Experimental investigation of accelerated low water corrosion of steel piling in harbours

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ABSTRACT. Accelerated Low Water Corrosion (ALWC) of steel piling used for port infrastructure such as wharves and bridge and jetty supports has become a topic of much concern. A review of the problem is given and a recent research project that examines the influence of bacteria and nutrients on corrosion is described. It is shown that evidence of ALWC is available after only a few years of exposure and is correlated with water (nutrient) pollution.

KEY WORDS: Corrosion, seawater, harbours, bacteria, nutrients, pollution.

1. Introduction

In some geographical locations steel piles and sheet piling exposed for many years to seawater without cathodic protection appear to be particularly prone to Accelerated Low Water Corrosion (ALWC). It is a high degree of corrosion below just the mean low tide (MLT) level. This may cause severe structural problems such as collapse of wharves or quays (Figure 1) with potentially significant economic implications (Christie 2001). The problem is of interest for structural engineers because of the need to predict likely durability and safe operation of such facilities.

Widespread discoveries of ALWC have occurred in the last two decade or so, mainly in sea harbours in the UK and in France, and also, recently, in Australia. It also has been detected in freshwater harbours, including at Duluth-Superior in the USA. However, it is not a new phenomenon. In a paper largely unnoticed in the ALWC literature, already in the 1960s Arup and Glantz (1963) reported high levels of corrosion between the mean tide (MMT) level and the mud-line in 20 Danish harbours for sheet piling 25-35 years old. The highest corrosion rates were observed immediately below MLT. They also noted, in passing, that corrosion rates were higher 'in harbors with fish industries'. However, no details were provided.
The marine tidal and the waterline zones are severe corrosion environments. Early electrochemical studies attributed this to differential aeration. Increasingly ALWC is associated with microbiologically-influenced corrosion (MIC) (Beech and Campbell 2008). The bacteria usually implicated are the sulfate reducing bacteria (SRB) (Hamilton 1985). They are thought to reside in anaerobic niches within the biofilm that forms almost immediately on the surface of a metal (or other material) when exposed to seawater. The SRB require suitable nutrients (trace elements) and energy (electrons) for metabolism, growth and regeneration. Despite considerable controversy in the past about the precise mechanisms relating SRB to corrosion, the SRB are now considered to influence corrosion primarily through their metabolites (waste products). The principal component is hydrogen sulfide (H$_2$S) which is aggressive to the iron in the steel to produce FeS.

The effect of this reaction is easily distinguished in practice. Any free S is seen as yellow or orange deposits, FeS is a soft, almost slimy, black corrosion product, easily removed from the surface of the steel. Its removal typically reveals bright shiny steel. In contrast, the usual oxidation products formed by the corrosion of steel, such as the ferrooxihydroxide FeOOH and magnetite Fe$_3$O$_4$, tend to be reddish brown or hard black respectively, and Fe$_3$O$_4$, that typically is found immediately adjacent to the metal, is very difficult to remove from the metal substrate.

2. Evidence of Bacterial Involvement

While the involvement of MIC in ALWC had long been suspected, it is not sufficient simply to observe bacteria to be present in the rust layers. This does not guarantee their involvement in the corrosion process. A better test is for specific corrosion products, such as the so-called ‘green’ rusts (GR). They can be created abiotically from the original oxidation product Fe(OH)$_2$ but also may be created under biotic conditions.

French researchers were some of the first to obtain clear evidence of biotic GR. In the tidal zone of steel sheet piling some 20 years old at Boulonge sur Mer, France. Genin et al.
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(1993) observed the corrosion product layer to be a black liquid film against the metal surface, overlain by a solid mineral layer of corrosion products with living organic matter on the outside, typically a layer of sea shells, the whole some 50mm thick. They found green rust in the black liquid as well as magnetite and goethite. Goethite is characterized by the distinctive orange colour often observed on corroded sheet piles (Figure 1). Genin et al. (1993) also detected FeS. With continued anaerobic bacterial mediation it transforms through to ferrous sulfide FeS$_2$ (pyrite). Typically it forms in biofilms and has been reported widely as an inner layer of the corrosion product under long-term immersion conditions.

Subsequently, Refait et al. (2003) reported little or no FeS but much magnetite (Fe$_3$O$_4$), an oxidation product that forms under oxygen-deficient conditions, for sheet piling exposed for more than 25 years in the Bay of Brest. They concluded that this could be the result of iron reducing bacteria. Similar inconsistencies were noted by Gubner (1998) for sheet piling observations in some 22 European ports, with some having apparently no evidence of AL WC even though both SRB and their usual corrosion product FeS were detected. For the sites where AL WC was evident, somewhat elevated levels of organic carbon, nitrogen and hydrogen were detected. However, no clear correlation was established between bacterial counts and AL WC.

The important conclusion from these studies is that bacterial action is likely to be involved in AL WC despite its complexity (Beech and Campbell 2008). In turn this means that it is likely to be affected by nutrient supply rates.

3. Progression of corrosion with time

Earlier studies of the longer term progression of corrosion of steel in marine conditions showed that mass loss has a 'bi-modal' distribution (Figure 2) (Melchers and Jeffrey 2008). Immediately after first exposure bacteria in the biofilm are involved (Phase 0, 1). This declines as the rust layers build-up on the surface of the steel. It also reduces the diffusion of oxygen from the water (or elsewhere) through the rusts to the corrosion interface (Phase 1), producing a gradual decline in the rate of corrosion (Phase 2). New anoxic niches may now form, this time within the rust layer and in which SRB and related bacteria can flourish provided there is a sufficient supply of nutrients and electrons (Phase 3). The longer-term corrosion behaviour, shown schematically as Phase 4 involves both bacterial activity and slow abiotic corrosion. Evidently, the AL WC of older piling is most likely associated with Phase 4.

Detailed analyses of field studies have shown that the rate of corrosion in Phases 0 and 1 and in Phases 3 and 4 is increased with higher levels of water pollution, and in particular with greater availability of nitrogenous material such as ammonia, nitrates and to a lesser extent nitrites (Hamilton 1985). The reason for nitrogenous materials being critical is simply the result of the order of availability of critical nutrients. Iron is limiting for much bacterial and micro-organism metabolic activity but in the corrosion of iron this is usually abundantly available. It is also one reason for bacteria to aggregate in steel corrosion.
regions. Organic carbon, the next limiting nutrient, is thought to be provided through the interaction of the bacteria in bacterial consortia, and not considered limiting for MIC. Phosphates, often associated with algal blooms, are abundant in seawater and thus not limiting.

Figure 2. Idealized progression of corrosion loss with time, showing various phases of the process as described in the text.

Taken together the above observations suggested two hypotheses: (1) If ALWC is indeed associated with the long-term effect of MIC (Phases 3 and 4), it also should be observable for short term observations as MIC is known to be involved in short-term marine corrosion (Phases 0, 1), and (2) If MIC is indeed involved, the severity of corrosion should depend on the level of activity of SRB in particular and this, in turn, should depend on the rate of nutrient supply - that is, the level of water pollution and in particular the concentration of N.

4. Australian field studies

To test the hypotheses, 3m and 6m long vertical strips of mild steel, untreated except for removal of grease, were exposed at 10 locations on the East coast of Australia at sites selected for their suspected levels of water pollution. The strips, 50 x 3 mm in cross-section, were attached to insulated supports and exposed for 1 and 2 years. Some tests are still in progress. The results reported below are interim results, but are unlikely to change significantly. At each site seawater samples were taken for water quality, mainly in summer and winter as these correspond to the extremes of seawater nutrient levels. The samples were tested for nutrients including total N at a commercial water-quality testing laboratory.

After each exposure period the marine growth, fouling and loose rusts were removed. The strips were guillotined to 100 mm long segments each sequentially number-punched as they were cut. The segments were cleaned to remove adherent rusts according to ASTM G3
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and weighed. The mass loss over the exposure period was then estimated, with the original mass derived from the density of steel and the original dimensions (including any fixing holes). An accuracy of about 1% of total mass was estimated. The equivalent corrosion loss was then calculated.

Figure 3 shows an example of the corrosion losses for individual segments plotted at its mid-height elevation. The mean (MMT), mean high (MHT) and mean low (MLT) tide levels are shown also. A best-fit curve was constructed through the data points. The ALWC region was identified and the corrosion loss there (A) measured. Similarly, the average immersion corrosion region was identified and the average immersion corrosion loss (I) measured. This was done for the strips recovered from all the test sites. The ratios \( R = \frac{A}{I} \) are plotted in Figure 4 against the average recorded nitrogenous nutrient concentration \([N]\) for each site.

![Figure 3](image)

**Figure 3.** Corrosion loss profile for one-year exposure at Williamstown, showing tide levels and parameters \(A\) and \(I\) used in the analysis.

5. Discussion

The sites used in the present study vary significantly in geographic location and thus have significantly different water temperatures. Water temperature has been shown to have a significant effect on corrosion loss and thus could not be ignored in the analysis. The use of the ratio \( R \) rather than the direct corrosion loss in the ALWC region is an attempt to allow for the differences in average water temperature, since this will affect both \(A\) and \(I\). Figure 4 shows that there is no obvious correlation of results with water temperature. Instead, there is a significant influence, as expected, of water nutrient level, represented by the critical nutrient \(N\). The trend line for \(R\) in Figure 4 is a reasonable fit to the data, with a correlation coefficient \(R = 0.83\). At zero nutrient concentration \(R\) is approximately unity as
would be expected for no ALWC effect since then immersion corrosion is roughly the same throughout the upper immersion zone and into the tidal zone. Also shown on Figure 4 are some historical experimental results for which there was no evidence of ALWC. These data were obtained during the 1950s at a US Atlantic coast site (Kure Beach) away from industrial activities and from domestic sewage and hence can be assumed to be reasonably unpolluted waters (e.g., Larrabee 1958).

**Figure 4.** Effect of nutrient concentration in bulk seawater on ratio \( R \) between maximum low water and immersion corrosion losses.

The second observation is that evidence of ALWC can be discerned already in short-term exposures (Figure 3) - after one or two years - rather than only in long-term corrosion losses as usually assumed. This is consistent with the observations, for immersion and tidal corrosion of coupons, that bacteria are involved in the corrosion process not only long-term as assumed for ALWC, but also short-term, as well-established (Lee et al., 1995, Melchers and Jeffrey 2008), and that therefore there ought to be some degree of correlation between them.

Evidently, there is considerable scatter in the observations plotted in Figure 3. In part this is the inevitable result of the use of field data. Experimental control over field experiments is very limited and variations in water temperature and nutrient levels throughout the year as well as other factors not directly considered will have some influence. On the other hand, artificial experiment in the laboratory increasingly are recognized as unable to replicate the influence of real seawater and in particular the influence of micro-organisms on corrosion. For engineering purposes only realistic results, even with large scatter, are appropriate. Further experimentation is in progress, particularly for refining the observations and estimation of the variability in water nutrient levels.
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The above results have important practical implications. One the one hand, the present results indicate that proneness to long-term ALWC can be predicted with a reasonable degree of accuracy from short-term (1-2 years) exposures of steel strips (or electrically connected coupons). Somewhat longer exposure periods may be required in cold water sites. On the other hand, if the duration of such 'short-term' exposures is too long relative to practical requirements, proneness to ALWC can be estimated from the level of average annual water pollution at the site of interest, using Figure 4 as a guide. Of course, ideally this requires the availability of water quality records. Less ideally, it follows that activities such as fisheries processing or nutrient pollution from, say, oil platform production or processing are likely to increase the likelihood of elevated levels of nutrients and hence to increase the likelihood of ALWC. Further research and field investigations are required to establish the necessary quantitative relationships.

Although ALWC conventionally is assumed to be a 'modern' phenomenon, the observations in Denmark (see above) suggest this is not the case. A more likely reason is a change in environmental conditions, with higher levels of seawater pollution being the prime cause. Since about the 1950's water pollution, and thus nutrient loading, in the North Sea and the North Atlantic coastal zones has risen considerably although this has peaked and is now declining (Cole 1979). The eventual corrosion outcomes, such as perforation of sheet piling, would occur much later since corrosion is a long-term integrative process. This is the most likely explanation for the common perception that ALWC is a 'modern' phenomenon – instead it is simply the result of earlier decades of high levels of water pollution.

Finally, the field observations show that different (horizontal) profiles of sheet piling when installed have different specific ALWC features. At present there is also no logical explanation why Larssen (U-shaped) sheet piling usually corrode through first in the trough of the U shape while Frodingham (Z shaped) piles corrode through in the middle flat of the Z shape. An experimental program currently is in progress to ascertain the reason(s) for this observation. Similarly, the observation that ALWC tends to occur first on one side of a harbour also awaits explanation.

6. Conclusion

Despite scatter in the data the results to date show correlation between bulk water nutrient content and ALWC. This offers a practical approach for assessing the risk of long-term ALWC problems. The potential for long-term ALWC can be estimated also from the corrosion profile of steel tests strips exposed for only a relatively short time period (one - to two years). This offers an alternative practical approach for estimating the risk of long-term ALWC. The apparently increased occurrence of ALWC most likely is the result of long-term elevated levels of water pollution, particularly in the North Sea and adjacent Atlantic coast but also in harbours generally. It is considered likely that ALWC in freshwaters also is the result of MIC.
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References


