

CORROSION & CHLORIDES



Severe corrosion has occurred in this under-roof area of an industrial facility due to continual exposure to chloride vapour from hydrochloric acid pickling facilities.

INTRODUCTION

Soluble salts, and chlorides in particular, are one of the prime drivers of corrosion on metal products and structures. In Australia, in particular, where 90% of the population live on or near the coast, the problems associated with corrosion due to the presence of soluble salts are significant.

Australia's eastern and southern coasts, and the south-west of Western Australia, with their endless surfing beaches, are also among the world's best airborne chloride generators.

This article highlights some of the issues associated with the presence of chlorides, design parameters that can moderate their effects and protective coating systems and materials that are up to the task of protecting steelwork in high chloride environments.

While this article deals primarily with ocean generated chlorides (largely sodium chloride, a small amount of magnesium chloride and a smaller amount of calcium chloride), other chlorides can arise from industrial activity (ammonium chloride and hydrogen chloride - hydrochloric acid).

SOME BASIC CHEMISTRY

Why do chlorides give rise to aggressive corrosion of steel? A review of the chemical reactions of chloride with steel tells the story. It should be noted that these reactions may not occur in sequence and there are differences of opinion amongst corrosion chemists regarding the basic mechanisms of chloride induced corrosion.

The following reactions are shown as examples of some of the corrosion mechanisms that can occur when chlorides are present.

Iron reacts with chloride ions to form ferric chloride.
($2\text{Fe} + 6\text{Cl}^- \rightarrow 2\text{FeCl}_3 + 6\text{e}^-$)

Ferric chloride reacts with water to form ferric hydroxide and hydrochloric acid.
($\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}(\text{OH})_3 + 3\text{HCl}$)

Iron then reacts with the hydrochloric acid to form ferrous chloride and hydrogen.
($\text{Fe} + 2\text{HCl} \rightarrow \text{FeCl}_2 + \text{H}_2$)

Also, the ferric hydroxide can react with hydrogen ions from the hydrochloric acid to form iron ions and water.
($\text{Fe}(\text{OH})_3 + 3\text{H}^+ \rightarrow \text{Fe}^{3+} + 3\text{H}_2\text{O}$)

The iron ions can then react with the chloride ions (from the hydrochloric acid) to form more ferric chloride.
($\text{Fe}^{3+} + 3\text{Cl}^- \rightarrow \text{FeCl}_3$)

The ferric chloride then can react with more water to form iron oxide and more hydrochloric acid.
($2\text{FeCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Fe}_2\text{O}_3 + 6\text{HCl}$)

This may not be as bad as it looks. While hydrochloric acid can be produced in these reactions, we should remember that salt is sodium chloride, and the sodium ions and extra electrons that the chloride ions do not want have to find something to do.

Where oxygen and water are available, which is most of the time, one of the reactions that occurs is that iron reacts with oxygen, water and sodium chloride to form ferrous chloride and sodium hydroxide.
($\text{Fe} + \text{O}_2 + \text{H}_2\text{O} + 4\text{NaCl} \rightarrow 2\text{FeCl}_2 + 4\text{NaOH}$)

The sodium hydroxide, being a strong alkali, will neutralise the HCl so there is little net acid formation in the corrosion cycle. It is pits and crevices that the acid is likely to remain active in as oxygen is not available to complete the above reaction. It is logical that where chlorides penetrate under coatings, acidic regeneration would be more likely to occur for the same reason.

This means that while chloride salts are present, the corrosion reaction can be regenerating.



This galvanized guardrail has failed in the overlapping areas as a result of chlorides accumulating in the joint.

AIRBOURNE INVASION

While there are many areas, particularly in Australia, where high chloride levels exist in the ground, it is the transport of chloride aerosols that is the main driver of chloride induced corrosion in building and construction.

The CSIRO'S Division of Manufacturing and Infrastructure Technology has developed corrosivity models for Australia that are based on factors such as time of wetness, ambient temperatures and chloride deposition rates. The last of these is by far the most important in determining the corrosivity of atmospheres with respect to steel and galvanized steel.

In a joint venture with Industrial Galvanizers Corporation, this information has been developed into a Corrosion Mapping System that can be accessed through Industrial Galvanizers' web site at www.ingal.com.au.

Depending on topography, prevailing winds, wind velocity and the proximity of ocean surf, the CSIRO model can provide chloride deposition rate data for any Australian location. This model has some limitations due to the complexity of local landscapes. The presence of hills, cliffs, bays and forestry can influence the transport of chlorides, and these factors need to be assessed in conjunction with the mapping data.

In general, the transport of high levels of chlorides from ocean surf is limited to about 1 kilometre from the coast. In some areas, this may be much further. Parts of south eastern South Australia subject to the Roaring Forties winds can be subject to significant levels of chloride deposition 20 kilometres or more from the coast.



The painted steel lintels on this oceanfront apartment block have been affected by chlorides within 2 years of installation. The rough render coating accelerates the problems as it facilitates the accumulation of chlorides in this unwashed area of the structure.

Chloride deposition rates are measured in mg/m²/day. The following table is extracted from AS/NZS 2699.3:2002. *Built-in components for masonry construction Part 3: Lintels and shelf angles (durability requirements).*

Section (f) Aerosol penetration, with the highest level of airborne salt deposited at the exterior of the masonry, as follows:

R0	nil mg/m ² /day
R1	10 mg/m ² /day
R2	20 mg/m ² /day
R3	60 mg/m ² /day
R4	300 mg/m ² /day
R5	See Note 2

NOTES

- 1. The extent of aerosol salt penetration depends largely on the distance from the coast; however, in practice, microclimatic effects may distort otherwise normal climatic patterns by many kilometres and should always be considered. The atmospheric salt deposition on the exterior face of the wall is double that normally experienced on the inner face. The values used in Appendix A reflect this situation.
- 2. The R5 durability classification refers to specific corrosive environments outside the above criteria. Where industrial fall-out, bacteria, chemicals or other environmental conditions exist, it is necessary for the manufacturer to test all unique coatings and materials to confirm their resistance to the particular environment for the expected life of the structure. Because such an environment cannot be specified in this document, suitable coating systems cannot be recommended.

Chloride ions are the most stable form of the element, chlorine. They do not deteriorate over time. It is this characteristic that can cause much more serious chloride induced corrosion of steel than the salt deposition data would indicate at face value.

While chlorides are extremely soluble, they obviously need water to dissolve them away. In sheltered areas of structures – lintels, under-roof and under-floor areas, facades, eaves, etc – chlorides accumulate over time if they are not washed off.

When the chloride aerosol is deposited on a sheltered surface, its moisture evaporates, leaving the salt behind. On steel surfaces, as soon as the steel's temperature drops to the Dew Point, the film of moisture dissolves the salt and forms an ever more concentrated salt solution.

In this way, high levels of chlorides can persist for long periods of time unless the sheltered areas of the structures can be washed down.

For this reason, corrosion stress in sheltered areas subject to any chloride deposition may be 2-5 times higher than adjacent exposed structures.

DESIGN FOR DEFENCE

Structures that are likely to be subject to chloride deposition can be better protected from premature chloride induced corrosion by considering detailed design features and ensuring that appropriate materials and coatings are used.

On the eastern seaboard of Australia, the eastern facing sections of structures are those at highest risk. Minimising exposure of steel components in sheltered sections of the structure that face the chloride source will significantly reduce corrosion stress.

The provision of barriers to prevent ingress of chlorides in the underside of roofs or suspended floors will also make a significant contribution to durability. In very severe marine conditions (ocean front), alternative materials (stainless steel, timber, concrete lintels) should be considered.

Most paint coatings used for residential or commercial coating applications may not be appropriate for use in areas subject to chloride deposition. This applies particularly to acrylic water-based house paints. Their use over steel components may actually accelerate corrosion problems if chlorides are present.

There are high-performance paint systems available from all the major paint manufacturers that can deliver marine-grade levels of protection to the underlying steelwork. It is unlikely that these paint system components will be available from your corner hardware store.

Metallic coatings such as hot dip galvanizing are specified for exposure conditions to Class R3 in AS/NZS 2699.3. In R4 environments, additional coatings should be applied over the hot dip galvanized steel. These industrial protective coatings are nominated generically in AS/NZS 2699.3.

Care should be exercised in marine exposures with pre-galvanized products that are commonly available as in-situ formwork for floors and decks, and as light structural hollow sections. These continuously galvanized products have relatively thin zinc (galvanized) coatings that are typically 20-30 microns in thickness, and they have no coating on their cut edges as they are galvanized prior to fabrication.

These types of products are almost always used in sheltered parts of the structure and providing them with adequate additional coating protection will ensure that the durability of the structure will not be prematurely compromised.



This building awning (shown top right) on the NSW North Coast is 2 kilometres from the ocean. Its south easterly orientation has resulted in its accumulating chloride aerosols under the awning. The photo above shows the chloride induced corrosion after less than 2 year. The upper side of the structure is still in excellent condition.

CHLORIDE CLEANLINESS

Chlorides are so persistent when they have contaminated a surface that precautions need to be taken when undertaking maintenance of steel structures to ensure that chlorides do not remain on the surface to be repainted.

It is well established that conventional abrasive blasting is not effective in removing chlorides from contaminated surfaces. AS 3894.6 *Determination of residual contaminants* contains a procedure for determining the level of residual chlorides on surfaces.

There are a number of methods of removing chlorides from surfaces to be painted. Wet abrasive blasting or dry blasting followed by high pressure water blasting is perhaps most commonly specified. There are some proprietary products that are designed to neutralise chlorides and the performance of these will be a matter for the suppliers to verify.

SUMMARY

With the dramatic reduction in industrial pollutants in the developed world, sulfates and nitrates are no longer major participants in salt-induced corrosion. The corrosivity associated with major heavy industries has fallen by over 95% in Europe over the past 25 years, and while it has not been as significant in Australia, environmental management system throughout the country have seen corrosivity drop to background levels in most industrial areas.

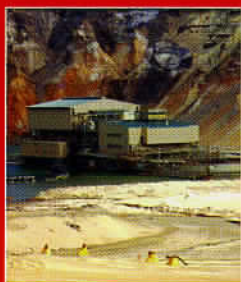
This will never be the case with chlorides however, and they will continue to be a major cause of steel deterioration that will need careful consideration in the design and construction of infrastructure and buildings wherever steel is used within the ocean surf zone of Australia's coast.

The cost of remediation due to the taking of shortcuts in dealing with protecting steelwork in structures exposed to chlorides, should premature corrosion occur, will be at least an order of magnitude higher than the any initial savings that might be made through not using the best available materials and coatings in the first place.



These galvanized steel salmon pens in Tasmania are subject to extreme marine conditions. While the grating deck that is constantly wet shows signs of corrosion, the handrails that are regularly rain-washed and out of the splash zone remain in good condition.

CORROSION MANAGEMENT

**Cover**

The Consolidated Rutile's Yarraman mine has created its own spectacular backdrop on Stradbroke Island and is the subject of a case history study on coating performance.

Photography: Trevor Murphy

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CORROSION MANAGEMENT is published for those interested in the specification, application and performance of protective coating systems.

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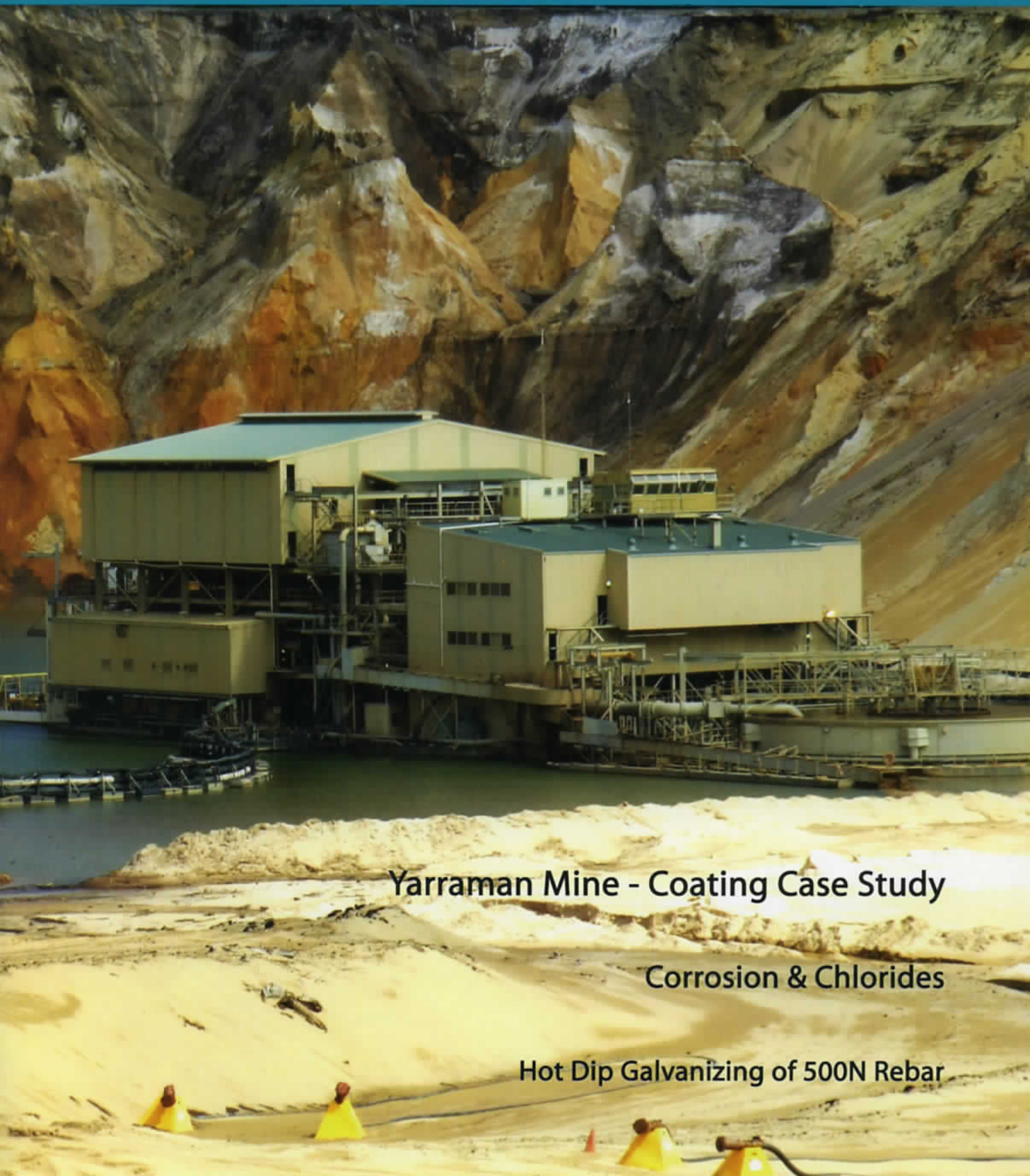
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