bare steel tends to decrease with time in most cases, the difference in corrosivity of different atmospheres for a particular product is tremendous. Similar ranges in corrosivity were determined by the ISO 9223 corrosion rates for steel. In a few cases, the corrosion rates of ferrous metals have been reported as increasing with time, and careful analysis of the exposure conditions generally reveals that an accumulation of contaminating corrosive agents has occurred, thus changing the severity of the exposure.

It is generally conceded that steels containing low amounts of copper are particularly susceptible to severe atmospheric corrosion. In one test over a 3 1/2-year period in both a marine and an industrial atmosphere, a steel containing 0.01 % copper corroded at a rate of 80 µm/y, whereas increasing the copper content by a factor of five reduced the corrosion rate to only 35 µm/y. Other tests comparing gray cast iron, malleable iron, and low-alloy steels indicated that their corrosion resistances were approximately the same.

Plain cast iron appears to have a corrosion rate about one half that of 0.2% copper steel in a marine atmosphere. One has to be careful in citing such differences to stipulate the composition of the carbon steel because corrosion behavior of carbon steels is influenced so markedly by small variations in copper and phosphorus content. In an industrial atmosphere, a structural carbon steel showed a penetration of about 20 µm, a copper structural steel about 10 µm, and a low-alloy steel about 4 µm after five years of exposure.

As indicated in ISO 9223, it is impossible to give a corrosion rate for steel in the atmosphere without specifying the location, composition, and certain other factors. If one can relate exposure conditions to those described in the literature, a fairly good estimate can be made of the probable corrosion behavior of a selected material. However, all aspects of the exposure of the metal surface must be considered. A high-strength, low-alloy (HSLA) steel may show an advantage in corrosion resistance of 12:1 over carbon steel when freely exposed in a mild environment. As the severity or the physical conditions of exposure change, the HSLA steel will show less superiority, until in crevices or the backside of structural forms in a corrosive atmosphere, it will be no better than carbon steel.

Very little needs to be said about the behavior of stainless steels (Types 200 and 300), which contain high percentages of nickel and chromium, except that they can keep their shiny aspect without tarnishing for many decades as illustrated in “The Mudra”, shown in the following Figure, which was erected in the busy part of Toronto in 1974. The steels containing only chromium (Type 400) as the principal alloying constituent tend to rust superficially, but the others are relatively free from surface atmospheric corrosion. Many of them are susceptible to SCC in many common environments.
Toronto stainless steel sculpture the ‘Mudra’ by Ted Bieler completed in 1974. (Photo by Tom Skudra courtesy of the Nickel Institute)

**Copper and Copper Alloys**

Copper and its alloys are not exposed to the atmosphere in great quantities when compared with steel. However, this material brings aesthetic value to building construction, in addition to excellent corrosion resistance. The black and then green patina formed on the surface provides an attractive decorative finish, while sealing the metal from further corrosion. As a consequence, some copper has been used for roofs, gutters, and as flashings on wood or composition shingled roofs.

**Example problem 9.6**

Find in your neighbourhood some structural elements made of copper and copper alloys and report on their
Extensive tests have been made of the corrosion resistance of copper and its alloys to various atmospheres. Various alloys were exposed in rural, industrial, and marine atmospheres for periods of up to twenty years. From data accumulated in these tests and the calibrations of relative corrosivity of the test sites, a fairly clear picture can be obtained of the corrosion behavior of copper. In addition to the corrosion penetration rates, one must be mindful of dezincification of brasses and selective attack on some bronzes, as well as SCC illustrated by season cracking of brass. These types of corrosion contribute to the failure of the material in mechanical respects without significant weight changes or losses in thickness.

Where copper is used as flashing on roofs, corrosion has been encountered at the edge of the shingles as a continuous groove. This effect is more pronounced when the atmosphere contains both chlorides and sulfides, and with wood shingles as compared with roofs of other composition. Tests indicate that all-copper roofs 0.5 mm or more in thickness such as the roof in the following picture would last several centuries in an industrial atmosphere.

Green copper roof on Quebec Armory

If the green patina on copper alloys is desired for aesthetic reasons, pre-treatment of the surface with appropriate
passivating solutions is recommended. If oxidation by sulfur compounds precedes the desired reaction, the surface will present only a dark brown color for many years.

**Nickel and Nickel Alloys**

Electrodeposited nickel and electroless nickel are widely used as a protective coating for atmospheric exposure, and some nickel alloys, while, selected for other reasons, are also exposed to atmospheric corrosion. The results shown in the following Table were obtained for several representative alloys. As can be concluded from the data, nickel tends to be passive in a marine atmosphere. The ratio between the corrosion rate for nickel exposed to the industrial atmosphere and that exposed to rural or marine atmospheres was 28:1.

<table>
<thead>
<tr>
<th>Material</th>
<th>New York/ Newark</th>
<th>State College, PA</th>
<th>Kure Beach/La Jolla</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nickel</td>
<td>0.15</td>
<td>3.66</td>
<td>0.22</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>1.65</td>
<td>0.23</td>
</tr>
<tr>
<td>Monel</td>
<td>0.16</td>
<td>1.57</td>
<td>0.17</td>
</tr>
<tr>
<td></td>
<td>3.56</td>
<td>0.81</td>
<td>0.21</td>
</tr>
<tr>
<td>Incoloy</td>
<td>0.06</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>Inconel</td>
<td>0.05</td>
<td>0.03</td>
<td>0.02</td>
</tr>
<tr>
<td>Nionel</td>
<td>0.03</td>
<td>0.02</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Corrosion in mm/year of nickel and its alloys in various atmospheres.**

**Aluminum and its Alloys**

Aluminum, in its many forms is exceeded only by steel in tonnage directly exposed to the elements. It is produced in the form of wrought products, extrusions, and castings with a large variety of alloying elements to impart desired mechanical properties. The atmospheric corrosion behavior of aluminum products fits into some fairly well-defined patterns that are related to composition.

While pure aluminum has excellent atmospheric corrosion resistance and is used extensively as a cladding materials for this very reason, alloys containing copper and silicon as the principal alloying constituents are susceptible and should be used with care. In a rural atmosphere, the corrosion rate for most alloys is approximately 0.06 µm/y, with those containing large amounts of copper about double this low rate. Changes in tensile strength because of corrosion vary from 0 to less than 1% for sheet material.

In a marine environment, the differences between alloys appear as a tenfold increase, from about 0.6 µm/y for the less corrosion-resistant materials, to about 0.7 µm per year for the better materials. Pitting also is about 10 times greater in marine atmospheres. Corrosion can be much greater in a severe industrial atmosphere than in the marine atmosphere.

Some aluminum alloys develop severe pitting and a voluminous white corrosion product under some exposure conditions in a marine atmosphere. Aluminum roofs have been known to corrode severely at the overlaps. Some aluminum alloys also can be attacked in their intergranular regions when exposed after certain metallurgical treatments (cold working or precipitation hardening). General intergranular attack or exfoliation can then occur. The attack tends to start at sheared edges or punched holes, but is not restricted to these areas. Aircraft manufacturers, in particular, must guard against this type of corrosion.

In designing aluminum equipment, care must be exercised to avoid dissimilar metal couples and the attendant galvanic corrosion. Copper and rusty steel are particularly bad in contact with aluminum. Due to the passive film on stainless steel, it can be used in contact with aluminum in the atmosphere with little expectation of accelerated corrosion, despite the differences in potential. In addition, designers should be aware of the possibility that some aluminum alloys may be sensitized to intergranular corrosion by heat treatment.

As would be expected, constant exposure to moisture with a limited supply of oxygen to the aluminum surface leads to the rapid corrosion of any aluminum apparatus or equipment component. This is due to the highly reactive nature of aluminum that leads to formation of oxides or hydroxides. In the presence of oxygen, a protective aluminum oxide film develops on any aluminum surface. This oxide film is substantially unreactive with the normal constituents of the atmosphere. If the film is removed by mechanical or chemical means and the aluminum exposed to water, a rapid reaction sets in and large quantities of the aluminum are converted to the hydroxide and subsequently to the oxide.

Most of the 1000, 3000, and 6000 series of wrought alloys, the magnesium, and the silicon magnesium casting alloys are relatively immune to SCC in normal atmospheres. However, the other alloys may be susceptible under some conditions. This subject should be investigated carefully by the designer or user if stresses are high and the atmosphere is corrosive.

The usual corrosion behavior in the atmosphere involves pitting and roughening of the surface with a fairly large decrease in the corrosion rate after the first one to three years of exposure. In a marine atmosphere, the maximum pit depth might reach 150 mm within 2 years, yet not exceed 200 mm in 20 years. In an industrial atmosphere, initial pits might reach 4 mils in the first period and not exceed 125 mm at the end of 20 years. In terms of average corrosion rate, the initial rate would be about 0.08 mm/y, dropping to less than 0.3 mm/y by seven years.

Severe pitting has been encountered where aluminum surfaces were contaminated by either alkaline dust or coral dust containing chlorides, followed by condensation. On some of the South Pacific islands, dust collected from the surfaces of sheltered structures, such as those inside aircraft wings, contained 67% chloride by weight.

In the design of aluminum structures, the usual precautions of avoiding crevices or pockets and coupling with dissimilar metals must be observed. An example of this is in the overlapping encountered between aluminum roofs and siding. In some marine or industrial atmospheres, the aluminum perforated at the laps within a few months. In addition, stress concentrations should be avoided, such as those found in some riveted structures, in the vicinity of welds, and at notches or inside corners. Where it is impractical to avoid dissimilar metals, the aluminum should be electrically insulated from the more noble metal by means of washers, sleeves, etc. In some instances, covering the noble metal with an organic finish is sufficient to greatly reduce galvanic couple corrosion.

To illustrate the problems encountered in designing aluminum structures, an amusing and fairly well-known, yet illustrative story comes to mind. A new processing plant was built having an un-insulated aluminum roof attached directly to steel support frames. This was known to have worked well in several instances. However, the high RH in the plant caused condensation on the cool roof during rainstorms, evenings, and cold spells in the winter.

**Zinc and its Alloys**

Zinc is exposed to the atmosphere in the form of galvanized sheet, as in flashings on roofs; as die castings, and as coatings on steel, either hot dipped or electroplated. Studies of the corrosion of zinc in the New York atmosphere indicated that there was less than a 10% difference between the corrosion rate of galvanized iron, zinc die castings, and three grades of rolled zinc. It was also found that the corrosion rate tended to be a linear function with time. In some instances, where the rate changed after a period of time, it was concluded that the amount of contamination in the atmosphere had changed.

The general behavior of zinc metal and zinc coatings is described in the ISO tables presented earlier. Note the particularly low rates of attack on zinc as compared with steel in marine exposures where chloride deposition is important. Such excellent resistance is acquired by the hard, dense, protective products of corrosion in a chloride atmosphere. Similar results cannot be obtained in a sulfurous atmosphere where the products are soft, voluminous, and non-protective.

**Example problem 9.7**

Find in your neighbourhood some structural elements made of galvanized steel and report on their state and condition.

Zinc-base die castings usually are not exposed boldly to the outside atmosphere without a protective coating. When
breaks or pits occur in coatings such as nickel and chromium, the corrosion of the die casting may be accelerated due to the dissimilar metal contact and thus give a false impression of the corrodibility of zinc. Many small parts of machinery, household appliances, and hardware are made of zinc-base die castings or "white metal" and are exposed to an indoor atmosphere where their corrosion behavior is very good (White metal is typically 93 to 96% Zn, 4% Al, 0.05% Mg, and sometimes 1 to 3% Cu). In these cases where severe corrosion is encountered in this relatively mild atmosphere, the cause may be improper alloy selection or the use of material containing too high a percentage of impurities.

**Galvanized steel** is the most important application of zinc. Worldwide, the use of zinc for galvanizing results in an annual consumption of more than three million tons of zinc, constituting nearly one-half of the world zinc production. Most of these are hot-dipped galvanized coatings containing a small amount of aluminum. Thickness of electroplated coatings is considerably lower than those applied by the hot dip process. Galvanizing produces a zinc coating on the steel surface and is one of the most effective methods for corrosion protection of steel. This is attributed to the excellent corrosion resistance of zinc coatings, particularly in atmospheric environments.

Corrosion rates for zinc, like other metals can vary by as much as two orders of magnitude in atmospheric environments depending on the specific environmental conditions. Therefore, it is important to know the specific corrosion rate in a given application environment in order to effectively use zinc coated steels in outdoor structures. The most commonly used method for corrosion life estimation of galvanized steels has been the use of generalized values for the different types of atmospheres as shown in the following Figure.

![Service life of hot-dip galvanized coatings as a function of zinc thickness and specific environments.](image)

This method uses a generalized value to represent the corrosion rates for five predetermined atmospheric environments as a function of zinc coating thickness. Service life in Figure 9.43 is defined as the time to 5% rusting of the steel surface. It can be used to estimate the service life of a given coating thickness or to specify a coating for a given environment.

**Example problem 9.8**
Use one of the [corrosivity maps](http://www.corrosion-doctors.org/Corrosion-Atmospheric/Corrosion-resistance.htm) to specify the thickness required of a galvanized coating to achieve a useful life of fifty years in the various environments described on that map.

The method is applicable to zinc-coated steel produced by batch or continuous galvanizing. It is applicable to hot-dip, electrogalvanized, and thermal sprayed coatings. However, it does not apply to coatings containing alloying elements **larger than 1%**. The method assumes that the galvanized product is free of significant defects that could accelerate corrosion. Additionally, the service life prediction does not consider issues of water entrapment that can create severe crevice chemistry.

**Miscellaneous Alloys**

Many other alloys are exposed to the atmosphere under a variety of circumstances. The resulting corrosion problems tend to be specific. Lead and tin alloys tend to be inert in the atmosphere unless some specific type of contamination exists. As far as exposure to the atmosphere is concerned, tin appears mostly as a coating on steel containers where it can accelerate the corrosion of the more anodic steel by pitting. Lead is sometimes used on roofs, but more often is found indoors in chemical plants.

Due to their inertness, silver and gold are used as alloys to confer corrosion resistance to more reactive metals. Silver reacts with sulfur compounds in the atmosphere to produce heavy coatings of black silver sulfide. This corrosion product is soft and rubs off of electrical contacts.

Titanium alloys have very good corrosion resistance in the atmosphere, as do the iron-nickel chromium alloys. There are many alloys that hold a specific place in the metal family, such as pewter, speculum, constantan, and the like, which possess certain atmospheric corrosion resistance properties, but are used so infrequently that they do not warrant general discussion.

**Metallic Coatings**

Any discussion of atmospheric corrosion should include consideration of the corrosion behavior of various metallic protective and decorative coatings. These are usually divided into two general categories:

- **Coatings that confer protection to the basic metal, and**
- **Coatings that are used for decorative purposes.**

As protective coatings, a distinction must be made between those such as zinc, cadmium, and aluminum on steel that protect by sacrificial behavior, and those that must provide a substantially continuous protective envelope around the protected metal. In the latter category are metals such as nickel, tin, silver, brass, and chromium.

Sacrificial metals corrode as coatings in much the same manner as they do as solid metals until the base or protected metal is exposed at pores or bared areas. The galvanic couple effect then begins to accelerate the corrosion of the protective coating. This galvanic couple effect tends to protect the base metal at the pores or bared spots. General corrosion of the sacrificial type of coating tends to follow a linear function that is peculiar to the particular site.

This reaction is in contrast to what happens in the case of the more noble protective coatings that act as an envelope and resist the atmosphere due to their inertness, passivity, or protective films. As soon as a pore or bare spot appears, the corrosion of the base metal is accelerated. Die castings of a metal such as zinc covered with a copper-nickel-chromium coating will suffer severe corrosion at large pores or discontinuities in the coating.

While most metal coatings are applied by electroplating, some are produced by flame or plasma spraying, hot dipping, electrostatic sputtering, or vapor deposition. The corrosion rate of a metal coating is largely independent of the method of application, except where impurities play a role. Powders of various metals have been attached to the surface of a base metal by either organic or inorganic binders. Where these metal particles are in mutual contact, and in contact with the base metal, they can perform much like a metallic coating. In noble types of coating, porosity is very important and tends...
Corrosion Resistance to Atmospheric Corrosion

to decrease rapidly as the coating thickness increases **beyond 13 mm**. No clear cut information is available on the factors that influence porosity in electrodeposited coatings.

**Polymeric Materials**

Essentially all polymers freely exposed to the elements will change in some manner. The active rays of the sun become potent agents of change in the organic materials. Further polymerization of the resin can occur to produce embrittlement. Other types of new bonding can be triggered to make polymers more crystalline. Any volatile component of the material, such as a plasticizer, can be evaporated. The polymer chains may be simply oxidized and broken up to destroy the product. Oxygen, ozone, and moisture act with the sunlight to degrade the plastics as illustrated in the following Figure.

![Plastic material degraded over a few years of exposure to sun rays on a window sill.](image)

The external evidence of attack may be blushing (loss of gloss), chalking, or change in color of the product. This is often observed on the epoxy and polyester polymers when they have been boldly exposed to the environment. However, only mechanical tests will reveal the extent of degradation of either thermoplastic or thermosetting resins. The effect of high atmospheric temperatures or heating from direct exposure to the sun can be particularly severe on thermoplastic polymers. Creep or distension of the polyvinyl chloride and polyethylene plastics will occur readily unless provision is
made to prevent overheating or stressing of the materials. Certain other thermoplastics can be dimensionally stable under normal atmospheric temperatures. The strength of these thermosetting resins is not noticeably changed.

Polymeric materials should be thoroughly tested if they are to be exposed freely in the atmosphere. ASTM Recommended Practice D1435 describes the appropriate conditions for such a test exposure and suggests tests that might be used to evaluate changes in the materials. Changes in mechanical and physical properties of the polymers are determined for definitive results. Weight gains or losses can be of interest, but do not provide substantive results. Accelerated cabinet testing of the materials can be performed with essentially the same validity as when testing metallic materials. Poor materials can be eliminated, but extrapolation of the data to forecast the life of plastic parts in the atmosphere should not be attempted. ASTM D1499, D 2565, and G26 may be used to ensure the controlled cabinet testing of the plastics. ASTM D750 should be used for the evaluation of the elastomers.

The preventive measures used to ensure the integrity of polymeric materials are similar to those for metals, i.e., the exterior should be covered. The exterior surfaces are painted or metal plated to provide a barrier between the material and the atmosphere. Alloying of the basic material with small amounts of other resins can often upgrade the stability of the material.

Answers to example problems