EVIDENCE FOR MICROBIOLOGICAL INFLUENCED LONGER-TERM CORROSION IN TIDAL AND COASTAL ATMOSPHERIC CORROSION OF STEEL ELEMENTS

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SUMMARY: This paper demonstrates recent evidence that bacteria are involved in the longer-term corrosion of mild steel in the tidal zone and in marine atmospheres. Bacteria are often associated with marine immersion corrosion but there appears to have been little attempt previously to associate bacterial activity with atmospheric corrosion in the coastal zone. The present paper describes observations of rust conditions on steel strips and coupons exposed in field tests conducted at several locations on the Eastern Australian seaboard. Careful examination revealed rust patterns and corrosion surface characteristics that could not have been caused by conventional oxidation with oxygen as the ultimate electron receptor. The patterns are consistent, however, with the activity of the sulphate-reducing bacteria in which sulphur acts as the electron receptor. Importantly, the most severe corrosion losses occurred away from coupon edges and revealed shiny, heavily pitted metal surfaces. There is evidence also that ferrous oxidizing bacteria are involved. These observations are consistent with the corrosion loss models previously proposed for longer-term immersion corrosion. An important aspect is that the evidence reported herein was obtained only as a result of the investigators expecting to find it, and then exercising unusual care in examining rusts and corroded surfaces.

Keywords: atmospheric, tidal, corrosion, microbiology, SRB, IRB, pitting

1 INTRODUCTION

It is now well-established that bacteria are involved in the corrosion of steels continuously immersed in natural seawater (i), and that this involvement occurs primarily during two phases (i) in the early exposure period when bacteria are harbored in sub- and anoxic niches in the biofilm and (ii) later when sufficient corrosion product has developed on the corrosion surface to provide appropriate local environmental conditions for bacterial metabolism, see Figure 1 (ii). The bacteria that have been of most interest to date are the sulphate reducing bacteria (SRB) that require (semi-continuous) anoxic environments. However, as will be seen, other bacteria that require merely sub-oxic conditions also are of interest.

Recently it was shown that the data for corrosion loss for marine tidal and coastal atmospheric exposure zones in many cases may be interpreted to have the same general features as the immersion loss curve shown in Figure 1. These curves all show the distinctive early decline in corrosion rate, followed by a later increase and then a long-term relatively low rate of corrosion. The similarity in the corrosion loss behaviour led to the proposition that bacteria also may be involved in the marine corrosion of steel exposed to tidal and to coastal atmospheric conditions (iii). For tidal corrosion at least, this has been suspected for some time, with the presence of SRB being associated with the corrosion of steel sheet piling in harbours (iv, v, vi, vii). However, the precise mechanisms involved have not yet been fully clarified.
The possibility of bacterial involvement in atmospheric corrosion appears not previously to have been considered in the corrosion literature. One exception is the work of Santana Rodriquez et al. (viii) who observed sulphate reducing bacteria (SRB) on surfaces exposed to marine coastal atmospheres. They proposed that this was linked to the presence of certain rust types found on corroded steel surfaces. In particular they observed sulphated Green Rust GR2(SO_4), akageneite (β-FeOOH) and magnetite (Fe_3O_4) as major rust constituents after one and two years exposure (ix). These rusts have been associated with SRB activity under marine immersion corrosion conditions (iv, v) but also can be generated abiotically (x, xi). It follows that the mere presence of these rusts cannot be taken as proof that bacterial activity contributed to the corrosion process. Moreover, the presence of bacteria (even in large numbers) also does not provide proof that they were actually involved. These qualifications are important for understanding the research approach taken in the present work.

Confining remarks for the present just to SRB, it is important to note that they are known to be ubiquitous in nature and that they occur in seawater and elsewhere. Most research for marine corrosion conditions has focused on the biofilm that forms almost immediately after first immersion and that eventually provides the anoxic niches suitable for the largely anaerobic metabolism of SRB (xii, xiii). The later provides the principal pathway now generally recognized as responsible for attack on steel (and other materials). The active metabolic product of SRB is hydrogen sulphide that, simply put, attacks the steel to form FeS. This generates highly acidic conditions at the steel surface and leaves a characteristic bright steel corroded surface. Since the pH tolerance range of the SRB involved typically is circum-neutral, they inhabit biofilm and corrosion product niches sufficiently far removed from the actively corroding surface.

Identification of FeS is possible in various ways. However, a key physical characteristic is that it is not adherent. This is in sharp contrast with oxidation products such as magnetite and iron oxi-hydroxides typical of conventional oxidation, both of which are very difficult to remove from the underlying metal. Another feature of corrosion by H_2S is the characteristic bright metal surface and often a characteristic pitting pattern revealed when the rusts are removed as shown in controlled laboratory experiments (xiv).

In this paper some observations are reported that provide support to the notion that bacteria are involved in a significant way in the corrosion of steel in marine atmospheres. As will be seen, they include the SRB and also the iron-related bacteria (IOB).

2 EXPERIMENTAL PROCEDURE

Bare steel coupons (100x50x3mm) and vertical steel strips (50x3mm cross-section) have been exposed in tidal and atmospheric zones for several years at several locations along the east coast of Australia. In each case the steel was electrically insulated from the support frames. The coupons and strips were recovered at various intervals in time, closely examined immediately on recovery. The rusts were carefully removed where possible although sometimes considerable mechanical impact or force was required. The surfaces thus revealed were photographed immediately. Subsequent examination included physical inspection, SEM, EDS and XRD analysis as well as optical microscopy. Samples of rust and bacterial swabs were taken for culturing purposes. For this commercial test kits, Sani Check for SRB and BART-IRB for iron-related bacteria (IRB) were used. The test conditions prescribed for these kits were followed, as much as was possible when dealing with rusts, including maintenance of sterile conditions.

Subsequently all the coupons were cleaned and weighed to determine mass-loss. For this purpose the strips were cut to a precise length of 100mm prior to weighing. Details of the corrosion losses as a function of time will be reported in due course.
3 OBSERVATIONS FOR ATMOSPHERIC CONDITIONS

Many observations were obtained in the course of the project. Only a small typical sample is given here. Figure 2a shows an edge view of two coupons recovered from the Belmont Beach site near Newcastle held together using one of the nylon fixing bolts. The laminations of the rusts are clearly visible. The rusts were removed simply by dropping the coupons on the concrete floor, revealing bright metallic surfaces away from the edges of the coupons (Figure 2b). The characteristic pitting of the bright metal surface is shown more clearly on a coupon recovered at a later time (Figure 3). As noted above, both the bright steel surface and the pitting of that surface are characteristic of attack by H₂S generated by SRB. It is noteworthy that this pitting is very closely spaced.

![Figure 2a](image1.png)

![Figure 2b](image2.png)

Figure 2 (a) Atmospheric coupons recovered from the Belmont Beach site after 14 months exposure, held together for photographing by the typical nylon bolt used to secure coupons. (b) Surfaces revealed by dropping the coupons on the concrete floor to remove all loose rusts. The bright metal surfaces are clearly visible. There is also some remnant rust. Note also the dark grey corrosion product that appears to have formed over the bright steel.

![Figure 3](image3.png)

Figure 3 Characteristic severe pitting of the bright steel surface revealed upon removal of rust layers by mechanical force.

Coupons recovered after some 3 years exposure revealed substantial corrosion over the whole surface, as might be expected, including at the edges. However, the most severe corrosion occurred in the central region of the coupons (Figure 4). This is consistent with the activity of bacteria such as SRB that require (semi-continuous) anoxic conditions and also with the activity of iron oxidizing bacteria that require sub-oxic conditions.
Figure 4 Typical coupon (100x50x3mm) recovered from Belmont Beach after standard acid cleaning procedures to remove all rusts.

Note the severe corrosion towards the centre of the coupon compared with the corrosion that occurred at the edges, where high free energy conditions ought to have lead to the most severe corrosion. The 2mm diameter holes at left, lower left and upper right are drilled identification holes. The large hole at centre left is the fixing hole. Note that some superficial surface corrosion occurred in the (short) time between cleaning the coupon and photographing it.

Corrosion in the tropics is known to occur at a greater rate. This can be seen in Figure 5 showing the remnants of 3 atmospheric corrosion coupons exposed at Belmont Beach for 3 years.

Figure 5 Views of three different corrosion coupons exposed for 3 years at Belmont Beach.

The remaining steel is very thin. Evidently most corrosion attack occurred generally away from the edges. The coupon on the right shows significant isolated spots of corrosion in the interior as well as metal loss at the top and bottom of the coupon but not at the left and right edges.

For XRD analysis the rusts of most interest were those that were located close to the corroding surface. These proved difficult to recover in sufficient quantity and invariably were mixed with rusts further out, thereby including also conventional iron oxihydroxides. This evident in the results, shown in Table 1. It shows that rusts conventionally associated with bacterial activity were present, including Green Rusts. SEM and EDS examinations were performed but did not reveal noteworthy results.
Table 1 – Summary of rust phases by XRD analysis

<table>
<thead>
<tr>
<th>Description</th>
<th>Dominant</th>
<th>Semi-dominant</th>
<th>Minor</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green rust (ex Townsville)</td>
<td>Ferrous chloride hydroxide</td>
<td>Green Rust GR1(\text{Cl}^-)</td>
<td>Green Rust GR1(\text{CO}_3^{2-}) FeCl_2·4H_2O</td>
</tr>
<tr>
<td></td>
<td>\text{Fe}_2(\text{OH})_3·\text{Cl}</td>
<td></td>
<td>Lepidocrocite \gamma-\text{FeOOH} Goethite \alpha-\text{FeOOH}</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Iron oxide chloride \text{FeOCl} Iron sulphide FeS</td>
</tr>
<tr>
<td>Red-brown rust (remaining on metal surface)</td>
<td>Sodium chloride NaCl</td>
<td>concerts \gamma-\text{FeOOH}</td>
<td>Akaganeite \beta-\text{FeOOH}, Cl</td>
</tr>
<tr>
<td>Rust sample</td>
<td>Lepidocrocite \gamma-\text{FeOOH}</td>
<td>Green Rust GR1(\text{CO}_3^{2-}) Goethite \alpha-\text{FeOOH}</td>
<td>Aragonite \text{CaCO}_3 Sodium chloride NaCl</td>
</tr>
<tr>
<td>Crushed rust</td>
<td>Lepidocrocite \gamma-\text{FeOOH}</td>
<td>Goethite \alpha-\text{FeOOH} Magnetite \text{Fe}_3\text{O}_4</td>
<td>Akaganeite \beta-\text{FeOOH}, Cl Green Rust 1 \text{Fe(OH,Cl)}_{2.55}</td>
</tr>
</tbody>
</table>

4 OBSERVATIONS FOR TIDAL CONDITIONS

Generally similar observations to those reported above were obtained for steel exposed in the tidal zone, but the localized attack appeared to be more severe. Figure 6 shows three different lengths each about 200mm long of 50mm wide mild steel strip, after the adherent rusts were removed. The pattern in each case is the same – severe localized corrosion, away from the edges of the metal, in many cases with perforation and spaced at roughly regular intervals of about 50mm. Figures 6(a) and (b) show the severely corroded regions being black or very dark grey in colour, with a small area of bright steel visible at lower centre in Figure 6(a). Similarly there are several very small spots of bright steel visible at about centre of Figure 6(b). All are within the highly corroded regions.

![Figure 6(a)](image1)

![Figure 6(b)](image2)

**Figure 6** Severely corroded areas with various corrosion products and small areas of bright steel, spaced along steel strip and all located away from its edges.

Enlargement of the small spots of bright steel seen in Figure 6(b) shows them (Figure 7) to be pitted with the characteristic closely spaced, roughly hemispherical pits also seen in the atmospheric coupons (e.g. Figure 3). Moreover, it appears that both the dark grey and the dark red-brown corrosion product have the same or very similar pitting topography, suggesting they were formed subsequently to the pitted topography.
Figure 7 Enlargement of areas of bright steel showing severe pitting and apparent overlay of subsequent dark grey and red-brown corrosion product, suggesting oxidation after corrosion under anoxic conditions.

A rather larger region of bright steel is seen in Figure 8. It shows, very clearly, the characteristic pitting seen earlier and also the dark grey corrosion product overlying part of the surface topography in the clearly defined area of severe corrosion. Both to the left and the right of this area the steel plate has perforated. Again the perforations and the severely corroded regions are all well away from the edges of the steel strip.

Figure 8 Larger area of heavily pitted bright steel with evidence of dark grey corrosion product with similar topography of the bright steel surface suggesting its later formation.

Finally, Figure 9a shows a much larger bright steel pitted region, again located well away from the edges of the steel strip. A close-up view (Figure 9b) shows dark grey material around the edges of the bright steel, particularly at the edges of the depression forming the severely corroded region. It also shows the severe pitting within that region. The dark grey material is most likely magnetite although this could not be confirmed by XRD because of the thinness of the layers.
Figure 9 Large area of bright metal surface with characteristic pitting and dark grey corrosion product around its edges.

5 BACTERIAL CULTURING TESTS

Although DNA testing for the presence of bacteria is in progress in our laboratory, the present observations were considered only against standard culturing tests for bacteria. The procedures are described in Section 2. The results were quite consistent across all samples tested. While IRB testing proved to be positive for all cases tested, SRB testing was positive in only some cases, despite the characteristic corrosion topography and rust compositions consistent with SRB activity. This low rate of success with culture testing was not unexpected since it is well-known because of bacterial diversity and the need to grow cultures in an artificial environment, only some 1-10% of organisms can be retrieved in this way (xiii). This has been a major problem also for other research areas and for this reason DNA studies are being explored in the present project. These will be reported on in due course.

6 DISCUSSION

Whereas most studies dealing with bacteria-induced corrosion consider the influence of bacteria residing in biofilms, the present project has been much more concerned with the effect of bacterial activity when the steel had already corroded a considerable amount, and the bacteria of interest were residing in the rust layers. This is a rather different situation, and demands the presence of relevant bacteria in the rust layers. The evidence provided both by the recognized laboratory tests (xiv) and by the above photographs suggests the presence of SRB (and by inference perhaps also other bacteria) on the surfaces of corroding steels, with seawater aerosols providing the bacteria. For bacterial activity, appropriate environmental conditions must exist and nutrients and energy must be available. Previous studies have shown that this can occur within biofilms (xv). The present study has focused on the longer-term exposure of steels and for this situation the metabolism of bacteria of interest is that which can occur when substantial rust layers have already been established. This is similar to the situation for immersion corrosion (ii) and for this the basic theory for the effect of bacterial metabolitic attack on the steel and the role of nutrients has been described previously in the context of SRB. It is considered likely that for tidal and coastal atmospheric corrosion essentially parallel theory will hold, a matter that will be considered in due course.

Some direct SEM observations of SRB and IRB were made for shorter-term exposures in the present study but it proved difficult to make similar observations for longer-term exposures. The reasons for this are being explored. However, it now seems likely that the problem is two-fold - the relatively quick die-off, particularly of SRB, once exposed to air and under ‘stationary conditions’ as would occur once bacteria are removed from their natural habitat (xvi) and the extremely high resolution microscopy required to observe the decomposition products of dead bacteria. The latter problem can be side-stepped by the use of DNA analysis. To tackle the first problem will require the design and application of an anaerobic chamber equipped with tools to break-open the rusts. Despite these deficiencies, the present observations provide sufficient evidence of the presence of bacteria in the rust layers for longer exposures of coupons, thereby providing support for the notion that bacterial activity is involved in phases 3 and 4 of the model (Figure 1).

Both SRB and IRB appear to be involved. The former was demonstrated through comparison to topography and corrosion surface characteristics and the latter at least by IRB culturing. But the case for IRB involvement, and in particular ferrous oxidizing bacteria, also is strong. As shown in Table 1 there is strong evidence of magnetite (Fe₃O₄) and akageneite (β-FeOOH) in the rusts, as well as Green Rusts. Although both may be formed abiotically, there is considerable evidence from a variety of sources that they are also formed biotically (xi). This is consistent with the culturing observations. It is also consistent with Figures 2b and 6-9 that show the apparent overlaying of thin dark rusts and also dark red-brown rusts over the
topography provided by H2S corrosion resulting from SRB activity. The most likely scenario is that these dark rusts were formed under widespread sub-oxic conditions as the exterior rust layers developed, with some localized areas developing anoxic conditions, largely as a result of the heterogenic nature of the overlying rusts and the greater likelihood of anoxic conditions away from coupon or strip edges. There are also the possible influences of patchiness in bacterial settlement and cultivation and in heterogeneity in nutrient deposition and diffusion through the rust layers.

Finally, it is noted that both the pitting and the bright steel on which it occurs are inconsistent with conventional notions of metal corrosion with oxygen as the electron acceptor (i.e. conventional oxidation). Pitting under these conditions is known to involve an anode (the pit) surrounded by a sizable cathodic region, thereby producing individual, somewhat isolated pits. This is not what is observed here – in fact the pitting seen in the above figures has close spacing and is similar to the pitting seen also under immersion conditions and previously associated with corrosion under localized anoxic conditions and SRB activity (joint paper on topography). Also, conventional oxidation of steel produces hard adherent rusts immediately adjacent to the metal, not the loose, easily removed rusts found in the present study. Moreover, the repeated evidence of the occurrence of bright steel under the rusts is completely inconsistent with conventional oxidation. On the contrary, it is consistent with laboratory observations under anoxic conditions involving controlled bacterial additions and nutrients (xiv). Remarkably, despite decades of atmospheric corrosion research and experimentation with coupons, in many parts of the world, observations similar to those given herein appear not previously to have been recorded. The present observations arose only because the Authors suspected bacterial involvement and set out to specifically look for it.

7 CONCLUSIONS

From the observations presented herein it may be concluded that

1. for steel exposed to tidal and to atmospheric marine corrosion conditions the most severe corrosion tended to occur in the interior regions of coupon or strips,
2. the severe corroded regions showed severe, closely spaced, pitting of relatively uniform size with often substantial areas of bright steel,
3. the pitting pattern and bright steel is consistent with SRB activity under anaerobic conditions, and
4. culturing tests also revealed the involvement of iron-related bacteria, most probably ferrous oxidizing bacteria.

These observations are considered to provide the first conclusive proof that microbiological processes can be involved in longer-term marine atmospheric corrosion and in corrosion in the tidal zone.

8 ACKNOWLEDGEMENTS

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9 REFERENCES


