THE EFFECT OF SEAWATER STERILISATION ON THE CORROSION OF MILD STEEL

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SUMMARY: Initiation of pitting of mild steel in seawater usually is attributed to anode-cathode reactions set up by the small manganese sulphide (MnS) inclusions present in most steels. On the other hand there is now considerable evidence that microbiological factors are involved in the early corrosion of mild steel in natural seawater. Presented herein are the results of a two year investigation of whether microbiological factors are likely to have a significant role in the pitting of mild steel exposed to seawater. In the experiment, natural seawater was pumped from a Port Stephens tributary and split into two streams. One stream flowed slowly through a tank in which 25 mm x 25 mm polished steel coupons were suspended and was then released back to the estuary. The second stream was passed through a series of filters and sterilized using ultra-violet (UV) lamps prior to entering a similar but sealed tank, also fitted with UV sterilization, where identical coupons were suspended, before being returned to the estuary. Coupons were removed at various time intervals and examined both visually and using a scanning electron microscope (SEM). In all cases the metal surfaces show a considerable difference in topography between those recovered from natural and those from sterilised seawater. Since the only significant difference between the exposure conditions was the removal of living microbiological material it is concluded that microbiological factors are responsible, directly or indirectly, for the more severe pitting observed on the coupons exposed to natural seawater.

Keywords: Steel, Seawater, Sterile seawater, Microbiological influence, Pitting.

1. INTRODUCTION

Initiation of pitting of mild steel in seawater usually is attributed to anode-cathode reactions set up by the small manganese sulphide (MnS) inclusions present in most steels (Wraglen 1974). More recently it has been proposed that the region immediately surrounding the MnS inclusion rather than the inclusion itself is responsible (e.g. Schmuki et al. 2005). Despite extensive research the precise electro-chemical, transport and diffusion mechanisms involved in the nucleation, initiation and growth of pits are still not completely understood (Szklarska-Smialowska 1986). Nevertheless, it is clear from the empirical corrosion literature that pits appear almost immediately upon immersion of a steel surface in seawater and that they grow quickly in depth to up to 100 microns (Butler et al. 1972). The topography of the surface changes considerably with time and includes pit growth both in depth and in area, with subsequent pit coalescence and eventually the initiation of newer pitting (Jeffrey and Melchers 2007).

It is now well-established that upon first immersion of a steel surface in natural seawater it is soon covered by a thin biofilm that harbours micro-organisms (Costerton 1992). The biofilm and the micro-organisms are recognized to have an interaction with the corrosion process (Beech 2004). This has been included in mathematical models for uniform corrosion as well as models for maximum pit depth (Melchers and Jeffrey 2008). The models have been found to be consistent with bacterial corrosion observations (Malard et al. 2008) as well as empirical studies of influences on longer term corrosion loss and pit depth (Melchers 2008). The first question that arises is whether bacteria are involved also in very early pitting, that is within a short period of time after a steel surface is first exposed to natural seawater. The second question is whether any such process continues with time. The present paper is concerned with these two issues.

Although a variety of techniques exist to study bacteria in biofilms (Biocorys 2007), it was considered highly desirable to interfere as little as possible with the biofilm and bacterial processes that occur on surfaces exposed to natural environments. It was also recognized that detailed observation of individual pit development under natural conditions would be difficult experimentally, in part also because it is well-known that the location of individual pits cannot be predicted with any degree of accuracy, even for small coupons or isolated surface areas. Given these factors, it was
considered that the most appropriate approach would be simply a comparison of the surface topography resulting from exposure to natural seawater and that resulting from exposure to seawater for which bacterial activity was in some way controlled (Melchers and Jeffrey 2008). While in principle the latter could be achieved by control over the rate of metabolism through control over nutrients essential for bacterial activity and survival, a more practical approach, consistent with earlier work, was considered to be the use of seawater from which all bacterial activity had been removed, preferably by killing all bacteria. Chemical or autoclaving means to do this were deemed unsuitable since these are likely to alter the normal chemical and physical characteristics of the seawater. In previous studies millipore filtering had been used to produce abiotic seawater (e.g. Dexter and Gao 1988) for use in laboratory experiments, but the volumes of water produced were very small. While this might be adequate for small scale, short-term testing in small containers, for the present work it was considered highly desirable to replicate field conditions as closely as possible, both for the natural exposures and for the exposures with controlled bacterial activity, and this precluded small test vessels and short-term tests. Increasingly it has become apparent that laboratory experiments that do not closely replicate field conditions may produce very misleading results (Lee et al. 2009). Closely realistic natural exposure conditions were achieved by using two parallel streams of low velocity seawater, one natural and one natural without bacterial activity, both sourced continuously from the one body of natural coastal seawater. The removal of bacterial activity in the second stream was achieved through the use of filtration and ultraviolet radiation to give a ‘sterile’ seawater.

The next section describes the experimental equipment and the conduct of the experiment. Several SEM images obtained for the natural and the sterile seawater streams at various exposure periods are given next. These are then discussed in the context of earlier observations of the changing topography of pitted steel surfaces in natural seawater exposures. As will be seen, these images present clear evidence that the topography of the steel surface is very different for natural and for sterile seawater, almost immediately from first exposure. Since the only difference between the two water streams is the presence of bacteria, it is reasonable to conclude that this is the cause of the difference in surface topography. The closing sections of this paper discuss the practical implications of this observations and conclusion.

2. EXPERIMENTAL OBSERVATIONS

A test rig was established in a specially constructed field laboratory within the Port Stephens Fisheries Centre site at Taylors Beach, located on a tributary of Port Stephens, a substantial coastal water body, approximately 150 kilometres north of Sydney. Earlier experiments conducted there have shown that the seawater at this location is similar to Pacific Ocean water in the adjacent coastal regions (Table 1). Seawater for the experiment was taken-off from a pumped supply of fresh seawater used by the Fisheries Centre for their fish breeding programme. The water was split into two streams. One stream went directly into a tank in which small steel coupons were suspended (see below). This was the ‘natural seawater’ stream in which the raw seawater was returned directly to the estuary after passing through the tank. The second stream was passed through a series of filters and sterilised using ultra-violet (UV) lamps prior to entering a similar but sealed tank, fitted with UV sterilization lamps as well as with coupons, before being returned to the estuary. This was the sterilised seawater stream. In both streams the water velocity was kept very low (< 1mm/sec) to ensure there were no velocity effects that would interfere with the desired observations. The filtration and sterilisation process consisted of settling tanks, primary and secondary filters, a battery of 20, 50 and 5 micron filter bags and finally through two ultra-violet light sterilising units. There was also a UV lamp in the tank. Figure 1 shows a schematic drawing of the test rig.

<table>
<thead>
<tr>
<th>Ammonia mg/l</th>
<th>Nitrate mg/l</th>
<th>Nitrite mg/l</th>
<th>Total P mg/l</th>
<th>Sulphate mg/l</th>
<th>Salinity ppt</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt; 0.05 – 0.080</td>
<td>0.017 – 0.034</td>
<td>&lt; 0.003- 0.011</td>
<td>&lt; 003 – 0.07</td>
<td>1600 - 2750</td>
<td>25.7 – 31.3</td>
</tr>
</tbody>
</table>

Figure 1 Schematic flowchart for natural and sterilised seawater trial at Taylors Beach.
The tanks in which the coupons were exposed were 200 litre fibreglass rectangular units with uniformly decreasing depth allowing water to discharge over a spillway to the drain. Water entered both tanks via an underflow weir to minimise ‘dead spots’. The sterilised tank had an airtight lid and the raw water unit had a similar but not airtight fitted cover.

The area available on the stage of the scanning electron microscope determined coupon size. The coupons were 25 mm x 25 mm x 1.3 mm thick and laser cut from mild steel plate mirror polished on both sides. The coupons were stored in a dessicator and sterilised with alcohol prior to exposure.

One coupon was recovered from each of the natural seawater and the sterile seawater tanks after 1, 4, 7, 50, 100, 135, 190, 280, 260 and 554 days. Upon recovery coupons were examined externally and the nature of the rust formation noted. They were then cleaned; typically a strong stream of water was sufficient to remove the rust layer back to bright steel. In cases where the rust layer was adhesive coupons were cleaned with dilute inhibited hydrochloric acid then rinsed in water and then alcohol before drying. All coupons were gold coated prior to being examined in the SEM.

The efficacy of the sterilization system was monitored at regular intervals by taking samples from the water stream immediately after various filtration and ultra-violet units. Samples were taken also from the sterile seawater tank. The samples were tested for sulphate reducing bacteria (SRB) spores and iron related bacteria (IRB) using commercial test kits. Over the 2 year test period no evidence of SRB or IRB was found in the sterile seawater tank. However, evidence of bacterial spores was found in the natural seawater tank on a regular basis. Water temperature in both tanks was monitored over a one-year period, as summarized in Table 2. The temperature in the sterile tank was on average 2° warmer than in the raw water tank. This is attributed to the water passing over ultra-violet lights as well as the UV light in the roof of the tank.

<table>
<thead>
<tr>
<th>Water temperature °C</th>
<th>Minimum</th>
<th>Maximum</th>
<th>Average</th>
<th>Typical range</th>
<th>Diurnal range</th>
</tr>
</thead>
<tbody>
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<td>33.6</td>
<td>21.5</td>
<td>1.0°-2.5 °</td>
<td></td>
</tr>
<tr>
<td>Raw Water tank</td>
<td>10.3</td>
<td>31.3</td>
<td>19.5</td>
<td>1.0°-2.0 °</td>
<td></td>
</tr>
</tbody>
</table>

3. EXPERIMENTAL RESULTS

The following gives a sequence of SEM images, photographs and descriptions of the observations made on the various coupons recovered during the course of the experiment.

3.1 1 Day

After one day the coupons had distinct anode-cathode regions where some regions of the surface had oxidised whilst other regions appeared to be unaffected. Similar behaviour has been observed previously (Jeffrey and Melchers 2007). There was some light-coloured, adherent rust that had to be removed with a very short (< 1 min) soak in acid. SEM images of the typical surface of coupons recovered after one day of immersion are given in Figures 2 and 3. These show that visible pitting occurred on both coupons within a period 24 hours exposure, entirely consistent with much earlier observations by Butler et al. (1972) who found pits of depth approaching 100 microns within days of exposure to seawater. Although Figures 2 and 3 show only a small part of the overall coupon surface, it was very clear that there were a greater number of pits for the natural seawater coupon. Figure 3 appears to show some steps or “benches” within the pit but this is not evident in Figure 2.

Figure 2 Mild steel surface of after 24 hours exposure in natural seawater showing a multitude of pits approaching 100 microns in diameter. Bar = 100 μm.

Figure 3 Mild steel surface of after 24 hours exposure in sterile seawater showing a pit already larger than 100 microns in diameter. Bar = 100 μm.
3.2 4 Days

After four days the pitting regime on both coupons was similar to that observed on the first day, however some perhaps unusual surface patterns were observed. Figure 4 is a 10 x higher magnification than Figure 2 but shows inchoate doughnut-like forms on an un-pitted area of the coupon exposed to natural seawater. Larger versions of this phenomenon have been observed previously by the authors on coupons in seawater immersion conditions (Jeffrey and Melchers 2003).

Figure 5 shows a different set of surface patterns, surrounding a pit on the surface of the coupon removed from sterile seawater. They may be described as distorted tori, many of them apparently ‘filled’, and irregular shaped flat formations, all of which have varying degrees of what might best be described as “mud-cracking”.

The cause of these surface patterns is not understood. They are not an oxide or biological feature as the samples have been acid cleaned immediately prior to SEM preparation. Energy dispersive spectrographic (EDS) analysis of the formations gives an identical trace to that of the original base steel.

Figure 4 Mild steel surface of after four days exposure in natural seawater. Note the toric surface topography. Bar = 10 \( \mu \)m.

3.3 7 Days

After a week of immersion the corrosion patterns were similar to those seen earlier. There is now more evidence of ‘steps’ or ‘benches’ for the surface of the natural seawater coupon (Figure 6). It has been proposed previously that such topography is the result of bacterial activity (Jeffrey and Melchers 2007). This suggests that the bacteria present in the natural seawater, as evident from the water quality, influenced the pitting corrosion process within the first week of immersion. As before, there was only relatively light pitting on the sterile seawater coupon (Figure 7).

Figure 6 Pitting of steel surface after a week in natural seawater. Note some evidence of the ‘pits within pits’, a possible result of bacterial influence. Bar = 100 \( \mu \)m.

Figure 7 Pitting of steel surface after a week in sterilised seawater. Bar = 100 \( \mu \)m.
Elsewhere on the surface of the natural seawater coupon there was evidence of unusual surface topography. Figure 8 shows growths that are roughly hemi-spherical, most of which are similar to the “mud cracking” noted above. An enlarged image of an area on the coupon from the sterilised tank shows formations described in Figure 4 as well as other previously undescribed formations that include plates and hollow tubes (Figure 9). As with all samples, these coupons were acid cleaned, so the surface topographical features are not calcareous or biological in nature. EDS analysis confirmed they have a high iron content.

**Figure 8** Hemispherical surface topographical features on the steel surface after 7 days exposure in natural seawater. Bar = 10 μm.

**Figure 9** Plates and tubes observed on steel exposed in sterile seawater for one week. Bar = 10 μm.

### 3.4 50 and 100 Days

After seven weeks immersion the pitting surface topography was similar for the coupons irrespective of the type of seawater. Figures 10 and 11 show typical images of pits observed on the coupons. Higher magnification images confirm the presence on both coupons of the toric shapes observed after 4 days exposure. Similar topography was observed on coupons recovered after 100 days exposure.

**Figure 10** Typical pit on steel surface after 50 days in natural seawater. Bar = 50 μm.

**Figure 11** Typical pit on steel surface after 50 days in sterilized seawater. Note higher magnification compared with Figure 10. Bar = 20 μm.
3.5 135 Days

Coupons recovered during the first three months had generally rust layers, irrespective of the type of seawater but this gradually changed after with time. The coupons from the sterilized seawater tank showed a much more regular rust build-up than did that the coupons from the natural seawater tank (Figures 12 and 13). The rust layer on the natural seawater coupons typically showed definite signs of biological influence with the presence of pustules and slime (Figure 12). In contrast, for the coupons from the sterilised water the rust layer appeared very uniform, and showed what appeared to be of lines of oxide (Figure 13). Again, it is reasonable to suppose that the difference is the result of the presence of microbiological components in the case of the rusts shown in Figure 12. Although there was an obvious change in the nature of the rusts, the surface topography of the steel surfaces after cleaning was generally similar although slightly more prominent, to what had been observed for shorter exposure times.

Figure 12 Coupon removed from natural seawater tank after 135 days of immersion. Note slimy oxide.

Figure 13 Coupon removed from sterile water tank after 135 days of immersion. Note relatively uniform oxide.

3.6 190 Days

After 190 days the coupons recovered from natural and from sterilised seawater exhibited similar surface topographies at a 100 x magnification, however at much higher magnification there were some interesting differences. Both surfaces contained the tori with “mud cracking” features noted above but both now contained crystalline features on inner areas (Figures 14 and 15). Interestingly, the sterile coupons had much larger (factor of 2) circular growths and plate-like crystal structures also observed occurred at a much denser than those seen on the surface of the natural seawater coupon. Similar platelet-like features have been reported previously (Jeffrey and Melchers 2003) but not inside the ‘mounds’ as noted herein. Once again, it might be noted that these coupons had been acid cleaned so the observed features are not biological in origin. EDS analysis confirmed them as iron.

Figure 14 Mud-cracked toric features observed on the steel surface after 190 days of immersion in natural seawater. Bar = 5 μm.

Figure 15 Mud-cracked toric feature observed on the steel surface after 190 days of immersion in sterilised seawater. Note the dense platelet-like formation at centre. Bar = 5 μm.
3.7 280, 360 and 512 Days

After ten months exposure quite different surface topographies were found on the steel coupons. The natural seawater coupon surface had a pock-marked appearance even at low magnification (Figure 16) that was seen to be irregular at higher magnifications. The surface of the coupon from sterile seawater was generally clear but, surprisingly, where crystalline features were present, they were much larger and more elaborate than seen for shorter exposure periods (Figure 17).

![Figure 16 Surface of steel immersed for 280 days in natural seawater at 200 x magnification. Bar = 200 μm.](image1)

![Figure 17 Surface of steel immersed for 280 days in sterilised seawater at 200 x magnification. Bar = 200 μm.](image2)

After 360 days (one year) of exposure the surfaces were generally similar to what had been seen at 280 days. The natural seawater coupon showed an irregularly pitted surface and the sterilised water coupon showed more and larger crystalline and irregular features. After 512 days all coupons in the natural water tank had a large tubercle on at least one face. The coupons from the sterilised water tank showed a more even rust layer than those from exposed to natural seawater.

3.8 554 Days

Eighteen months of continuous exposure produced prolific rust on both sets of steel coupons. However, much of the oxide on the natural seawater coupon was contained in a large orange tubercle (Figure 18). When this was broken open it contained a black oxide (probably magnetite) that is often found in similar tubercles. The black oxide layer was readily washed off to reveal a bright steel surface. In contrast, for the sterilised seawater the recovered coupon showed an oxide layer that was less regular than that observed at, say 135 days exposure (Figure 13). There also was no evidence of tubercles (Figure 19). Removal of the outer orange crust revealed a black oxide underneath that readily washed off to expose a bright steel surface.

![Figure 18 Mild steel sample recovered from natural seawater tank after 554 days exposure.](image3)

![Figure 19 Mild steel sample recovered from sterilised seawater tank after 554 days exposure.](image4)
When the coupons were cleaned there was an obvious difference in the condition of the surfaces of the two coupons (Figure 20). The sample on the left is from the sterilised tank. The only pitting on the coupon from this tank is around the top attachment hole. This probably is a result of differential aeration. Otherwise the surface is relatively flat and free of pitting. The coupon on the right is from the natural seawater tank. It is clearly more uneven in surface texture and also more heavily pitted than the coupon on the left.

Figure 20 Mild steel coupons recovered after 554 days of immersion. The sample on the left is from the natural water tank and that on the right is from the sterilised water tank. The difference in surface topography is evident.

Closer observation (500 x magnification) of the two surfaces showed the reason for the apparent differences in surface texture. At this magnification there is considerable pitting on the surface of the coupon exposed to natural seawater immersion (Figure 21). The pits in Figure 21 also appear to show pitting within the pits, a phenomenon previously associated with bacterial activity (Jeffrey and Melchers 2007). This is in contrast to there being no significant pits on the surface of the coupon from the sterilised seawater tank when seen at high magnification (Figure 22).

Figure 21 Surface of mild steel coupon immersed in natural seawater for 554 days. Bar = 100 μm.

Figure 22 Surface of mild steel coupon immersed in sterile seawater for 554 days. Bar = 100 μm.

Further magnification (2500 x) of the two surfaces revealed more detailed differences in surface features. The raw seawater surface showed patterns that suggest evolvemnt from distorted tori that later appeared to have ‘filled’ with crystal forms, with later evolvement into a flower-shaped formation. It almost appears as though petals formed from the split torus and the central crystalline mass became the stamens. Various phases of this analogy can be seen in Figure 23. The surface of the sterile seawater coupon showed only small broken shale-like plates (Figure 24). The mechanisms that cause these various surface topographies remain matters for further exploration.
4. MASS LOSS

Coupons were not individually weighed prior to deployment because they were all laser cut and drilled, however there was a slight variation in original mass so 20 fresh samples were weighed and their average mass used as an exposed weight. The coupons were weighed after recovery and cleaning. The derived mass losses are shown in Figure 25 as a function of exposure period. It is evident that at any one exposure period there is little difference in the mass loss between the steel coupons that corroded mainly by pitting when exposed in natural (raw) seawater and the mass loss of coupons that corroded much more uniformly when exposed to sterilised seawater.

![Figure 25](image)

Figure 25 Mass loss of coupons exposed in natural (raw) and sterilised seawater as a function of exposure period.

5. DISCUSSION

The above systematic set of observations of the topography of the surfaces of the steel coupons shows a clear difference between those surfaces exposed to natural seawater and those exposed to sterilised seawater. Apart from a very small difference in average water temperature resulting from the UV lamps, the only known or detected difference in the seawaters is their living microbiological content. This has been shown in various previous investigations to have an influence on the corrosion of steel in seawater both in the period soon after immersion (e.g. Melchers 2007, Malard et al. 2008) and subsequently (Jeffrey and Melchers 2003). Microbiological presence also has been associated with pitting, particularly in stainless steels (Dexter and Gao 1988) and also for mild steels in seawater (Melchers 2004) but direct, clear evidence particularly in relation to pit development, such as shown in the comparisons between Figures 2 and 3, 6 and 7,
16 and 17, and 21 and 22, has been lacking. There also has been no direct, clear evidence to date that the overall corrosion products can be significantly different between seawater with and without living microbiological content, such as shown in the comparisons between Figures 12 and 13, 18 and 19. The characterization of these corrosion products will be undertaken in a project currently underway.

To date maximum pit depths have not yet been measured. Whether this will produce results that are not qualitatively obvious from the figures presented herein remains to be seen. What is clear, however, is that the size of pits increases with increased exposure period and that the pits are deeper for the natural seawater exposures. Given what has been shown earlier regarding the growth pattern of pit depth (Melchers 2004), it is entirely plausible that Figure 25 also represent, qualitatively, the growth pattern for average and for maximum pit depth.

The present project has not characterized specifically the bacteria involved in the natural seawater stream, although it is known from earlier work that for immersion conditions the SRB are likely to be the most influential (cf. Melchers 2007). In a sense detailed information about the bacteria involved is not particularly relevant for engineering decisions – what is probably more important is information about how corrosion is influenced by changes in bacterial activity, from that seen in ‘normal’ natural seawaters as herein used, and seawaters polluted to various degrees by nutrients that can stimulate bacterial activity and numbers and thereby influence corrosion losses and maximum pit depths as functions of exposure time. This includes levels of nitrogenous materials as well as sources for organic carbon. A study of the effect of nutrient levels in seawater on corrosion loss and pit depths is currently in progress at Taylors Beach.

6. CONCLUSION

In all cases the topography of the cleaned steel surfaces and the rust products show a considerable difference for those coupons exposed to natural seawater and those exposed to sterilised seawater. Since the only significant difference between the exposure conditions was the removal of living microbiological material it is concluded that microbiological factors are responsible, directly or indirectly, for the more severe pitting observed on the natural water coupons.

7. ACKNOWLEDGMENTS

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8. REFERENCES


Szklarska-Smialowska Z (1986) Pitting corrosion of metals, Houston: NACE.

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Robert Jeffrey is a research scientist at The University of Newcastle, Australia where for the last ten years he has been investigating corrosion in marine, tidal and atmospheric conditions. Robert is also principal consultant for Pacific Testing Pty Ltd, a company specializing in corrosion problems. He is a past president of the ACA and has been on the committee of the Newcastle branch for twenty years. He co-authored a paper that won the prestigious T P Hoar Prize (Institute of Corrosion, UK) and has twice been presented with the ACA’s Marshal Fordham award for corrosion research.

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