

# Atmospheric Corrosion

G O Lloyd

Atmospheric corrosion is not a very clearly defined subject. It occupies the territory between immersed corrosion and dry oxidation, since metals may be exposed to damp atmospheres or may be subjected to the full force of the weather. It is usually taken to include packaging and storage, painting and preparation for painting, and the effects of climate and air purity. This contribution will concentrate mainly on corrosion of iron and steel, with sideglances at other metals where necessary.

Metals exposed to uncontrolled “normal” atmospheres may corrode more rapidly and by different mechanisms than those kept in pure, dry air – even if they are not exposed to rain. In dry atmospheres, the growing oxide film usually protects the underlying metal, giving rise to a logarithmic or square-root time law. In uncontrolled atmospheres, the rate usually remains constant for a period, but may fall off when the film has grown to an appreciable thickness. If the metal is exposed to rain, it may corrode while it is wet at the rate appropriate to immersion in impure, well-aerated water, but the rate will fall when it dries. Equations for predicting rates of atmospheric corrosion must therefore contain a term for “time of wetness” as well as for average temperature, average relative humidity, atmospheric purity and so on. These equations are of limited value because it is almost impossible to specify the local conditions sufficiently precisely. At ten sites within a few hundred metres of the promenade at Biarritz, rates of corrosion of steel varied by an order of magnitude. The following rates for ingot iron were found by Ambler and Bain at Lagos, where there is a tropical surf beach.

Approx Distance from surf (M)	Salt content of air (mg NaCl/dm <sup>2</sup> )	Rate of rusting (mm/year)
50	11.1	0.95
200	3.1	0.38
400	0.8	0.055
1300	0.2	0.04
25 miles	-	0.048

Average rates in the UK vary between 0.048 mm/year at rural sites, 0.079 mm/year at marine sites and up to 0.170 mm/year in some industrial atmospheres. In the driest atmospheres, e.g.

at Khartoum, the rate can be as low as 0.003 mm/year. Detailed results are often difficult to rationalise but in general it is clear that persistent wetness, high temperatures and contamination by strong electrolytes are responsible for the highest rates of corrosion.

Rates of rusting in impure controlled atmospheres without the complication of rain are low if the relative humidity is kept low, and remain fairly low even at 100% RH in the absence of strong electrolytes. The rate increases sharply at some RH in the region of 60-80% if the surface is contaminated with particles of sodium chloride, or ammonium sulphate, or if the atmosphere contains sulphur dioxide.

Vernon showed that there was an increase in rate at about 60% relative humidity even in pure air, and a further sharp increase at 80% in the presence of 0.01% of sulphur dioxide. The increase was larger and the corrosion product less protective if the surface was contaminated with particles of charcoal. More recent evidence suggests that the SO<sub>2</sub> content in this work was unrealistically high, and that higher RH is needed to initiate rapid corrosion with 1 ppm SO<sub>2</sub> or less. In general, it seems that the "critical" relative humidity is set by the vapour pressure of some salt hydrate in the corrosion product, and that chlorides and sulphates are the most effective corrosive agents.

The effect of moist atmospheres is to set up droplets of some strong electrolyte with the classical pattern of corrosion with a small anode in the centre of the drop acting as a source of ferrous ion and oxygen-reduction cathodes at the edges producing hydroxyl ion. Such droplets become covered by a transparent skin, presumably of ferrous hydroxide, which darkens and thickens and eventually runs through the range of hydrated ferric oxides up to Goethite and lepidocrocite. According to atmospheric conditions, these droplets may remain as discrete scabs, or may spread, or produce tracks that wander over the surface. When the rust layer is completed, the metal surface may become starved of oxygen, and it is quite common for a layer of Fe<sub>3</sub>O<sub>4</sub> to form under the hydrated rust. The presence of corrosive salts will, however, prevent this layer from becoming very protective.

Vernon showed that a carefully cleaned steel specimen would not rust even in a normal laboratory atmosphere if it was enclosed by muslin stretched over a wire frame. The protective oxide film continued to develop, and if the specimen was removed from the

enclosure after, say, a year, it would remain unaffected by dust particles, perhaps for several weeks, before spots of rust appeared.

Other metals than iron and steel show rather similar phenomena on exposure to uncontrolled atmospheres. Copper produces a green film of corrosion product containing hydrated sulphate, or carbonate, or chloride. It shows a rather similar variation of rates of corrosion with relative humidity: rates are, however, much lower than for iron and steel, and copper sheeting on roofs has survived for well over 100 years. Aluminium shows low rates of corrosion in most circumstances, but may corrode rapidly when exposed to alkaline solutions of copper salts derived from copper roofing or from wood preservatives is also deleterious. Rates of corrosion of completely exposed zinc are considerably lower than for iron and steel: the metal becomes covered with a protective layer of basic carbonate or basic sulphate. It may corrode comparatively rapidly if it is subjected to heavy condensation, or to high concentrations of sulphur dioxide. Nickel exposed to moist air containing sulphur dioxide becomes coated with a wet layer of nickel sulphate: nickel catalyses the oxidation of sulphur dioxide to sulphur trioxide. Silver is rapidly converted to the sulphide by hydrogen sulphide; this reaction is unusual in not being impeded by drying the air.

Stainless steels (i.e. steels containing at least 12% chromium) show greatly improved resistance to atmospheric corrosion. The austenitic alloys containing 8% nickel and 18% chromium are still more resistant, and alloys containing in addition 2-3% molybdenum are almost completely unaffected by weathering in industrial atmospheres.

“Weathering” or “slow-rusting” low-alloy steels containing 0.2-0.3% copper with minor additions of other elements corrode at about  $\frac{1}{3}$  to  $\frac{1}{4}$  the rate of plain steels. They have been used unprotected in some structures, but in rainy climates they tend to produce rainwater stains on other materials.

Factors conducive to rusting of iron and steel are therefore:

Sensible moisture

High RH (above 70-80%)

Salt mist

Surface contaminants (dust, sweat residues, soldering fluxes, etc)

Atmospheric contaminants (SO<sub>2</sub>, HCl, organic acids)

High temperature.

Means of prevention include:

Cleaning, and protection from dust

Drying the atmosphere, and preventing condensation

Purifying the atmosphere

Use of corrosion inhibitors

Protective coatings (wrappings, temporary protective materials, paint films, surface coatings of metals, polymers or vitreous enamels, conversion coatings)

Sacrificial coatings.

Coatings If oxygen, water and strong electrolytes are required to produce rapid corrosion, one or more of these agents may be excluded by a variety of coatings, ranging from noble metals and vitreous enamels through thick polymeric coatings (e.g. polyethylene, nylon and PVC) and paint films to paper wrappings and thin coatings of polymer or greases.

Metal films In principle, electrodeposits of metals might provide completely impervious barriers: gold, silver, nickel and chromium deposits are used both for decorative and for protective purposes. In practice, however, electrodeposits are invariably porous, and are also liable to mechanical damage. Exposure of the base metal leads to the damaging combination of small anode and large cathode, so that intense corrosion forms a bulky corrosion product in the pore, which may further damage or detach the coating. Thick deposits produced by high-temperature process (“chromising”, “calorising”, etc) are comparatively robust.

Polymer coatings A number of commercial processes are available for applying polymeric materials from either sheet or powder, and comparatively thick, robust coatings can be obtained which give protection against corrosion and mechanical damage. Like metallic barrier layers, they may, however, allow rapid corrosion if portions of the metal are exposed.

Vitreous enamels Comparatively thick layers of borosilicate glass can give excellent protection against corrosion and oxidation up to about 900 °C. Again, mechanical damage leads to failure of protection against corrosion.

Conversion coatings Chemical reaction to produce layers of corrosion-resisting sales (particularly phosphate and chromate) can produce a wide range of coatings, suitable both for enhancing the corrosion resistance of the metal or as a preparation for painting. Anodising treatments for aluminium may incorporate phosphate or chromate ion, and so-called “chemical anodising” may be used to enhance the resistance of aluminium to atmospheric attack. Chromate treatments are also used to improve the resistance of zinc and cadmium plating.

Painting Paints provide easily applied and versatile organic coatings, which can be adapted to a wide range of requirements. They do not act by excluding water and oxygen; their action depends partly on excluding strong electrolytes and partly on the fact that paint materials usually contain corrosion inhibitors, often in the form of heavy-metal organic salts. Paint films are porous, and they are liable to mechanical damage. Even if corrosive salts penetrate breaches in the paint, however, the inhibitive species will often suffice to prevent serious attack on the underlying metal. If the damaged area is too large, or the contamination too heavy, and corrosion proceeds, the cathodic alkali may soften and detach the paint film, leading to the formation of a blister which remains wet long after the rest of the surface has dried.

A successful protective system should therefore include a priming layer containing a corrosion inhibitor and preferably a layer of metal that can protect the underlying surface by sacrificial action. Steel to be painted may therefore be aluminium – or zinc-sprayed, or primers containing metallic zinc particles may be employed.

Thorough cleaning of the metal surface is extremely important, especially if it has previously been corroded. Abrasive treatment should be sufficiently severe to remove the whole of any previously formed corrosion product. It has been shown that on rusted steel, crystals of ferrous sulphate are present at the base of quite deep pits. Since paint films are permeable to

both water and oxygen, corrosion cells can be set up under the paint unless the preparation is sufficiently thorough.

Sacrificial coatings Zinc, cadmium and aluminium can protect steel by sacrificial action: being anodic with respect to iron, they hold the potential of the latter at a value at which it will not corrode. Since the corrosion product is usually highly protective, these metals build up a surface layer which limits corrosion and prolongs the life of the coating. These coatings can be used alone, or as a foundation for a paint system, and their effect can be enhanced by chemical conversion coatings.

Temporary protectives Apart from wrapping papers, which may be greased or waxed, temporary protective materials can be applied to metal surfaces to exclude moisture and dust. They may take the form of greases or slushes, pastes, thin films applied with solvents, or thick films of soft thermoplastic materials which give mechanical protection. All these types of protective may contain corrosion inhibitors (see temporary protection guide).

Design The normal considerations of design against corrosion apply to atmospheric exposure. Parts should be designed to avoid trapping moisture in hollow sections, crevices or joints, all of which may lead to locally increased time of wetness. Suitable drain-holes should be provided for hollow sections. Structures should also be designed to avoid setting up “poultices” of moisture-retaining debris, and to prevent insulating materials from becoming soaked with water. Many corrosion-inhibiting putties, slurries, pastes and impregnated tapes are available for avoiding vulnerable design features.

Fastenings should preferably be of the same material as the components they secure, or if this is impracticable, they should not be more anodic; “small cathode/large anode” is better than the reverse. It is usually better to avoid even small differences in material if possible.

Control of RH Most atmospheric corrosion can be prevented by maintaining RH below 60%. Desiccators and dehumidified stores can therefore be used for storage. In store-rooms and warehouses it is important to maintain the air temperature at a reasonable level and to avoid large variations in temperature; a fall in temperature overnight or at the weekend may lead to heavy condensation of moisture. Condensation may also occur if massive metal parts are placed while cold into a warm room if the air is not saturated at the prevailing

temperature. Stoves and gas heaters must be provided with adequate flues. The air in store cupboards may be dried by the use of desiccants or by refrigerating plant. For special purposes, including display cabinets, where it is essential to ensure immediate access to complex equipment refrigerated surfaces may be the most practical means of protection.

Packaging Packages may employ desiccants: the two most common agents are silica gel and activated alumina, both of which are non-corrosive and can be regenerated by heating. Desiccated packages need careful design to take account of the permeability of the wrapping material to water vapour, the water content of the interior of the package, and the absorptive capacity of the desiccant.

The metal parts should be carefully cleaned before packaging, to minimise damage if the package is breached or the desiccant becomes exhausted after prolonged storage. It should be remembered that some packaging materials may contain appreciable quantities of soluble chloride or sulphate, or may liberate corrosive vapours. The choice and specification of materials should take these factors into account. Maximum permissible levels are: chloride (as NaCl) 0.05%, sulphate (as sodium sulphate) 0.25%, pH of water extract 5.5 to 8.0.

Desiccated packages are often the best choice for delicate scientific equipment since this can be packed in assembled form without greasing or dismantling, and therefore without the need for cleaning and reassembly. Military stores, which may need a guaranteed life in package of many years in poor storage conditions, are often packed in elaborate desiccated containers.

Volatile Corrosion Inhibitors See guide to temporary protection.

Atmosphere control Unforeseen problems sometimes arise because variations in temperature lead to heavy condensation of moisture on steel parts, or because of some source of pollution. Troubles of this kind can often be overcome only by identifying and removing the causative agent.

Degreasing solvents and the equipment used for recovering them frequently cause outbreaks of rusting in engineering plant, since heating or chlorinated hydrocarbons may produce hydrochloric acid either in the air or in the solvent. Water extracts should be checked for acidity.

Fingerprints and traces of soldering or welding fluxes occasionally cause rusting in moist air, and precautions may be needed to prevent or remove contamination, e.g. by the use of non-corrosive fluxes.

PVC insulating materials and other polymers may produce corrosive vapours which lead to heavy attack on metal parts. Acid vapours are produced by some types of wood used in packaging. See guide to corrosion of metals by wood.

Ozone, produced by sparks from electrical contacts, may attack polymers to produce organic acids.

Sulphur compounds liberated by some synthetic rubbers may cause heavy corrosion of silver relay contacts.

Organic acids used in dyeing plastics components may be liberated during the life of the equipment and cause severe corrosion.

Traces of ammonia in the air may cause stress-corrosion cracking of brass or copper.

## **Conclusion**

It is probably true to say that satisfactory means are available for preventing all forms of atmospheric corrosion so long as the conditions of exposure are specified and considered at the design stage. It is far easier and cheaper to select materials and protective systems in advance than to clean up corroded components and apply protection after corrosion has set in. If this does become necessary, thorough cleaning is essential, and this involves removing the corroded material down to the base of the pits. It is difficult and expensive to recondition corroded components, and it is better to take precautions in advance.