THE EFFECT OF INCREASING AMOUNTS OF NUTRIENT ON THE CORROSION RATE OF MILD STEEL

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SUMMARY: It is known that nutrients can increase corrosion loss and increase the severity of pitting corrosion, both for short and for longer term exposures. However, the quantitative relationships involved are not well-defined nor is the effect of high nutrient loadings well-understood. Nutrient loadings for natural coastal seawater can occur through run-off of excess fertilizers and waste products from adjacent agricultural lands, either as a result of fertilizers applied for crop improvement or as a result of animal husbandry. It is known also that relatively high amounts of oxidised nitrogen, such as in nitrites, can inhibit corrosion. Herein a report is given of observations for highly polished mild steel coupons 25 mm x 25 mm in size exposed to different concentration levels of fertilizer. The coupons were exposed continuously for up to 546 days to low velocity streams of natural seawater in 200 litre tanks. There was no intervention in the first tank but the other two were dosed periodically with agricultural fertilizer, with the third tank being dosed at twice the rate of the second tank. For the first three months corrosion losses were similar in all three tanks but then began to diverge. After about twelve months corrosion loss in the second and third tank was around 90% and 75% respectively of that observed in natural seawater and this continued for the rest of the experiment.

Keywords: Steel, Seawater, Nutrients, Corrosion.

1. INTRODUCTION

It has long been recognized in agriculture that nutrients in the soil contribute to the yield of the harvest, whether that be crops or livestock. For millennia crops were rotated and swathes of farmland left fallow to allow the soil to rejuvenate. For centuries legumes have been planted as a winter or rotational crop to improve soil fertility. The legumes contain biologically fixed nitrogen (N). The planting of legumes was necessary to provide fodder for draft animals. However, with the advent of fossil fuels at the turn of the 20th Century it no longer was necessary for farmers to commit up to 25% of their land to forage. As a result, many farmers eliminated all livestock from their operations, moving to cash grain enterprises. One consequence was that they became entirely dependent upon using fertilizers on to their farms to obtain the necessary source of nitrogen for their crops (Power 1987). For current Australian broad-acre farming it is estimated that only about 10% of crops and pastures utilize legumes as a biologically fixed N supply, the rest being derived from fertilizers. While this may be economically beneficial, one of the disadvantages is that fertilizer overuse can result in excess run-off into waterways. That this is an issue is illustrated by regulation in, for example, New Zealand and in some European countries to attempt to minimize or even eliminate nutrient run-off into streams, rivers and eventually coastal waterways. However, agricultural fertilizers are not the only problem and particularly sewage discharges or effluents can cause raised nitrogen loads since most sewage treatment plants do not remove organic nitrogen. In the Australian context septic tanks have similar disadvantages, and is a recognized issue (e.g. EPA 2002). In the North Atlantic region, with high coastal region population densities, elevated levels of nutrient loadings to coastal waterways has caused much concern and investigation, primarily because of eutrophication and related concerns (OSPAR 2000). However, the impact of water pollution is wider than this. Long suspected, and demonstrated recently (Melchers 2005, 2007a), for steel infrastructure the presence of nutrients in the seawater or in seawater spray can elevate corrosion losses. This also applies to freshwaters although the critical nutrients appear to be different (Melchers 2007b). Practical implications include corrosion of harbour infrastructure such as through accelerated low water corrosion of steel piling (Melchers and Jeffrey 2010).

The most important macro-nutrients for microbiological activity are carbon, hydrogen, nitrogen, oxygen, phosphorous and sulphur. Micro-nutrients necessary as trace elements include manganese, zinc, nickel and iron. Bacteria in seawater utilize...
these in various forms, depending on the type of bacteria. Seawater is rich in organic carbon, in sulphates and if aerated in oxygen. Nutrients such as nitrogen may be available though nitrates, nitrites and ammonia from pollution sources, although the latter two usually are quickly oxidized in aerated seawaters to nitrates. For fresh water, sulphates often are the limiting nutrient (Maynard 1976). Previous research has shown that for seawater corrosion the availability of nitrates can be considered the critical nutrient (Odom 1993, Melchers 2007a). In contrast, it is known also that nitrites can inhibit the corrosion of steel in seawater (Evans 1966).

Since both nitrate and phosphate are significant components of agricultural fertilizer, it was considered appropriate to investigate whether there is a link between fertilizer level in seawater and corrosion of steel. In the following a long-term (546 day) exposure experiment is described that was aimed at elucidating the effect of fertilizer dosing on the corrosion of steel in coastal seawater. It was assumed, based on earlier work (Jeffrey and Melchers 2003), that microbiological material was present in the natural seawater used as input for all exposures. The only matter of direct interest, therefore, was the effect of nutrient content.

2. EXPERIMENTAL

2.1 Equipment

The rig used for the present investigation is shown schematically in Fig. 1a with an overview in Fig. 1b. It uses fresh coastal seawater drawn from Nelson Bay at Taylors Beach, about 50 km north of Newcastle, NSW. The rig consisted of three 200 litre sloping fiberglass tanks flushed at low water velocity with natural coastal seawater every 12 hours. The first tank remained undosed throughout the experiment. The second was given one unit of fertilizer dose during the early stage of every flushing. The third tank was given two units of fertilizer dose every flushing.

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Figure 1a. Schematic layout of test facility
Figure 1b. Overall view of tanks.
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2.2 Nutrient dosing

The fertilizer used for the test programme was a commercial lawn fertilizer with composition as supplied shown in Table 1. The doses were composed of 300 grams of the fertilizer prills dissolved in 60 litres of fresh potable water in a mixing tank (or 5 grams/L). After sustained stirring, 300 millilitres (mL) of the resulting solution was pumped into tank two. As the seawater volume of this tank is 200 litres, the net diluted concentration of fertilizer is around 7.5 mg/L for this tank. Immediately afterwards tank three was given a 600 mL dose of solution, giving a concentration of around 15.0 mg/L. Dosing occurred within minutes after fresh seawater was flushed into the tanks. Since all three tanks were flushed simultaneously and both tanks 2 and 3 dosed from the same feed tank, any variation in dissolution or mix composition would be the same for both tanks.
Table 1. Nutrient Analysis as Shown on the fertilizer packet (Lawn Food)

<table>
<thead>
<tr>
<th>Nutrient</th>
<th>Form</th>
<th>% by weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>N (nitrogen)</td>
<td>Ammonia</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td>N Total</td>
<td>9.1</td>
</tr>
<tr>
<td>P (phosphorous)</td>
<td>Water soluble</td>
<td>3.0</td>
</tr>
<tr>
<td>P</td>
<td>Citrate soluble</td>
<td>0.7</td>
</tr>
<tr>
<td></td>
<td>Citrate insoluble</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>Total P</td>
<td>3.9</td>
</tr>
<tr>
<td>K (potassium)</td>
<td>As sulphate of Potash</td>
<td>4.9</td>
</tr>
<tr>
<td></td>
<td>Total K</td>
<td>4.9</td>
</tr>
<tr>
<td>S (sulphur)</td>
<td>As sulphate</td>
<td>17.7</td>
</tr>
<tr>
<td>Ca (calcium)</td>
<td>As super-phosphate</td>
<td>8.6</td>
</tr>
</tbody>
</table>

2.3 Corrosion coupons

The corrosion coupons were laser cut from a sheet of mild steel that had been electro-polished to a mirror finish. Table 2 shows the results of composition analysis of the steel.

Table 2. Composition of mild steel coupons % (by weight).

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>P</th>
<th>S</th>
<th>Ni</th>
<th>Cr</th>
<th>Mo</th>
<th>Al</th>
<th>Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>%</td>
<td>Balance</td>
<td>0.06</td>
<td>0.01</td>
<td>0.21</td>
<td>0.006</td>
<td>0.017</td>
<td>0.03</td>
<td>0.01</td>
<td>0.01</td>
<td>0.059</td>
<td>0.03</td>
</tr>
</tbody>
</table>

The size of all coupons used was 25 mm x 25 mm x 1.4 mm. This small size was selected to facilitate access to the scanning electron microscope (SEM) stage. The coupons were weighed to the nearest 0.01 mg and immediately individually identified (Fig. 2). Sets of coupons were suspended below water level using plastic cable-ties secured from rigid plastic tubes spanning the tanks (Fig. 3).

Eighteen retrievals of sets of coupons were made over a total period of 546 days. The trial commenced in February 2010 (summer) and the last sets of coupons were recovered in August 2011. After each retrieval the coupons recovered at that time were washed in clean water to remove loose corrosion product. Any adherent product was removed using the minimum soaking time (typically less than 30 seconds) in inhibited 16% HCl. The resulting steel surface was then rinsed in clean fresh water, dried and further rinsed in acetone and allowed to dry before being reweighed. Corrosion loss was derived from the mass loss.

Figure 2. Coupon with identification tag.  
Figure 3. Coupons as suspended in one of the tanks (during filling).
3. EXPERIMENTAL OBSERVATIONS

3.1 Up to 120 days

A light corrosion product was evident from the first recovery, as shown in Fig. 4 for exposure in the natural seawater. Similar rusts developed on the coupons exposed to the two dosed tanks. However, after about two months a soft orange corrosion product had developed on the surface and judging from the colour (Waseda and Suzuki 2006), probably consisted of mostly lepidocrocite with some goethite (Fig. 5). Again this was the case for coupons drawn from all three tanks.

The mass losses due to corrosion for the first six recoveries (up to 120 days’ exposure) are shown in Fig. 6. It is evident that shortly after first recovery the corrosion losses in the dosed tanks are somewhat lower than in the natural seawater tank.

![Figure 4. Coupon showing corrosion product after one day of exposure in natural seawater.](image)

![Figure 5. Coupon showing corrosion product after 60 days’ exposure in natural seawater.](image)

![Figure 6. Corrosion losses of coupons exposed for up to 120 days in (i) natural (raw) seawater, (ii) seawater with 300 mL fertilizer dose and (iii) with 600 mL dose.](image)

3.2 Between 120 and 239 days’ exposure

After about 6 months’ (180 days) exposure a significant build-up of corrosion product had occurred on the coupons in all three tanks. The corrosion product was slime-like and was a darker shade of orange than was observed earlier, after the first few weeks of exposure. This indicates an increasing amount of goethite (α-FeOOH) in the outer rust layer (Misawa et al. 1974). When the outer layer was removed a black oxide (magnetite) was observed underneath. This was readily removed. Fig. 7 shows the typical corrosion product on coupons recovered between 100 and 200 days’ of exposure. The corrosion losses remained similar in all three tanks for the first 6 months (180 days) or so but then began to diverge, showing considerable differences at 239 days’ exposure (Fig. 8). At that stage the corrosion loss in the tank with 300 mL dosing was about 10% less than that in the natural (raw) seawater tank. Corrosion in the tank with 600 mL dosing was about 25% lower.

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Figure 7. Coupon recovered from the tank with 600 mL dosing after 184 days’ exposure, showing the slimy dark orange corrosion product.

Figure 8. Corrosion losses of coupons exposed for up to 239 days in (i) natural (raw) seawater, (ii) seawater with 300 mL fertilizer dose and (iii) with 600 mL dose.

3.3 Between 239 and 546 days

After about 12 months continuous exposure the rusts on all coupons started to show signs of the formation of ‘bubbles’ that on further examination were seen to comprise tubercles (Fig. 9). These occurred on coupons exposed in each of the three streams. In each case the outer orange oxide layer washed off easily to reveal a black magnetite sub-layer. When in turn this was removed the metal surface thus exposed showed extensive irregular localized corrosion (Fig. 10).

Fig. 11 shows the progression of corrosion loss for each of the three streams up to 546 days’ exposure. It is seen that the relativity between the corrosion losses for the 0 mL, 300 mL and 600 mL dosings is maintained but that the results do show some irregularity in trend. The reason for this fluctuation currently is not understood and will be investigated.
Figure 9. Coupon recovered from 300 mL dosed tank after 395 days showing tubercles and slimy dark orange corrosion product.

Figure 10. Surface topography of the coupon recovered from the natural seawater tank after 395 days’ exposure and after cleaning.

Figure 11. Corrosion losses of coupons exposed for up to 395 days in (i) natural (raw) seawater, (ii) seawater with 300 mL fertilizer dose and (iii) with 600 mL dose.

3.4 At conclusion (546 days, about 18 months)

At the completion of the experiment all remaining coupons were covered in slimy tubercles. Fig. 12 shows the corrosion product in the 300 mL dosed tank. Although the chemical composition of the rusts involved was not investigated in the present study, similar observations have been made previously and the chemistry recorded (Jeffrey 2008). As before, it can be expected that the tubercle consists essentially of an outer layer of orange and red oxides and hydroxides with an inner core composed largely of black magnetite.

Figure 12. Tubercles on the exterior of the coupon recovered from the 300 mL dosed tank after 449 days’ exposure.
When the last of the samples were recovered after 546 days’ exposure the maximum difference in steel corrosion loss between the three exposure streams was almost 40%. The coupons exposed in the tank with 600 mL dosing showing the largest difference in mass loss and those in the 300 mL dosed tank about half of this (Fig. 13).

Figure 13. Corrosion losses of coupons exposed for up to 546 days in (i) natural (raw) seawater, (ii) seawater with 300 mL fertilizer dose and (iii) with 600 mL dose.

3.5 Water Chemistry

At regular intervals throughout the total experiment samples of water were collected from each of the 3 tanks. These were analysed for nutrients at a commercial water quality testing laboratory. Table 3 shows typical results. It can be seen that the conservative components of sea water, namely the sulphates, calcium and salinity, remained relatively the same throughout the whole experiment whereas the non-constant components (nitrates and phosphates) increased significantly after dosing.

Table 3. Results of analyses of seawater, natural and dosed.

<table>
<thead>
<tr>
<th></th>
<th>Natural seawater</th>
<th>+ 300 mL dosing</th>
<th>+ 600 mL dosing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Conservative components</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sulphate (mg/L)</td>
<td>3000, 1800</td>
<td>3000, 1900</td>
<td>2800, 1900</td>
</tr>
<tr>
<td>Calcium (mg/L)</td>
<td>355</td>
<td>373</td>
<td>349</td>
</tr>
<tr>
<td>Dissolved Oxygen (%)</td>
<td>83.6</td>
<td>79.8</td>
<td>64.6</td>
</tr>
<tr>
<td>Salinity (mg/L)</td>
<td>30.9</td>
<td>31.3</td>
<td>31.5</td>
</tr>
<tr>
<td><strong>Non-conservative components</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ammonia (mg/L N)</td>
<td>0.033, 0.009, 0.035, 0.032</td>
<td>0.82, 0.83, 0.74, 0.49</td>
<td>2.2, 1.7, 3.8, 1.3</td>
</tr>
<tr>
<td>Nitrate (mg/L N)</td>
<td>0.039, 0.020, 0.015, 0.009</td>
<td>0.28, 0.17, 0.14, 0.15</td>
<td>0.26, 0.080, 0.57, 0.11</td>
</tr>
<tr>
<td>Nitrite (mg/L N)</td>
<td>0.004, &lt; 0.003, 0.005, &lt; 0.003</td>
<td>0.015, 0.033, 0.053</td>
<td>0.27, 0.091, 0.062</td>
</tr>
<tr>
<td>Total oxidized Nitrogen (mg/L N)</td>
<td>0.043, 0.082, 0.009</td>
<td>0.30, 0.19, 0.15</td>
<td>0.53, 0.63, 0.13</td>
</tr>
<tr>
<td>Total Phosphorous (mg/L N)</td>
<td>0.005, 0.014, 0.027</td>
<td>0.25, 0.13, 0.14</td>
<td>1.4, 0.92, 0.37</td>
</tr>
<tr>
<td>pH</td>
<td>7.9</td>
<td>7.9</td>
<td>7.6</td>
</tr>
</tbody>
</table>

Since nitrates (and ammonia and nitrites) in natural coastal seawater are normally very low, the 300 mL dosing gave a very large percentage increase in nitrates (and ammonia and nitrites). The 600 mL dosing produced roughly twice the concentration of nitrates, ammonia and nitrites but there is a wide variability. Similarly, the phosphate content, which is normally very low in natural coastal seawater, increased markedly with 300 mL dosing and roughly twice that amount with the 600 mL dosing, again with considerable variation. The reason(s) for the variability are not clear at the present time and are under investigation.

3.5 Water Temperature

Water temperature was monitored for the first twelve months of the trial. The plot of the data is set out in Figure 14.
The average annual water temperature being 20.9° C, the minimum 9.6 °C and the maximum 32.9 °C. Diurnal temperature variation was typically 1.5 °C to 2.5 °.

4. DISCUSSION

The purpose of the experiment reported herein was to investigate the effect of fertilizer added to natural coastal seawater on the corrosion of mild steel. Whereas previously increased concentrations of nitrates have been associated with increased corrosion in otherwise natural seawaters, this appears not to be the case here. One reason for this could be the way the experiment was conducted. Under natural conditions components such as nitrites and ammonia are seldom present in the concentrations shown in Table 3, since both typically are oxidized to nitrate through natural oxidation processes in seawater. Nitrite is a well-known corrosion inhibitor (Evans 1960), largely because it competes for the oxygen that would otherwise be available for corrosion by oxidation. By not having been oxidized earlier by natural processes it is likely that nitrites were available in the vicinity of the steel coupons and thus able to inhibit the corrosion process while under control of oxygen as the electron acceptor. This inhibiting influence is unlikely to be effective when the corrosion process becomes gradually anoxic as the oxygen is no longer the main electron acceptor (Melchers 2011). Fig 13 tends to support this interpretation since it shows, despite considerable fluctuations in the trends, that the corrosion inhibiting effect is most pronounced in the period prior to about 350 days’ exposure, with the three trends diverging. After this time the trends diverge less and are roughly parallel.

Phosphates also increased with higher dosing (Table 3). It is known that phosphates are used as inhibitors for corrosion of steel in fresh water immersion conditions (Evans 1960) but their effect in seawater is unclear. Unfortunately, their influence as an individual variable cannot be determined from the present results.

The present results do show that the influence of nutrients is not necessarily a simple matter and may depend on the relative availability of other nutrients and the overall chemical composition of seawater. Previous results have shown that nitrates increase the amount of corrosion loss and the severity of pitting (Melchers 2005, 2007a, 2007b). This was attributed to microbiological influences that were both possible and important for corrosion in natural seawaters. Importantly, previous field studies all involved natural exposure conditions such that there was sufficient time lag for nitrites and ammonia to be oxidized and for these to be negligible in the seawater to which the steel was exposed. In addition, laboratory studies under controlled conditions have shown the influence of nitrates, without the complications of the presence of nitrites and phosphates.

The present results also show that the addition of fertilizer or agricultural runoff that is fresh and therefore not oxidized to any significant extent is unlikely to increase corrosion and may decrease it somewhat, largely as a result of the influence of nitrites in the fertilizer. Where nitrates are not present or significant or are oxidized to nitrates the inhibiting effect is not available and in that case the previous results for the effect of nitrates on enhancing corrosion through microbiological influences would appear to be applicable.

Finally, whether tubercles (Fig 12) are the result of microbiological influences and if so what bacteria are involved is an open question (Ray et al. 2011). The represented results tend to suggest that tubercles will form, at about the same time, irrespective of the concentration of fertilizer added to the seawater and without correlation to corrosion mass loss. This suggests that tubercle formation may be primarily the result of mechanisms other than microbiological, although the severity may be influenced by microbiological influences. The possibility that tubercles form under abiotic conditions is not inconsistent with the recent proposition that the severe increase in longer-term corrosion (after about one year at

![Figure 14 Plot of water temperature for the first year of the trial showing seasonal variation](image-url)
Taylors Beach) is largely the result of severe localized (autocatalytic crevice or pitting) corrosion under anoxic conditions (Melchers 2011, 2012).

5. CONCLUSION

The addition of commercial fertilizer containing nitrogen, phosphorous, potassium and calcium, and with a high proportion of sulphates, reduced the corrosion of steel coupons continuously over an 18 month period. For the first 6 month the effect of adding fertilizer to a concentration of 15.0 mg/L of the 200 litre tank content reduced corrosion loss by about 25% compared to corrosion loss in natural seawater. Thereafter, until about 9 month’s exposure, the corrosion loss was about 75% of that in natural seawater. This relative loss continued at about this rate for the remaining time.

For a dosing rate giving about 7.5 mg/L the reduction in corrosion losses at all times were approximately half those for the 15 mg/L dosing rate. This showed that the reduction in corrosion loss is approximately proportional to the amount of fertilizer added. However, there was considerable variation in all the trends, for reasons not yet ascertained.

The results appear to be inconsistent with previous observations that addition of nitrates to seawater tends to boost the influence of microbiological activity and hence increases both corrosion loss and severity of pitting. It is proposed that this was not observed in the present experiment because of the relatively high content of nitrite (a recognized electro-chemical corrosion inhibitor) that would under natural exposure conditions have been oxidized to nitrate.

6. ACKNOWLEDGMENTS

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7. REFERENCES


8. AUTHOR DETAILS

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He is an honorary life member, a past president of the ACA and has been on the committee of the Newcastle branch for over 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 and also the AC Kennet award for corrosion research.

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