structural practices

Corrosion and Protection of Structures in Marine Atmospheres

By Bop S. Phull and Robert M. Kain

Corrosion in marine environments is usually classified in terms of one or more "zones" to which a structure is exposed, i.e. atmospheric, splash-and-spray, tidal, immersion, or mud zone. Each zone has various characteristics that can influence corrosivity, form of corrosion, and rate of attack on any given material. The choice of corrosion-control methods available and applicable for each zone are dictated by a number factors. Carbon steels and low-alloy steels continue to be the most widely used materials for structural materials applications in marine environments due to their excellent mechanical properties, ease of fabrication/welding, and usually lower initial cost. However, due to their poor corrosion resistance, they typically require protection by one or more methods. This article summarizes the important factors involved in marine atmospheric corrosion of structures and describes examples several some successfully used corrosion-control methods.

Characteristics of Marine Atmospheres

In the marine atmospheric zone, solid surfaces are exposed to airborne sea salt "mist". Corrosion of susceptible materials, like unprotected carbon steel, is initiated primarily by chloride ions from the dissolved salt particles and sustained by oxygen that diffuses readily from the atmosphere, through the moisture film, to the metal surface. Corrosion is influenced by numerous factors such as the amount of salt deposition, wind speed and direction, elevation of the structure, distance from the shore (for land-based structures), degree of sheltering, time of wetness, relative humidity, metal-surface temperature, and frequency and amount of rainfall. For example, the critical relative humidity of sodium chloride (NaCl) at 70°F (20°C) is ~ 74%. This means that whenever the relative humidity of air is > 74% (common in coastal, especially tropical areas), the NaCl particles will absorb moisture from the atmosphere. This hygroscopic property of salt will result in "wetting" of metal surfaces (that are not sufficiently hot for moisture evaporation) and initiate corrosion. Since sea salt is a complex, its critical relative humidity is < 74%.

"Corrosion is influenced by numerous factors…"

Industrial and automotive emissions generated in the vicinity, or transported long-range in the atmosphere, can increase corrosivity of marine atmospheres due to deposition of additional aggressive species such as SO_x and NO_x. Bird droppings, which tend to be alkaline and contain ammonium compounds, can also contribute to accelerated corrosion, especially for aluminum and copper alloys. Runoff of copper salts can adversely affect corrosion of materials such as aluminum, zinc, and carbon steel. Dissimilar metal (i.e. galvanic corrosion) effects are not addressed in this article because of space limitations.

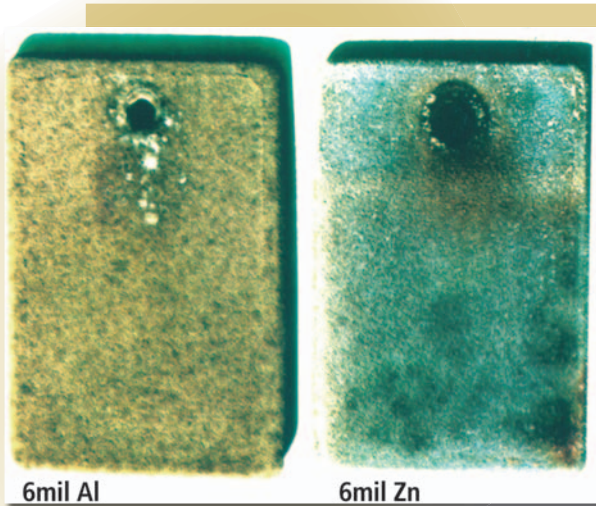

Figure 1

Corrosion Protection in Marine Atmospheric Environments

Carbon steels structures are generally protected in this zone with paint coatings. However, due to degradation in service, such coatings typically require periodic maintenance and, eventually, recoating. An alternative, but a much more effective method for corrosion control is application of thermally sprayed zinc, aluminum, or mixtures of the two, to marine structures in the field. The coating materials are generally in wire form and applied using either an arc or flame-spray gun. Thermal spraying, also known as metallizing, produces coatings with barrier (Zn and/or Al) as well as sacrificial properties (mainly Zn or Zn-rich). Exposures in the LaQue Center's marine atmospheric test site at Kure Beach, NC, have shown that 6-mil (0.006-inch) Zn, Al or Zn+Al thermal spray coatings can provide effective protection for 50+ years, as illustrated by *Figure 1*. This type of long-term data developed in real-world environments, which cannot usually be reproduced in accelerated salt-fog-type cabinet tests, has allowed selection of thermal spray coatings for many new and rehabilitation applications. There are, however, two divergent schools of thought on the importance of applying a topcoating on the thermal spray coating.

In the unprotected condition, corrosion products on carbon steel tend to develop as poorly adherent, exfoliating layers. Buildup of such corrosion products in confined spaces is sometimes referred to as packout rusting, which can generate sufficient stresses to produce warping or outright material failure. These high stresses are caused by the fact that rust on carbon steel is ~ 3 times the volume of the corroded metal. In contrast, there is a class of materials known as "weathering steels" which develop a protective rust patina in specific environments. In other words, unlike carbon steels, the corrosion products on weathering steels are dense and adherent, and capable of impeding ingress of moisture, oxygen and corrosive species. These are high-strength, low-alloy steels that offer the advantages of lighter weight, low long-term corrosion rates, and elimination of coating or maintenance painting.

However, it is very important to recognize that weathering steels cannot be used indiscriminately in marine atmospheres. Factors that are considered deleterious to good performance include high concentrations of hygroscopic salt deposits from sea spray or coastal fogs, high humidity, poor air circulation, insufficient rain washing to remove contaminants (especially salt), poor drying, and water ponding due to poor drainage. A sculpture made of CORTEN® weathering steel and exposed ~ 0.5 mile (0.8 km) from the ocean in Wrightsville Beach, NC appears to be performing very well even after 21, years as shown in *Figure 2*. The sculpture is actually only a few hundred yards from a seawater channel, but "sheltered" from direct sea spray by buildings and therefore subjected mainly to airborne salt.

"…can generate sufficient stresses to produce warping or outright material failure."

For conventional weathering steels (e.g. ASTM A709 used for bridge applications) a general rule-of-thumb is that the structure should be located > 1.25 miles (2 km) from the coast. In lieu of distance, criteria based on airborne salt content are also cited in the literature. However, divergent views indicate permissible average airborne chloride levels ranging from < 50 to < 300 mg/m^2/day. Corrosion data for a new weathering steel, containing ~ 3% nickel, developed in Japan indicate that it gives notably superior performance in coastal atmospheres compared to conventional weathering steels (whose Ni content is an order of magnitude lower). Even with effective weathering steels, the original thickness of material should include a sufficient corrosion allowance over the life of the structure.

Chloride, moisture, and oxygen migration through concrete results in corrosion of ordinary carbon steel rebar. Packout rusting of the rebar ultimately causes spalling of the surrounding concrete as shown in *Figure 3*. A number of methods have been researched and used to alleviate this problem. *Figure 4* shows a 2.1 km (~1.3 mile) long marine pier in Progreso, Yucatan (Mexico), constructed between 1937 and 1941, using Type 304 stainless steel rebar. Even after 60+ years, the stainless steel rebar is performing well. This is in dramatic contrast with a pier built in the 1960s, using unprotected carbon steel rebar, whose remnants are visible in the foreground in *Figure 3*. Even if the stainless steel incurs

Figure 2

Figure 3

Figure 4

pitting, it will not suffer from packout rusting because, unlike carbon steel, no voluminous corrosion products are produced. It should be recognized that the 300-series stainless steels do not usually remain stain free, particularly in long-term marine atmospheric exposures. However, despite staining, they generally exhibit very low corrosion rates.

"…a protective current is supplied to the steel from an anode material…"

Cathodic protection is a very effective electrochemical technique for mitigating corrosion of carbon steel rebar in concrete structures such as bridge columns and oceanfront residential/commercial building balconies. In cathodic protection, a protective current is supplied to the steel from an anode material, either by design in the original construction or as retrofit for rehabilitation of existing structures. A variety of anode materials are available commercially, e.g. thermal-sprayed zinc, conductive polymer, conductive cement, etc., that are usually applied to the exterior concrete surfaces. Anodes can also be embedded in the concrete (e.g. on bridge decks) but this is generally more expensive. DC power is used to energize the anodes. Even though Zn is more active than steel, Zn anodes have to be driven by DC power to overcome the high electrolytic resistance of the concrete. A schematic illustration is this is shown in *Figure 5*.

Figure 6 shows a 6061-T6 aluminum guard-rail on a concrete bridge over a seawater channel after 32 years of exposure. The extruded aluminum stock material and stainless steel fasteners (used for anchoring to the concrete) are in excellent condition, requiring little maintenance. A bulkhead made from the same material, without any long-term protection, would be highly susceptible to localized corrosion (pitting and crevice attack) in seawater immersion conditions, especially under biofouling, and in man-made crevices.

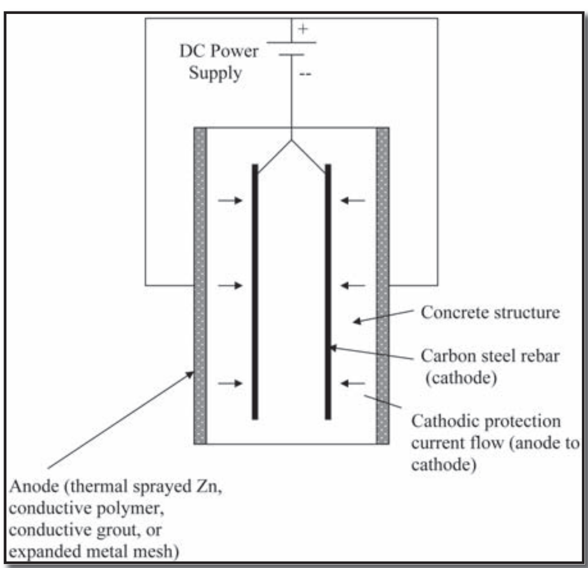

Figure 5

Conclusions

- Marine atmospheric corrosion is commonly associated with deposition of salt from sea spray, ocean fogs or airborne transport.
- Chloride is the most significant corrosive specie in the salt particles.
- Corrosion is influenced by the amount of salt on the metal surface, and related to wind speed and direction, elevation and distance of the structure from the shore, degree of sheltering, and frequency and amount of rain washing.
- Other factors that can influence corrosion include time of wetness, relative humidity, metal-surface temperature, industrial and automotive emissions, the subject metal, dissimilar metal contact, and copper runoff.

Figure 6

- Carbon steels have poor resistance in marine atmospheres and hence require protection for durability. For protection, alternatives to conventional paint coatings include thermal sprayed coatings of Zn, Al, or Zn+Al mixtures.
- Weathering steels are an attractive alternative to carbon steels because of their higher strength and preclusion of coating and maintenance painting.
- High chloride levels, frequently wet conditions, and unprotected crevices, can result in poor performance of conventional weathering steels. A 3% Ni-containing weathering steel is reportedly superior in coastal conditions than conventional weathering steels.
- Rebar in concrete can be protected by cathodic protection, or the carbon steel substituted with stainless steel rebar.
- Specific aluminum alloys can provide good long-term corrosion protection in marine atmospheres.
- Selection of materials and corrosion-control techniques should be based on cost-benefit analysis.▪

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