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MN James  School of Engineering, Computing and Mathematics

DG Hattingh

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Case Studies in Marine Concentrated Corrosion

M N James\(^1\), D G Hattingh\(^2\)

Abstract

This paper outlines the problem and analysis techniques in three exemplary case studies of marine concentrated corrosion. The intended audience is failure analysts or forensic engineers, who might occasionally come across examples of concentrated corrosion and are seeking relevant background information. In particular, it demonstrates the advantages in problem identification and solution that can accrue from the use of the highly sophisticated spectrographic instrumentation that is currently available. These techniques include energy dispersive spectroscopy (EDS) mapping in a scanning electron microscope (SEM), Fourier transform infrared (FT-IR) and Raman spectroscopy. Confocal laser scanning microscopy (CLSM) is also useful in surface metrology. The main case study presented is one of accelerated low water corrosion (ALWC) on the tubular steel piles of a marina. The paper includes an outline of some of the relevant literature relating to the use of these modern techniques in identifying marine corrosion products.

Keywords: Marine concentrated corrosion; accelerated low water corrosion (ALWC); intergranular corrosion (IGC); de-alloying; dezincification; stainless steel; alpha-beta brass

INTRODUCTION

Marine environments include a number of ‘zones’ in which materials may be exposed and suffer corrosion, i.e. atmospheric, splash and spray, tidal, immersion, or submerged and

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\(^1\) Marine Science & Engineering, University of Plymouth, Drake Circus, Plymouth, PL4 8AA, England

\(^2\) Department of Mechanical Engineering, Nelson Mandela Metropolitan University, Port Elizabeth, 6031, South Africa
bottom sediment [1]. Metals are widely used as structural materials in these various environments and there are a multitude of factors which influence the rate and severity of corrosion mechanisms, including temperature, nutrient level, water velocity and depth.

In terms of their effect on structural integrity, marine corrosion problems range from localised issues affecting individual ship or marine fittings, for example shackles, bolts and chains, to much more severe issues associated with phenomena such as accelerated low water corrosion (ALWC) of port structures.

The present paper gives an introductory outline of marine corrosion issues and influential factors before focusing on specific case study examples of ‘concentrated’ corrosion chosen as exemplars of interesting mechanisms where the use of modern techniques and instrumentation is useful in their identification and prevention. The case studies chosen comprise two examples of classic problems, namely intergranular corrosion of stainless steel, and dealloying (dezincification) of α-β brass. Whilst these are well known mechanisms of corrosion, some more recent work has advanced understanding of mechanisms and of alloy design to mitigate their influences; it therefore seems useful to review some of this work in the context of case studies.

The paper then goes on to present an outline of the more interesting case of accelerated low water corrosion (ALWC) of steel piling on a harbour structure. ALWC is a topic of significant current interest in Europe [2 - 5]. As noted in the summary sections of references 3 - 5, it is a particularly aggressive form of localised corrosion on marine structures which occurs typically at, or below, the low water level in tidal and brackish water. It is a form of Microbiologically Induced Corrosion (MIC) that leads to unusually high rates of metal wastage (a corrosion rate perhaps in the order of 0.3 – 1.0 mm/wetted side/year) and holing, potentially leading to loss of backfill for sheet piling, structural weakening and other integrity problems on much shorter timeframes than envisaged in the original structural design. It is known to affect port structures, in particular steel piling, and is a global phenomenon that is
currently detected via visual inspection. Typically, ALWC is evidenced as lightly adherent orange patches localised in a narrow band above Lowest Astronomical Tide (LAT) or occasionally extending down to bed level. Under these orange outer layers, a black sludge can be observed which covers a bright and extensively pitted steel surface (Figure 1). If timely remedial action is not taken, extensive and expensive (and unbudgeted) repair and maintenance works may have to be undertaken. Figure 2 illustrates typical corrosion loss rates on steel structures as a function of the marine environment zones and shows the ALWC zone.

The ALWC case study in this paper will cover identification of the problem, the choice and implementation of remedial works, and the subsequent observation and identification of a thick calcareous deposit which forms on steel piles above the high water mark under cathodic protection. It is emphasised that this case study should be seen in the forensic context of marina operators involved in litigation with the design consulting engineers, and who were seeking to understand the problem that they faced and the necessary remedial measures.

MARINE CORROSION

The topic of marine corrosion has received significant attention in the literature, e.g. [1], and the intention here is simply to briefly recall several key issues about marine environmental zones and corrosion rates and to point the reader to some of the relevant literature. Table 1 summarises data given in BS 6349-1 [6] for typical uniform corrosion rates on structural steels in a temperate environment, as a function of the marine environment zones. Corrosion rates in excess of these values can be caused locally by several forms of accelerated or 'concentrated' corrosion, which include:

- Galvanic or bi-metallic corrosion where one metal is connected to a more 'noble' metal, i.e. one with a more positive electromotive force (EMF) value, or where weld metal is significantly less noble than the parent plate. A particular form of
galvanic corrosion occurs as localised corrosion at grain boundaries caused by the anodic dissolution of (i) regions depleted of alloying elements, (ii) second phase precipitates, or (iii) regions with segregated alloying or impurity elements. This is known as intergranular corrosion which can occur in pure metals or engineering alloys [7] and will be demonstrated in this paper through an example observed on 316 stainless steel shackles used to attach a buoy to riser chain on a river mooring point. Dealloying is another form of selective electrolytic dissolution of a less noble metal from a metallic solid solution or intermetallic compound [8] and will be illustrated in a case study of dezincification of α-β brass studs used to attach copper sheathing to the hull of a sailing yacht.

- Microbial activity in concentrations around and below the low water zone leading to a particularly aggressive form of concentrated corrosion that has become known as accelerated low water corrosion (ALWC) and which, as noted above, is a mechanism of increasing concern to port and waterway authorities around the world, as well as to marina or berth owners. The forensic case study outlined in this paper relates to tubular steel piles used to construct a marina on the South Coast of the UK.

Immersion corrosion is also influenced by a number of other factors, including temperature, nutrient level in the water [9], compositional variations [10] and seawater-related issues such as salinity, dissolved oxygen content and pollutants such as sulphides [1]. Melchers discusses the influences of low levels of nutrient pollution on corrosion in reference [9] and the effect of elevated nutrient level in reference [11]. Inorganic nutrients such as nitrogen and phosphorous occur in inland and coastal waters typically as nitrites, nitrates, ammonium, phosphates and orthophosphates, with nitrates and ammonium appearing to be the most important [9].
Pollutant effects on corrosion include (i) an influence on the marine growth that forms soon after immersion, (ii) the dissolved oxygen content of the water which affects the aerobic phase of corrosion, in which the initial rate-controlling step is oxygen leaving the water and attaching to the corroding surface and the subsequent controlling step is the rate of oxygen diffusion through the layers of corrosion product on the steel surface. This diffusion rate is directly proportional to the concentration of dissolved oxygen in the water. The third major influence derives from the effects of sulphate-reducing bacteria (SRB) which are known to influence long-term anaerobic corrosion. Biological factors such as marine growth and bacterial activity are influenced by nutrient levels (in particular, the dissolved inorganic nitrogen [11]) and the environment and in turn affect the initial aerobic phase corrosion. There is hence a correlation between nutrient levels and early corrosion rates [9]. It is also the case that microorganisms are able to change the electrochemical conditions at the metal-solution interface through biofilm formation. Such changes can either inhibit or accelerate corrosion, depending on the specific biofilm-corrosion product interaction, which is linked to nutrient level [12]. However, probably the most important influence of nutrient level is on activity of SRB under anaerobic conditions in the later phases of corrosion. In anaerobic corrosion of steel the production of sulphide metabolites is the critical feature of both corrosion and inhibition processes; the chemical and physical nature of these sulphides is influenced by environmental parameters that condition the relative concentrations of free sulphide and soluble iron [12]. Thin adherent biofilms are protective, whilst bulky precipitates stimulate localised corrosion and the introduction of oxygen both accelerates corrosion and leads to the transformation of primary sulphide metabolites into pyrite (FeS$_2$) and elemental sulphur [12].

Melchers notes that the most likely rate-controlling mechanism in longer term corrosion is diffusion of nutrients through the rust layers and states that, as a first approximation, this is governed by diffusivity of the rusts and the concentration of nutrients in the bulk water [11].
Inorganic anions such as chromate or nitrite either form their own passive surface films or enhance the resistance of intrinsic passive films, and this underlies the extensive historical use of chromate as a corrosion inhibitor (which is now severely restricted owing to its harmful effects on animals and human beings). Reference 12 discusses mechanisms of corrosion inhibition in some detail, covering anodic and cathodic inhibitors as well as film-forming inhibitors, concluding that corrosion resistance is due to the formation of thin surface films under oxidising conditions and high anodic polarisation. Melchers [11, 13] has presented a non-linear model for the progression of uniform or general corrosion through a series of sequential phases which can deal with dissolved oxygen concentration, seawater velocity and the influence of steel composition. The model is suitable for tidal and marine coastal atmospheric exposure.

Current understanding of role of the alloys themselves in interactions with the marine environment, and the use of corrosion control measures remains somewhat empirical. Shifler [14] has recently reviewed the interaction between structural materials and the marine environment in terms of issues associated with selection of an appropriate structural material, whilst the effect of alloy compositional influences on corrosion has been considered by Melchers [13, 15]. Shifler notes that appropriate material selection is based on surface properties, bulk properties and fabrication and joining capability [14]. Surface properties revolve around the nature of the any passive film that is formed and its influence on corrosion rate. Passive films such as oxides, hydrated oxides or oxyhydroxides reduce ionic transport of reactive species through the layer. The physical and mechanical properties of the bulk material can strongly influence the ability of passive films to resist corrosion, while joining effects can encompass crevice corrosion, hydrogen interactions or galvanic corrosion. Shifler discusses all of these influences and effects in some detail [14] and puts them into the context of the various corrosion zones relevant to a marine environment. Melchers considered the effects on corrosion of small compositional variations in alloy content of chromium, molybdenum, copper, aluminium, nickel, manganese, silicon,
phosphorous, titanium, and vanadium, in terms of a multi-phase model of corrosion mechanisms [15] and showed that the compositional influence could differ between the early kinetics-controlled stage of corrosion and the later anaerobically-controlled stage. Melchers and Wells [13] present mathematical models for the diffusion of nutrients out of the rust layer and through the rust layer, which can be converted to corrosion loss as a function of time by assuming that longer-term corrosion under anaerobic conditions is governed by the rate of supply of nutrients for the metabolism of SRB. This model applied to carbon and copper-bearing steels.

CORROSION CASE STUDIES

Galvanic Intergranular Corrosion

As noted above, intergranular corrosion is a form of localised corrosion that proceeds along grain boundaries and the corrosion rate depends on factors such as the diffusion of chemical species to or from the anodic front that governs the dissolution kinetics. Reference 7 provides detailed information on intergranular corrosion in aluminium alloys, stainless steels, nickel and nickel alloys, as well as briefly considering ICG in other metals and alloys. Three main mechanisms have been proposed for IGC [7]:

(i) Local depletion of an alloying element, such as chromium in a region of chromium-rich carbides. In austenitic stainless steels this is referred to as sensitisation and occurs through the formation of chromium-rich precipitates during reheating or slow cooling through a critical temperature range typically 800°C to 500°C. It is also well-known that plastic deformation prior to the sensitising heat treatment increases the degree of sensitisation [7, 14] although the sensitivity depends on factors such as grain size, temperature and time-at-temperature.
(ii) The microcell or electrochemical theory based on the formation of a local electrochemical cell between matrix and precipitate, followed by dissolution of the less noble element or phase. A typical example is the anodic dissolution of second phase precipitates, e.g. \( \text{Al}_3\text{Mg}_2 \) in 5XXX aluminium alloys.

(iii) The segregation theory based on the presence of an increased concentration of alloying or impurity elements at or in the vicinity of the grain boundaries, such as sulphur or phosphorous in stainless steel. Dissolution of these regions is related to the adsorption of these elements at the grain boundary, thus changing the chemical and electrochemical activity.

The example of IGC chosen for this paper occurred in a shackle manufactured from grade 316 austenitic stainless steel that was used to secure a mooring buoy to a riser chain. The shackle is shown in Figure 3 in which the region of severe localised IGC and associated cracking is clear. The region of corrosion attack may also be associated with prior plastic deformation during manufacture. The mooring was located in an estuarine river subject to regular flows of well-aerated seawater and the shackle was stated to have been in service for approximately 6 months before the problem was noticed. Grade 316 stainless steel is known to be susceptible to both IGC and to pitting corrosion, and it would have been wiser to have specified grade 316L with lower carbon content and hence a lower susceptibility to carbide precipitation and the associated grain boundary chromium depletion. It should be noted however, that IGC can still occur in grade 316L stainless steel [e.g. 16]. Metallographic specimens cut from this shackle were polished and etched to show the intergranular nature of the attack (Figure 4). A sample that included part of the corroded surface of the cavity was examined in a scanning electron microscope (SEM) and this revealed the intergranular appearance (Figure 5) typical of IGC, with significant corrosion pitting evident on the IG facets.
The metallographic specimen was then examined using energy dispersive analysis (EDS) in a scanning electron microscope to see if any evidence could be found to support the chromium depletion hypothesis. Figures 6 and 7 show evidence of selective near-boundary corrosive attack which has left carbide particles of the $M_23C_6$ type standing alone near a grain boundary (and presumably still attached to the steel at a lower point). The latest generation of EDS systems allow much better characterisation of chromium content than is shown here, and can also provide advanced elemental mapping, which would reveal depleted grain boundary zones more clearly. References 17 and 18 provide more information on the use of quantitative microscopy techniques to study precipitation, chromium depletion and IGC susceptibility of grade 316 stainless steel, whilst reference 7 discusses strategies to avoid sensitisation in austenitic stainless steels. These strategies include the use of low carbon grades (L grades with <0.03 wt % C); the addition of alloying elements such as Ti or Nb that bind carbon into MC-type carbides (stabilised grades, e.g. 321 and 347), hence reducing the free carbon in solid solution and preventing the nucleation of $M_23C_6$ carbides; and the application of solution annealing treatments that dissolve existing carbides and quench sufficiently fast to avoid carbide nucleation.

**Dezincification of α-β Brass**

Some 10 mm and 14 mm diameter yacht studs, used to attach copper sheathing to the wooden hull, reportedly showed reduced toughness under impact with a hammer and suffered a 'banana-skin' failure mode whereby a brittle whitish-coloured outer layer of metal peeled away from an inner ductile core. The stud alloy was stated to be either brass or bronze. A number of these studs were supplied for a failure investigation, which included Charpy impact testing, metallography and chemical analysis. The impact testing demonstrated that the outer brittle layer had a variable thickness ranging from 0.5 mm to virtually the complete depth of the specimen. Figure 8 shows an example of the type of delamination observed during impact testing. EDS in an SEM using an Oxford Instruments Aztec system indicated that the alloy had a composition comprising approximately 58% Cu
and 40% Zn and 2% Pb and was thus a leaded free-machining and forging brass alloy corresponding with CuZn40Pb2 (C377) as detailed in BS EN 12167:2011 [19].

Metallographic specimens were prepared from some of the studs and etched in alcoholic ferric chloride to reveal the microstructure. The inner uncorroded region of the studs indicates that this alloy is a quenched leaded alpha-beta brass whose microstructure consists of a darker etching distribution of the zinc-rich beta-phase in a dendritic copper-rich alpha-phase matrix (Figure 9). The microstructure of the outer region is shown in Figures 10a and 10b where it can be seen that the beta-phase has been preferentially attacked. These brass studs have therefore experienced dezincification (selective galvanic corrosion) of the zinc-rich (less noble) phase. This was confirmed through EDS elemental mapping as shown in Figure 11 which showed the β-phase to be zinc-depleted. The copper enrichment in the zinc-depleted β-phase of the brass alloy arises because the conditions for dezincification of brass are quite specific; corrosion has to have been proceeding for some time (usually in an aerated chloride solution) and then dealloying starts under the resulting porous corrosion product. This leads to an enrichment of copper ions under the corrosion product and the exchange current density somehow enhances the mobility of copper exposing more zinc for dissolution [8].

As noted in references 8 and 20, the addition of small amounts of tin (~1-2 wt%), or arsenic, antimony and phosphorous (typically in amounts <0.05 wt%) improve the resistance of brass alloys to dezincification, although certain combinations of alloying additions, e.g. As + Sb and As + Sb + P make brass alloys more brittle. Reference 8 also points out that the role of these minor alloying elements in dealloying is related to nanoporosity, which has attracted considerable attention in recent years because of the remarkable properties of nanoporous materials and the potential applications of such dealloyed materials in catalysis and sensing.

Accelerated Low Water Corrosion (ALWC)
A quay extension, intended to act as a boat storage area, was added to an existing marina structure and was built on a number of circular steel piles, with outer diameter (OD) of 473 mm, wall thickness of 16 mm and a design life of 50 years calculated on the basis of metal loss from generalised corrosion. The piles were manufactured from S355 J0H steel to BS EN 10210-2 [21] which specifies that a 10% variation in wall thickness is acceptable. Some 5 months after practical completion, visible evidence of corrosion was noticed during times of low water. An investigation was therefore commissioned by the owners into the cause of the observed corrosion which differed in appearance from the uniform corrosion observed on other parts of the marina piling. The initial intention was to seek redress from the design engineers or fabricators if material properties were found to be out of specification. Subsequently, the case was settled by insurers on the basis that the piles should have had corrosion protection from installation. Hence, whilst techniques to analyse ALWC are now well-established and models for the influence of bacteria have been proposed [22 – 25], it seems to the present authors that there is likely to be considerable interest in the forensic engineering community in an ALWC case study set in such a context, rather than dealing with the fundamental research issues.

Arrangements were made with the original building contractors to remove several samples from both corroded and uncorroded regions of several piles in order to analyse the corrosion products and to accurately assess the reduction in wall thickness. This had to be performed during a neap tide and the sites of specimen removal were then immediately repaired with welded patches.

Samples of the red and black corrosion product from the affected piles as well as samples of the sediment at the exposed bed level (see Figure 12) were acquired at the same time for SRB DNA fingerprinting trials. An initial analysis of the DNA results from the samples (Figure 13) showed bacterial DNA fingerprints from replicates of the sediment samples (lanes 1-3) but not from the control sites (lanes 4-6), which are free from SRB.
extraction was unsuccessful from samples taken from the piles. The results are summarised below:

- SRB were confirmed in the sediment taken underneath one of the piles at 1200 colonies per gram (wet weight). This compares to figures of 460 SRB/cm$^3$ found in previous ALWC studies [22, 23].
- Other samples have less than 100 SRB/gram/ml (based on the sensitivity of the methods used).
- A bacterial DNA fingerprint of the ‘contaminated’ sediment showed statistical differences in speciation when compared to the control sediment.

The results of this DNA fingerprinting are best presented via a dendrogram, which is a tree diagram frequently used in computational biology to illustrate the arrangement and similarities among samples produced by hierarchical clustering. The lower the clustering distance on the ordinate axis, the greater the similarity. Figure 13 shows the DNA fingerprint image and the dendrogram indicating the linkages between samples. The results from sediment samples 1-3 are clustered together and are statistically different from the control samples 4-6 which do not contain SRB.

This data indicates that SRB did exist in the sediment around the piles and could be cultured to numbers significant enough to give rise to corrosion, as also found in reference 26, but could not be positively identified on the corrosion product taken from the pile surface, at least in the limited analysis performed.

The corrosion product was also analysed with Fourier transform infrared spectroscopy (FT-IR) on a Bruker IFS66 spectrometer. The FT-IR spectra from piles that show evidence of ALWC are compared with those where the corrosion appeared to be uniform in Figure 14. The top two traces (piles with presumed ALWC) show peaks in similar positions to those reported from other FT-IR work on SRB corrosion of steel [26, 27]. These include an intense
peak at 1448 cm\(^{-1}\) reportedly showing the presence of carboxylate group, and several peaks in the ranges of 1660 cm\(^{-1}\) and 1200-900 cm\(^{-1}\) that indicate the presence of polysaccharides associated with the metabolism of SRB [26, 27].

The specimens cut from the tubular piles were examined in a scanning electron microscope using EDS to characterise the corrosion product associated with the pitting. They were then cleaned to reveal the steel surface (Figure 15) and the depth of typical pits measured using an Olympus LEXT confocal laser scanning microscope (CLSM). EDS spectra acquired from pits in the specimens taken from piles showing evidence of ALWC typically exhibited a sulphur peak, which was absent from piles which did not show the red and black corrosion product on their surface. Pit were measured by CLSM as having maximum depths of around 0.2 mm, indicating an annual rate of perhaps 0.4 mm which is in the expected range for ALWC and well above the anticipated rates of corrosion for unprotected steel pilings in a marine environment (Table 1).

Having established that ALWC was occurring on these piles, the question asked by the owners was how to mitigate this problem and achieve the anticipated structural life of around 50 years. Reference 5 provides a comprehensive guide to the phenomenon of ALWC and its management in ports and harbours and other marine locations. It contains a brief background to ALWC, covers its geographic distribution in the UK (fairly uniform in the south), and then devotes the bulk of its attention to asset management for ALWC, condition appraisal, repair and protection (of new build and existing structures) and monitoring of the performance of repairs. Points of particular note in the guide include:

- That ALWC is a multi-stage process involving an incubation period, possibly lasting years on some structures, with subsequent stages producing attack at different rates which may be linear, exponential or stop-start, depending on circumstances. The early occurrence of ALWC on the piles is therefore a cause of some concern.
• That condition appraisal is important, as the earlier ALWC is detected and addressed the less extensive, and expensive, the remedial works. Condition appraisal is part of the asset management cycle. As part of this condition appraisal it is important to identify and accurately record the exact locations of ALWC damage using a survey drawing with grid system. Reference points on the piles are located using permanent marking paint, and a ‘clock positions’ approach for tubular piles. This enables accurate monitoring of damage sites on an ongoing basis. This was done for these piles.

• A programme of regular monitoring inspections should be implemented, to record the condition of the structure and the effectiveness of any remedial work.

• Protection options for existing structures are based on the well-established conventional corrosion protection methods, i.e. galvanic cathodic protection, coatings, welded patch plates, impressed current cathodic protection and concrete encasement. Coatings and cathodic protection can be used together provided that they are compatible.

In this particular case, as there were some legal issues to resolve with the contractors and their insurers, implementing the preferred solution of cathodic protection via sacrificial anodes took another 18 months, so a diving inspection was commissioned to monitor the problem some 12 months after this first analysis was performed and pile thickness measurements were made using a handheld Tritex 3000 underwater ultrasonic thickness gauge. The results of this survey are shown graphically in Table 2 as the range of thickness allowed by in BS EN 10210-2 [21] for such steel piles, the range measured on pile sections where ALWC was not present, and the range of thickness in regions where ALWC was observed to be present as patches of orange-coloured soft biofouling covering a black gel-
like layer of microbiological corrosion products which itself covered shiny pitted steel. These measurements suggested that in areas undergoing ALWC, an average reduction in wall thickness of 1.13 mm had occurred in the period of approximately 3 years since completion of the marina extension. The area of ALWC stretched from 2.3 m below the LAT datum (Figure 2) to 1.2 m above this datum line.

Following this report, and an agreed settlement from the insurers of the civil engineering contractor, the owners of the marina implemented a cathodic protection solution involving sacrificial zinc anodes attached the steel piles in critical positions, in accordance with Appendix 10 of reference 5.

Some 6 months after this cathodic protection system was installed, the owners became concerned over the presence of a thick white-coloured scale which was forming on the steel piles (Figure 16) and commissioned an investigation into its composition and cause. Samples of the scale were removed from the piles and subject to analysis using EDS in an SEM and Raman laser spectroscopy using a Horiba XploRA Raman microscope. Initial examination using EDS revealed that the major elements in the scale were oxygen and calcium (see Table 3) followed by silicon from the skeletons of marine animals and then aluminium, iron, sodium and magnesium as expected from a harbour seawater environment.

The formation of a thick calcareous scale is quite widely documented in the published literature as consequence of cathodic protection (CP) applied to structural alloys in a marine environment of natural seawater [e.g. 28, 29]. CP is especially attractive in marine environments because the conductivity of the seawater is high enough to obtain a reasonably uniform current distribution over the surface of the steel structure to be protected. The cathodic current promotes the oxidation of dissolved chloride ions at the anode and hydroxide is produced at the steel cathode. \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) at the cathode surface react with carbonate and hydroxide to produce calcium carbonate and magnesium hydroxide. These
precipitate to form the calcareous film on the metal surface. This mixed deposit appears as a calcareous scale on the protected surface [29] and is beneficial to CP by acting as a physical barrier against oxygen diffusion and hence decreasing the required current for efficient protection.

The formation of a calcareous deposit depends on a number of factors, including such parameters as applied potential, substrate nature, flow rate, temperature, pH, pressure, marine sediments and seawater composition [29]. The microscopic appearance of the scale seen on these steel piles (Figure 17) is very similar to that shown in reference [29] and it has a similar chemical composition. Raman laser spectroscopy was also used to examine a sample of the scale and Figure 18 shows a Raman spectrum acquired from the scale deposit. The intensity peaks observed at wave numbers of around 200, 400, 700 and 1085 are very similar to those reported by Rousseau et al [29] for a calcareous deposit formed on steel immersed in natural seawater for 6 months. The Raman spectra present a strong fluorescence background (which has been subtracted from the data shown in Figure 5) which reference 29 states to derive from clays in the sediment particles. The very strong Raman band at a wavenumber of 1085 is characteristic of calcite which is the most stable polymorph of calcium carbonate (CaCO3) [29]. Calcite is white in colour which explains the white appearance of the deposit of the steel piles.

The conclusion from this analysis is that the scale observed forming on the steel piles following cathodic protection is beneficial, and a concomitant part of cathodic protection. The recommendation to the marina owners was that there was no immediate cause for concern, although a regular annual or biennial inspection of the remaining thickness of the steel piles was recommended to ensure that the CP was reducing the rate of corrosion.

Conclusions
Several classic examples of marine concentrated corrosion have been discussed in this paper in the context of forensic engineering case studies. The intention has been to provide a brief review of the mechanisms and influences underlying their occurrence and to indicate how the use of advanced analytical spectroscopic techniques can be of significant assistance in identifying chemical constituents of corrosion deposits and in clarifying the mechanism of corrosion. The problem of ALWC has been given the greatest amount of coverage in this paper, reflecting its increasing importance in harbour installations around the world. Coverage of some relevant literature has also been provided in this paper to assist interested parties in locating useful mechanistic information.

A NACE corrosion costs study has identified that the total cost of corrosion on the US economy in 2013 exceeds $1 trillion or over 6% of the GDP [30], while the World Corrosion Organisation estimates that the annual cost of corrosion is some $2.2 trillion or over 3% of the world's GDP [31]. Clearly, corrosion and its mitigation are important forensic engineering concerns for through-life performance of maritime structures.

Acknowledgements
Dr Graham Bradley for his assistance with the DNA fingerprinting of the SRB, Andrew Tonkin for his help with the FT-IR spectroscopy, Dr Roy Moate for assistance with EDS and Tony Tapp for assistance with the diving survey.

REFERENCES


Table 1  Typical rates of corrosion for structural steels as a function of the marine environment zone [6].

<table>
<thead>
<tr>
<th>Marine Environment</th>
<th>Corrosion Rate</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean</td>
</tr>
<tr>
<td>Atmospheric zone</td>
<td>0.04</td>
</tr>
<tr>
<td>- above splash zone where direct wave or spray contact is infrequent</td>
<td></td>
</tr>
<tr>
<td>Splash zone</td>
<td>0.08</td>
</tr>
<tr>
<td>- above mean high water line</td>
<td></td>
</tr>
<tr>
<td>Tidal zone</td>
<td>0.04</td>
</tr>
<tr>
<td>- between mean high water and mean low water spring level</td>
<td></td>
</tr>
<tr>
<td>Intertidal low water zone</td>
<td>0.08</td>
</tr>
<tr>
<td>- between low water spring and 0.5 m below LAT</td>
<td></td>
</tr>
<tr>
<td>Continuous seawater immersion zone</td>
<td>0.04</td>
</tr>
<tr>
<td>- from 0.5 m below LAT to seabed level</td>
<td></td>
</tr>
<tr>
<td>Below seabed level or in contact with soil</td>
<td>0.015 max</td>
</tr>
</tbody>
</table>
Table 2  Summary of the thickness measurements taken in the underwater survey (in mm):

Range of thickness allowed by BS EN 10210-2:2006 (Min Max):

Thickness measured on uncorroded sections of piles (Min Average Max):

Thickness measured on corroded sections of piles (Min Average Max):

Table 3  Composition of the calcareous scale formed on the steel piling after the commencement of cathodic protection.

<table>
<thead>
<tr>
<th>Element</th>
<th>O</th>
<th>Ca</th>
<th>Si</th>
<th>Al</th>
<th>Fe</th>
<th>Na</th>
<th>Mg</th>
<th>K</th>
<th>S</th>
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</thead>
<tbody>
<tr>
<td>Weight %</td>
<td>36.3</td>
<td>35.2</td>
<td>10.2</td>
<td>6.4</td>
<td>4.1</td>
<td>2.4</td>
<td>1.4</td>
<td>1.4</td>
<td>0.9</td>
</tr>
</tbody>
</table>
Figure 1a  Typical appearance of ALWC observed during a diving inspection underwater - bright appearance of the steel under a lightly adherent orange and black deposit.

Figure 1b  Appearance of ALWC observed on the same steel piles above water during a neap tide – this has occurred in the region corresponding with the range of low water variation.
Figure 2  Schematic showing a cross-section through steel sheet pile showing corrosion zones.  HAT = highest astronomical tide; MHWS = mean high water spring tide; MLWS = mean low water spring tide; LAT = lowest astronomical tide.  The zone of ALWC usually ranges from the MLWS to the LAT region of the pile (adapted from reference 4).
Figure 3  Grade 316 stainless steel shackle that has experienced severe localised IGC. The inset diagram shows the dimensions typically used to characterise shackles, which in this case are \( A = 35 \text{ mm} \), \( B = 10.5 \text{ mm} \), \( S = 11.6 \text{ mm} \).

Figure 4  The intergranular attack typical of ICG is clearly visible in this metallographic image. 200x magnification.
Figure 5  Scanning electron microscope image of the corroded surface. This is very clearly intergranular in nature and the IG facets have themselves suffered localised corrosion pitting. A 20μm marker line is given on the image.

Figure 6  This SEM image clearly shows preferential attack around a grain boundary precipitate phase identified by EDS as likely to be $M_{23}C_6$. 
Figure 7  M_{23}C_{6} carbides left at the grain boundary by selective IGC of the near-boundary region. The EDS X-ray spectrum is taken from the larger particle identified by the arrow.
Figure 8  Delamination of yacht studs observed during impact testing.

Figure 9  As-cast microstructure of the unaffected 60/409 brass alloy showing some small inter-phase lead particles and darker etching beta phase in a matrix of dendritic alpha phase. 500x magnification.
Figure 10a  Microstructure around the interface between the outer and inner regions of one of the brass studs, showing that the beta-phase has been preferentially attacked. 1,000x magnification.

Figure 10b  SEM examination clearly shows the effects of the dealloying attack on the zinc-rich beta phase.
Figure 11  EDs elemental maps showing the distribution of (b) copper, (c) zinc and (d) lead in the microstructural region shown in the SEM image given in (a). Examination reveals that the beta-phase is Zn-depleted and hence also Cu-rich.
Figure 12  Region of sediment collection from the bed stratum. The red deposit corresponds with the region of ALWC on the pile and can be seen to have occurred just above the LAT position on the pile (which corresponds with bed level in this case).
Figure 13  DNA finger-printing of bacteria in the sediment samples. Lanes 4-6 (control) and 1-3 (sediment) in the top image show statistically significant differences, as indicated in the dendrogram or tree-diagram in the lower image.
Figure 14  FT-IR spectra for the various samples of corrosion product taken from piles showing no evidence of ALWC (bottom three traces) and those showing the typical red-black deposit associated with ALWC (top two traces). The top two traces show intense peaks at wavenumbers associated with the presence of SRB.
Figure 15  Bright shiny steel surface of a cleaned sample cut from the wall of one of the piles, showing the ALWC pitting.

Figure 16  Typical appearance of the thick white scale forming on the steel piles after cathodic protection was implemented.
Figure 17  Typical region of the scale deposited on the steel piling and the associated elemental composition.

Figure 18  Raman spectrum from the scale deposit, with the base-line corrected to a horizontal to compensate for the high observed levels of fluorescence.