MIC AND PITTING CORROSION ON FIELD RECOVERED MOORING CHAIN LINKS

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SUMMARY: Forensic investigations were performed on chain links recovered from two FSO mooring systems in West Africa and Indonesia. Although these links were in tropical seawater for only 7 years, they experienced extremely severe pitting corrosion not previously seen in any available records. The material presented has direct application to ensuring the integrity of mooring systems as it provides insight into the mechanical behaviour of highly corroded chain links, statistics of the observed corrosion rates in these locations and guidelines for examining chain links. Corrosion on the surface of the links was mapped using 3D photogrammetry. The observed long-term corrosion rate is significantly higher than the average corrosion rate of 0.4 mm/year given in API RP-2SK. Analysis of the elementary composition of the rusts indicates that the large pits observed were most likely associated with Microbiologically Influenced Corrosion (MIC). The obtained results represent a breakthrough in the field of corrosion of mooring chains deployed in tropical seawater, corroborating the latest models that have been developed taking into account MIC. This work was conducted under the scope of the SCORCH JIP which involves ExxonMobil, Chevron, BP, Total, Shell, BHP Billiton, ConocoPhillips, Petrobras, Statoil, BSEE, DNV, ABS, Bureau Veritas, INPEX, SOFEC, InterMoor, KBR, SBM, Franklin Offshore, Vicinay Cadenas, Bridon, Arcelormittal, Arrium and Vryhof Anchors.

Keywords: CORROSION, PIT, MIC, SRB, CHAIN, STEEL, SCORCH

1. INTRODUCTION

Corrosion is a key consideration in the design of long-term mooring systems. Current codes of practice recommend designing for uniform corrosion (typically factoring in a concurrent allowance for wear). These codes are based largely on cold-water experience. Corrosion of steel in seawater exhibits both uniform corrosion and pitting corrosion. Experience in tropical waters indicates that corrosion in warmer waters, particularly with high nutrient levels, give rise to more aggressive pitting which is not addressed by design codes. A review of the US NRL long-term study of corrosion in carbon steel and low-alloy steel (Wang & D’Souza 2004) indicated long-term average pitting rates around 2-3 times greater than the observed uniform corrosion level of the plate specimens in the exposure trials. The SCORCH JIP has investigated lengths of mooring chains at different points within the water column from working FPSO’s in tropical waters.

This paper summarizes some of the work performed by the SCORCH JIP on corroded/pitted chain links that were recovered from two Floating Production Units (FPU) based in West Africa and Indonesia. The chain links were donated by Chevron to the SCORCH JIP for examination. Although these links were in service for only seven years, they exhibited severe corrosion to an extent not noted previously in available records. Severe uniform corrosion was found to occur in the splash zone, whilst large-scale pitting corrosion was found on chain links just below the sea surface. In some cases the corrosion (uniform or pitting) caused an effective reduction in cross-sectional area of up to 35%. The severe corrosion was judged most likely attributable to Microbiologically Influenced Corrosion (MIC).

2. BACKGROUND TO MIC

MIC describes corrosion that involves the presence and activities of micro-organisms (Little & Wagner 1992), (Beech & Gaylarde 1999), (Little & Lee 2007). Owing to the abundance of micro-organisms in nature, MIC has been encountered across a wide range of environments. MIC has been identified in metals, alloys and composites exposed to seawater, freshwater, de-mineralized water, process chemicals, aircraft fuels and sewage environments.
MIC, and in particular the corrosion caused by sulphate reducing bacteria (SRB), has gained much attention due to observed severe and rapid damage to steel structures. The main types of bacteria associated with corrosion failures of cast iron, mild and stainless steel structures are:

- Sulphate-reducing bacteria (SRB)
- Sulphur-oxidising bacteria
- Iron-oxidising/reducing bacteria
- Manganese-oxidizing bacteria
- Bacteria secreting organic acids and exopolymers or slime.

Micro-organisms require the presence of water, nutrients and electron acceptors for survival and are found in the form of bacteria, fungi and micro-algae. Seawater often contains suitable forms of carbon, nitrogen, phosphorus and sulphur to support microbial metabolism (Little & Lee 2007), (Melchers 2007). These organisms can coexist naturally in the biofilms that form on surfaces almost immediately upon exposure, often forming synergistic communities (sortoria) that are able to affect electrochemical processes through co-operative metabolism not seen in the individual species. Bacteria may be classified according to their shape, requirements for oxygen, source of energy or type of environment in which exist (see Table 1). Some bacteria require the presence of oxygen; others require its complete absence, while others need low oxygen levels. Micro-organisms gain energy from electron transfer processes (e.g. oxidation, as in the corrosion process). Sources of energy can also be light or organic molecules and environments in which they can survive may depend on temperature and pH.

Table 1. Type of Respiration and Examples of Electron Acceptors

<table>
<thead>
<tr>
<th>Electron Acceptor</th>
<th>Product(s)</th>
<th>Organisms</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Aerobic respiration:</em> O₂</td>
<td>H₂O</td>
<td>Strictly aerobic or facultative anaerobic organisms</td>
</tr>
<tr>
<td><em>Anaerobic respiration:</em></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>NO₂⁻, N₂O, N₂, SO₄²⁻</td>
<td>Denitrifying bacteria</td>
</tr>
<tr>
<td>S²⁻</td>
<td>S²⁻</td>
<td>Facultative and obligate anaerobic bacteria</td>
</tr>
<tr>
<td>CO₂</td>
<td>Acetate</td>
<td>Acetogenic bacteria</td>
</tr>
<tr>
<td></td>
<td>Methane</td>
<td>Methanogenic bacteria</td>
</tr>
<tr>
<td>Fe³⁺, Mn⁴⁺, Cr⁶⁺</td>
<td>Fe²⁺, Mn²⁺, Cr³⁺</td>
<td>Metal-reducing bacteria</td>
</tr>
</tbody>
</table>

2.1 Mechanisms of MIC

The mechanisms of MIC include (Little & Lee 2007), (Melchers 2007), (Liengen et al. 2014):

- Production of chemicals that create a corrosive environment
- Creation of concentration cells on the metal surface
- Attack of surface films
- Acceleration of anodic or cathodic reactions
- Alteration of the chemical environment

Bacteria can reproduce quickly and when metal is immersed in seawater, a biofilm as shown in Figure 1 develops within the first few hours (Melchers 2010). A biofilm is a layer of bacteria that adheres to the surface of the metal, which may later grow to form biodeposits. Bacteria in biofilms can create favourable conditions for the support and growth of other bacterial species. For example, bacteria at the biofilm-water interface are supplied with nutrients and oxygen from the seawater, which they can break down into simple polymers, fatty acids or other waste products. These waste products can act as a supply of nutrients to other bacteria deeper in the biofilm. As they are simultaneously consuming oxygen at the water interface this creates an anaerobic environment adjacent to the metal surface (Figure 2), which can allow anaerobic bacteria to survive (Little & Lee 2007), (Liengen et al. 2014).

2.2 Sulphate Reducing Bacteria (SRB)

Because SRB are most commonly associated with corrosion in the oil and gas industries, it is useful to provide a brief review focusing on the corrosion effects rather than microbiology. SRB have been associated with pitting corrosion in areas such as ballast tanks, sheet piling and pipelines (Odom 1993). Anecdotal reports have indicated that SRB may have also caused rapid corrosion damage to mooring systems in the North Sea, SE Asia and off Brazil.
SRB are usually present in the rusts on or close to the steel surface. They do not directly attack the steel but the corrosion effect is the result of the bacterial metabolic products (metabolites) attacking the steel. For SRB corrosion to occur, the SRB require an anaerobic environment and essential nutrients, including iron (available through the corrosion process), organic carbon (available in seawater and also available through the corrosion process and other bacterial involvement) and nitrogen, such as through nitrates, nitrites or ammonium. Sulphates normally are abundant in seawater and phosphates usually are not limiting (Little & Lee 2007), (Melchers 2007). SRB metabolize the (calcium and magnesium) sulphates abundantly present in seawater to hydrogen sulphide (H$_2$S) which is highly aggressive to iron. SRB are often found in areas where hydrocarbons such as methane are present.

![Image 1: Progression of SRB Involvement](image1.png)

![Image 2: Dimpling Indicative of anoxic niches and SRB activity underneath rust layer](image2.png)

3. FIELD OBSERVATIONS OF RECOVERED MOORING CHAINS

Chevron recovered chain links from a mooring replacement on a floating production facility off West Africa in 2010. These links exhibited severe corrosion and were donated by Chevron to the SCORCH JIP for examination. The facility was moored in water depth of 42m with a prevailing average water temperature of 28°C. The mooring arrangement of the vessel was a 6-leg all-chain system comprising 76mm stud-link ORQ and R3 chains sourced from three manufacturers. Chain properties are listed in Table 2. All chains were replaced after 12 years in service, though some had earlier been replaced at the age of 5 years. The examined samples that have been reported herein were all exposed for 7 years.

Chevron also performed a replacement of the mooring lines on a FPU in Indonesia in 2010 after 7 years of service in 1000m water depth. The mooring consisted of 12 lines of combined wire and chain in a (4 x 3) 12 leg mooring system. Chain samples were donated to the SCORCH JIP for examination and destructive testing. The chain samples were studless 70mm ORQ, with chain properties listed in Table 2. The recovered links exhibited extensive corrosion. The mooring lines, numbered from F1 to F12, were split in 4 clusters of 3 lines each, F1 to F3 for Cluster 1, F4 to F6 for Cluster 2, etc. Whilst the water depth was approximately 1000m, the chain links were recovered from four water depth locations; the fairlead, before and after the upper and lower wire rope sockets respectively, and the lower ground catenary. The chain links were cleaned, and eight sets of three links were retained for high-resolution 3D laser photogrammetry, including 7 from the splash zone and one from the lower zone.

Water quality results for West Africa and Indonesia are summarised in Table 3. Nitrate levels were very high for both sites - much higher than for normal coastal seawaters. This is likely to result from high agricultural fertilizer runoff, providing large doses of NO$_3$, which generally has the effect of increasing bacterial activity. However, very high nitrogen does not necessarily mean very high bacterial activity, since once there is sufficient nitrogen, other nutrients such as phosphorus may become the limiting factor for algal/bacterial growth (Little & Lee 2007). The phosphorus levels observed in the present results are not very high.
Table 2. Recovered FPU Mooring Chain Properties

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chevron West Africa</th>
<th>Chevron Indonesia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>ORQ/R3</td>
<td>ORQ</td>
</tr>
<tr>
<td>Link diameter (nominal)</td>
<td>76 mm</td>
<td>70 mm</td>
</tr>
<tr>
<td>Width</td>
<td>274 mm</td>
<td>235 mm</td>
</tr>
<tr>
<td>Length</td>
<td>456 mm</td>
<td>420 mm</td>
</tr>
</tbody>
</table>

Table 3. Water Quality Summary

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Chevron West Africa</th>
<th>Chevron Indonesia</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitrate (as N)</td>
<td>12.08 mg/L</td>
<td>1 mg/L</td>
</tr>
<tr>
<td>Sulphate (total)</td>
<td>2024 mg/L</td>
<td>2500 mg/L</td>
</tr>
<tr>
<td>Phosphorus (total)</td>
<td>0.22 mg/L</td>
<td>Not detected</td>
</tr>
</tbody>
</table>

The effect of elevated nitrogen levels on corrosion has been given considerable research attention in the corrosion literature. In brief, corrosion at pitting locations tends to become more severe relative to the level of uniform corrosion as the nutrient level increases (Melchers & Jeffrey 2012), (Melchers & Jeffrey 2013). In addition, it has been shown that uniform corrosion also increases markedly with increased nutrient concentration in the seawater (Melchers 2014).

The observed extent and form of corrosion of the recovered chain links could be readily characterised into three groupings of results based on the location of the links within the mooring lines, as summarised in Figure 3:

- **Splash Zone** - Uniform corrosion was observed over the whole link, diameter shrinkage readily apparent, as seen in Figure 4 and Figure 5.
- **Submerged Near-Surface Zone** – Pitting corrosion was observed with deep pits, with pre-clean links shown in Figure 6 and Figure 7 and post-clean in Figure 8 and Figure 9. The characteristic black deposit and foul smell observed during recovery were indicative of MIC.
- **Lower Catenary Zone** – Three links were retrieved from a fully submerged position further down the line. There was very little corrosion visible.

![Figure 3 Changing corrosion mechanisms through zones of a mooring](image)
3.1 Investigation of Recovered Chain Links

As part of the SCORCH JIP, a detailed program of investigations were undertaken of the recovered chain links based on uniform procedures developed within the JIP. The investigations included the following:

- Physical examination prior to recovery
- Rust and biofilm sampling of chains immediately following recovery, and prior to cleaning
- X-Ray diffraction (XRD) tests of the rust samples
- Water quality and composition analysis, including biological cultures
- Detailed dimensional analysis using conventional measurement techniques
- High-resolution 3D laser photogrammetry of chain links
- Image recognition of the photogrammetry results to characterise the geometry of the chain link and surficial loss of metallic area, including uniform and pitting corrosion
- Detailed statistical analysis of the distribution and extent of uniform corrosion, and the depth and location of corrosion pits
- Residual break strength tests of 12 sets of primarily three links, with some longer sets included.
4. CIRCUMSTANTIAL EVIDENCE OF MIC

Several mechanisms were considered as potential contributors to the severe corrosion pits that were found on the West African and Indonesian recovered mooring chains, including intergranular corrosion, selective corrosion (the removal of one element from a solid alloy) and MIC.

MIC was considered the major contributing mechanism. The circumstantial evidence for this is summarized as follows:

- Removal of marine growth and corrosion products usually is relatively difficult for normal corrosion and relatively easy for cases involving serious MIC. The latter was the case for the recovered chain links.
- The base of the deep pits included evidence of smaller pits. These could be indicative of selective corrosion of iron. As these were a considerable depth below the current metal surface it is likely they were not oxygen induced, indicating they could be the result of anoxic corrosion conditions that would most likely include MIC since MIC favour anoxic conditions.
- X-Ray Diffraction (XRD) testing of the rust samples indicated materials not usually associated with uniform corrosion, such as Szomolnokite, an iron sulphate compound, and Sjoegrenite, a magnesium-iron carbonate hydroxide. There is a sufficient quantity of sulphates in seawater to allow the formation of the iron sulphates. These oxidized sulphur compounds could have developed from FeS, the typical product from MIC in seawater.

5. 3D PHOTOGRAMMETRY OF RECOVERED CHAIN LINKS

The photogrammetry of the chain links was performed with 2 hand-held laser scanners as seen in Figure 10, with an accuracy of up to 0.04mm, and resolution of 0.05mm. Pattern recognition of the cloud of points from photogrammetry (Figure 11) was used to create a reference frame for the corroded link, starting with a theoretical backbone of the link geometry. The backbone (Figure 12) served as a reference point to which subsets of the point cloud data could be taken as a slice of points around the backbone. Slices of points constructed sequentially around the backbone formed a mesh of the link surface as shown in Figure 13. The normalized loss of material around the link (R/Rref - measured radial loss/nominal radius) was shown as a function of the normalized arclength around the link (s/D), and the normalized arclength around the bar cross-section (Circumferential Distance/D), as in Figure 14. It shows an isometric view and contour map on the horizontal plane of the link surface topography. The red peaks in Figure 14 correspond to severe corrosion pits. Figure 15 shows a contour of the link topography for the severe corrosion pits above a threshold of 15mm. The raw pit contours in Figure 15 exhibit near elliptical profiles. The description of these pits as ellipses is employed in subsequent analyses, where characteristic radii a and b (as shown in Figure 15) are used in the statistical analysis of the population of pits.
6. UNIFORM VERSUS PITTING CORROSION

6.1 Underwater Versus Splash Zone Corrosion
When all chain links were recovered and marine growth was removed, severe loss of metallic area due to corrosion was observed on the fully submerged chain links as well as the splash zone links, although the form of corrosion degradation differed. Figure 16 shows link F5SZ from above the waterline, with substantial uniform corrosion, while Figure 17 shows link F3SZ that was submerged near the splash zone and has severe localized pitting.

6.2 Comparison of Corrosion Rates
Uniform corrosion was calculated for all links using the median radial loss from the reconstructed mesh, and by integrating the
volume loss and calculating an average radial loss. The results were very similar, and are shown for West Africa in Figure 18 and for Indonesia in Figure 19, with the maximum pit depth for each link. Since the links from Indonesia spanned the lower catenary to submerged near-surface zone to splash zone, the relative severity of uniform corrosion relative to pitting corrosion with respect to the link location within the mooring line can be seen in Figure 19.

As observed during visual examination and physical measurements of the links, there is a difference between the nature of corrosion observed between links F3, F10 and F12, which are in the submerged near-surface zone, and F5 and F8, which are in the splash zone. The submerged near-surface zone has generally larger pits, and lower uniform corrosion, while the reverse is true of the splash zone. There is a step change for Link 4, which is expected to have been situated at a transition point in the line. The lower links F10 had very little corrosion of either type.

![Figure 18 Uniform and pitting corrosion for Chevron West Africa chain links](image)

![Figure 19 Uniform and pitting corrosion for Chevron Indonesia chain links](image)
6.3 Comparison of Pit Statistics

The entire population of pits for all scanned links was characterised in a database with information on elliptical proportions, depth and location. This enabled a comprehensive analysis of the statistics of the corrosion pit population.

Pit depths are conventionally described using Gumbel statistics. Figure 20 shows the pit depths from West Africa and Indonesia on a Gumbel scale. It is apparent that the Indonesian pits were smaller than the West African pits, which may be attributed to differences in water quality and available nutrients. Based on experience of corrosion of steel in seawater for long exposures (>1 year) (Melchers 2014) the distribution of the pitting depths on a Gumbel plot is expected to have a transition between the depths of shallower and earlier-formed pits, which plot as a straight line on a Gumbel plot, and deeper, more severe pits, which plot in a curve on the Gumbel plot.

The latter has been shown to be described by a Frechet extreme value distribution (Melchers 2014). This is seen in Figure 20 for the pits from both West Africa and Indonesia, where at separate transition points, the pit sizes from both locations change from a Gumbel to Frechet distribution. This appears to occur for approximately the top 20% of maximum pits from both sets of links, and corresponds to a decreased likelihood of encountering larger pits compared to an extrapolation of the Gumbel distribution. The transition points at which this occurs (for pits sampled at a particular time) may be linked to the relative nutrient levels at the sites.

Figure 21 shows distributions of pit transverse and longitudinal radius, which are the dimensions of the ellipses fitted to each pit for West Africa links. The pits show steadily increasing pit size with pit depth, with most of the pits having a transverse/longitudinal radius of about 0.5-0.7 as shown in the ovality PDF’s. The distributions of pit locations were derived for around the link circumference and around the link cross-section, as shown in Figure 22 and Figure 23 respectively. Pitting was generally uniformly distributed along the link, both in link position, and around the cross-section.

![Gumbel Plot of pit depth data](image-url)
Figure 21 Chevron West Africa Pit Shape

Figure 22 Distribution of pits around link

Figure 23 Distribution of pits around link cross-section
7. CONCLUSIONS

An investigation was conducted during the SCORCH JIP into corrosion at different points within the water column on lengths of mooring chains from working FPU’s in tropical waters. The corroded/pitted chain links recovered from West Africa and Indonesia exhibited severe corrosion to an extent not previously reported in the literature. Severe uniform corrosion was found to occur in the splash zone, whilst large-scale pitting corrosion was found on chain links just below the sea surface. Where pitting occurred, the pit depth growth rate was found to be 1.5-10 times the uniform corrosion rate of links in the same zone, depending on the site and location along the line.

The observed extent and form of corrosion of the recovered chain links could be readily characterised into three groupings of results based on the location of the links within the mooring lines:

- Splash Zone - Uniform corrosion was observed over the whole link, diameter shrinkage readily apparent.
- Submerged Near-Surface Zone – Pitting corrosion was observed with deep pits associated with MIC.
- Lower Catenary Zone –There was no pitting and minimal uniform corrosion.

Innovative techniques were developed to map and characterise pitting corrosion on a complex chain geometry. Detailed statistics of pit depth, location and shape were derived. The pits that formed on the West African and Indonesian links were elliptical in shape, and were distributed uniformly around the link bar, and the bar circumference, with the only exception being at the interlink contact area. The pit depth distributions transition between Gumbel for shallower and earlier-formed pits, to Frechet for deeper, more severe pits. The distributions vary between the West African and Indonesian sites, which most likely is the result of differences in water quality and nutrient concentrations.

The investigations identified that the pitting was primarily associated with MIC, most likely SRB. The pitting corrosion was found to be strongly correlated with the nutrient concentration in the water. Nitrate levels were high to very high at the two sites - much higher than for normal coastal seawaters. This is likely the result of high agricultural fertilizer runoff, providing large doses of NO₃, and also other nutrients which are known to have the effect of increasing bacterial activity. The MIC degradation of chain links has been found to be significant at certain locations within the submerged near-surface zone and may be the governing mechanism for chain life. Whilst it was not the focus of the SCORCH JIP, MIC has been identified and warrants further investigation particularly with regard to characterising the association between MIC and nutrient level, and the driving mechanisms behind the transition from Gumbel to Frechet pit depth distributions.

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9. REFERENCES


10. AUTHOR DETAILS

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Jeremy has extensive experience in reliability analysis, fluid-structure interaction and the corrosion of chain links and wire ropes used offshore.

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In addition to Andrew’s extensive experience in fixed and floating offshore structures, he is an authority in the area of steel wire ropes and fibre rope systems used in marine applications.

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