An Evaluation of Carbon Steel Corrosion under Stagnant Seawater Conditions

JASON S LEE*, RICHARD I RAY*, EDWARD J LEMIEUX*, ALEXANDER U FALSTER* and BRENDA J LITTLE*

*(Naval Research Laboratory, Stennis Space Center, MS 38529, USA; Naval Research Laboratory, Key West, FL 33040, USA; University of New Orleans, New Orleans, LA 70148, USA)

(Received 23 July 2004; in final form 20 September 2004)

Corrosion of 1020 carbon steel coupons in natural seawater over a 1-year period was more aggressive under strictly anaerobic stagnant conditions than under aerobic stagnant conditions as measured by weight loss and instantaneous corrosion rate (polarization resistance). Under oxygenated conditions, a two-tiered oxide layer of lepidocrocite/goethite formed. The inner layer was extremely tenacious and resistant to acid cleaning. Under anaerobic conditions, the corrosion product was initially a non-tenacious sulphur-rich corrosion product, mackinawite, with enmeshed bacteria. As more sulphide was produced the mackinawite was transformed to pyrrhotite. In both aerobic and anaerobic exposures, corrosion was more aggressive on horizontally oriented coupons compared to vertically oriented samples.

Keywords: seawater; aerobic; anaerobic; sulphate-reducing bacteria

INTRODUCTION

Hamilton (2003) recently proposed a model for corrosion of carbon steel due to sulphate-reducing bacteria (SRB) in which sulphate, an intermediate electron acceptor, is reduced to sulphide. In his model, sulphide reacts with iron to form a corrosion product that ultimately transfers electrons to oxygen. Hamilton's theory provides insight into electron transfer reactions within a biofilm containing both aerobic and anaerobic niches. Consistent with that model, most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium (Hamilton & Maxwell, 1986; Hamilton & Sanders, 1986). Key West, FL, seawater typically contains 2 g l⁻¹ sulphate and 5–7 mg l⁻¹ dissolved O₂. Lee et al. (1993a; 1993b) and Hardy and Bown (1984) demonstrated that the most aggressive corrosion due to SRB occurs when carbon steel is exposed to alternating oxygenated/anaerobic conditions. Hardy and Bown (1984) conducted experiments in an artificial seawater medium to which they added 1.0 g l⁻¹ NH₄Cl, 0.1 g l⁻¹ KH₂PO₄, 0.1 g l⁻¹ Fe(NH₄)₂(SO₄)₂.6H₂O, 0.4 g l⁻¹ Tris[tris-(hydroxy methyl) amino methane], 4.5 ml 60% sodium DL lactate, 0.5 g l⁻¹ yeast extract, 1.0 g l⁻¹ ascorbic acid in 750 ml synthetic seawater and 250 ml distilled water. The experiments were conducted using a single marine isolate, Desulfovibrio sp. Corrosion rates of mild steel foils (25 μm thick, undefined surface area and finish) were determined by weight loss measurements and by electrical resistance probe measurements. In their experiments corrosion rates in anaerobic media were low (1.45 mg dm⁻² d⁻¹). Exposure to air caused corrosion rates to increase (129 mg dm⁻² d⁻¹) and localized corrosion was observed. The experiments of Lee et al. (1993a; 1993b) were conducted with an artificial seawater medium containing 10 mg l⁻¹ glucose, 25 mg l⁻¹ sodium lactate, 25 mg l⁻¹ sodium acetate, 10 mg l⁻¹ yeast extract, 10 mg l⁻¹ NH₄Cl and 2 mg l⁻¹ Na₂HPO₄ inoculated with Pseudomonas aeruginosa, Klebsiella pneumonia and Desulfovibrio desulphuricans. Lee et al. (1993a; 1993b) used electrochemical techniques to evaluate corrosion of 1018 carbon steel (polished to 600 grit) and concluded that the corrosion rate under
**4. TITLE AND SUBTITLE**
An Evaluation of Carbon Steel Corrosion Under Stagnant Seawater Conditions

**6. AUTHOR(S)**
Lee, Jason S., Ray, Richard I., Lemieux, Edward, Alexander, Falster, Little, Brenda J.

**14. ABSTRACT**
Corrosion of 1020 carbon steel coupons in natural seawater over a 1-year period was more aggressive under strictly anaerobic stagnant conditions than under aerobic stagnant conditions as measured by weight loss and instantaneous corrosion rate (polarization resistance). Under oxygenated conditions, a two-tiered oxide layer of lepidocrocite/goethite formed. The inner layer was extremely tenacious and resistant to acid cleaning. Under anaerobic conditions, the corrosion product was initially a non-tenacious sulphur-rich corrosion product, mackinawite, with enmeshed bacteria. As more sulphide was produced the mackinawite was transformed to pyrrhotite. In both aerobic and anaerobic exposures, corrosion was more aggressive on horizontally oriented coupons compared to vertically oriented samples.

**15. SUBJECT TERMS**
seawater, aerobic, anaerobic, sulphate-reducing bacteria
**Title of Paper or Presentation**

An Evaluation of Carbon Steel Corrosion Under Stagnant Seawater Conditions

**Author(s)**

Jason S. Lee, Richard I. Ray, Edward Lemieux, Alexander Falster, Brenda J. Little

It is intended to offer this paper to the [Name of Conference] (Date, Place and Classification of Conference)

and/or for publication in [Biofouling, Unclassified] (Name and Classification of Publication) [Name and Publisher]

After presentation or publication, pertinent publication/presentation data will be entered in the publications data base, in accordance with reference (a). It is the opinion of the author that the subject paper [is X is not ] classified, in accordance with reference (b). This paper does not violate any disclosure of trade secrets or suggestions of outside individuals or concerns which have been communicated to the Laboratory in confidence. This paper [does X does not ] contain any militarily critical technology. This subject paper [has X has never ] been incorporated in an official NRL Report.

Jason S. Lee, 7330

**FILING/APPRAISAL**

<table>
<thead>
<tr>
<th>CODE</th>
<th>SIGNATURE</th>
<th>DATE</th>
<th>COMMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lee</td>
<td></td>
<td>7/12/04</td>
<td></td>
</tr>
<tr>
<td>N/A</td>
<td></td>
<td>7/12/04</td>
<td></td>
</tr>
</tbody>
</table>

1. Release of this paper is approved. 2. To the best knowledge of this Division, the subject matter of this paper [has X has never ] been classified.

1. Paper or abstract was rejected. 2. A copy is filed in the office of E.O. Hartwig, 7000.
A - Approved for public release, distribution is unlimited.

B - Distribution authorized to U.S. Government agencies only (check reason below):
- Foreign Government Information
- Contractor Performance Evaluation
- Critical Technology
- Proprietary Information
- Administrative/Operational Use
- Premature Dissemination
- Test and Evaluation
- Software Documentation
- Cite "Specific Authority ____________________________" (Identification of valid documented authority)
- Date statement applied ____________________________
- Other requests for this document shall be referred to ________(Insert Controlling DOD Office*)

C - Distribution authorized to U.S. Government agencies and their contractors (check reason below):
- Foreign Government Information
- Software Documentation
- Administrative/Operational Use
- Critical Technology
- Cite "Specific Authority ____________________________" (Identification of valid documented authority)
- Date statement applied ____________________________
- Other requests for this document shall be referred to ________(Insert Controlling DOD Office*)

D - Distribution authorized to DOD and DOD contractors only (check reason below):
- Foreign Government Information
- Critical Technology
- Software Documentation
- Administrative/Operational Use
- Cite "Specific Authority ____________________________" (Identification of valid documented authority)
- Date statement applied ____________________________
- Other requests for this document shall be referred to ________(Insert Controlling DOD Office*)

E - Distribution authorized to DOD components only (check reason below):
- Proprietary Information
- Premature Dissemination
- Foreign Government Information
- Software Documentation
- Direct Military Support
- Administrative/Operational Use
- Contractor Performance Evaluation
- Test and Evaluation
- Cite "Specific Authority ____________________________" (Identification of valid documented authority)
- Date statement applied ____________________________
- Other requests for this document shall be referred to ________(Insert Controlling DOD Office*)

F - Further dissemination only as directed by ________(Insert Controlling DOD Office*)
- Date statement applied ____________________________ or higher DOD authority

G - Distribution authorized to U.S. Government agencies and private individuals or enterprises eligible to obtain export-controlled technical data in accordance with regulations Implementing 10 U.S.C. 140c.
- Date statement applied ____________________________
- Other requests for this document shall be referred to ________(Insert Controlling DOD Office*)

*For NRL publications, this is usually the Commanding Officer, Naval Research Laboratory, Washington, DC 20375-5320

Classification Review
(Initial/Date)

Classification Review Substantive changes made in this document after approval by Classification Review and Public Release Invalidate these reviews. Therefore, if any substantive changes are made by the author, Technical Information, or anyone else, the document must be returned for another Classification Review and Publication Release.

Author completes and submits this form with the manuscript via line channels to the division head for review and approval according to the routing in Section 4.
1. NRL Reports Submit the diskette (if available), manuscript, typed double-spaced, complete with tables, illustrations, references, draft SF 298, and proposed distribution list.
2. NRL Memorandum Reports Submit a copy of the original, typed manuscript complete with tables, illustrations, references, draft SF 298, and proposed distribution list.
3. NRL Publications or other books, brochures, pamphlets Handled on a per case basis by Site Technical Information Office. proceedings, or any other printed publications.

HQ-NRL 5219/1 (Rev. 5-97) (e) (Back)
totally anaerobic conditions was negligible compared to that under aerobic conditions. Both sets of experiments were used in the formulation of Hamilton's unifying theory of microbiologically influenced corrosion (MIC) with oxygen as the terminal electron acceptor. However, it is not clear that the results from Lee et al. (1993a; 1993b) and Hardy and Bown (1984) can be directly transitioned to exposures of carbon steel to natural seawater with no additives and a natural microflora. Furthermore, Hamilton's theory (2003) does not address corrosion rates in oxygenated and deoxygenated waters. The details of carbon steel corrosion in stagnant natural seawater are significant because of proposals to remove oxygen from seawater ballast as a corrosion control procedure for tanks that are not protected by coatings or cathodic protection (Matsuda et al., 1999; Tamburri et al., 2002). In this paper laboratory experiments are described which were designed to test the hypothesis that oxygen is required for aggressive corrosion of carbon steel exposed to natural seawater. Uncoated carbon steel was maintained under the following stagnant conditions: i) natural seawater open to air and ii) anaerobic natural seawater stripped of oxygen.

MATERIALS AND METHODS

Identical chambers were built to expose 1020 carbon steel and natural seawater to the defined operating conditions (Figure 1). Cylindrical chambers (35.5 cm diameter and 27.9 cm high) were constructed from heavy gauge, chemical resistant, opaque polyethylene. Corrosion coupons were descaled, non-polished 1020 carbon steel (Table I), 1.5 cm diameter × 0.16 cm thick (Metals Samples®, Munford, AL) with an as-mill finish. Individual insulated wires were attached to the back of each sample and held in place using conductive silver adhesive (Electron Microscopy Sciences®, Fort Washington, PA) and carbon tape. The exposure side of the coupon was coated with vacuum grease and centred face down inside a plastic mount (3.175 cm diameter × 2.54 cm high). Samples were mounted in Epothin® epoxy.

<table>
<thead>
<tr>
<th>AISI-SAE designation</th>
<th>C</th>
<th>Mn</th>
<th>P max</th>
<th>S max</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>0.17–0.24</td>
<td>0.25–0.60</td>
<td>0.04</td>
<td>0.05</td>
<td>remainder</td>
</tr>
</tbody>
</table>

![FIGURE 1](image1.png)  
Heavy gauge plastic experimental chambers each containing an Ag/AgCl reference electrode, a Pt/Nb mesh counter, a cylindrical electrode holder and 36 individually addressable C1020 electrodes (27 vertically orientated, 9 horizontally orientated).

![FIGURE 2](image2.png)  
Electrode holder and individual electrodes orientated both horizontally (bottom) and vertically (sides).
(Buehler, Lake Bluff, IL) with the wire connection exposed to the epoxy. Vacuum grease prevented intrusion of epoxy between the sample face and the bottom of the mount and allowed the as-mill finish to be preserved. Epoxy-mounted carbon steel coupons were oriented in rows both vertically (27 samples) and horizontally (9 samples) in each chamber to simulate tank sidewalls and bottoms, respectively, for a total of 36 samples (Figure 2). A heavy gauge plastic cylinder (17 cm diameter × 23 cm high) held the electrodes in place with the vertically oriented samples positioned inwards and the horizontally oriented samples positioned upwards. Prior to seawater exposure, coupons were rinsed in acetone, ethanol and distilled water and dried with nitrogen gas to removed vacuum grease and residual surface debris. A Ag/AgCl electrode and a platinum/niobium mesh were used as reference and counter electrodes, respectively (Figure 1). Exposure chambers were filled with natural seawater collected at the Naval Research Laboratory (NRL) Corrosion Facility, Key West, FL. Natural Key West, FL seawater was deoxygenated using a premixed inert gas containing CO₂.

Chambers containing stagnant seawater were sealed and transported to NRL, Stennis Space Center, MS. The chamber filled with natural, oxygenated seawater was open to air via a 1-inch tube in the chamber cover. The chamber filled with anaerobic water was maintained in an anaerobic hood with an atmosphere of 5% CO₂, 10% H₂ and the balance N₂. Water samples from the midsections of each stagnant chamber were collected monthly using a sterile 20 ml pipette. The following parameters were measured using standard techniques (Acculab® Incorporated, Marrero, LA): dissolved oxygen, ammonia nitrogen, nitrate and nitrite, bulk pH, sulphate concentrations and turbidity. Sulphide concentrations were determined in triplicate using the methylene blue method 228 C (Standard Methods, 1971) and Hach® Odyssey DR2500 spectrophotometer/software. A sterile 5 ml syringe was used to remove 4 ml from the 20 ml water sample. One ml was used to inoculate serial dilutions (10⁵) of each of the following seawater media (Dixie Testing and Products Incorporated®, Houston, TX): phenol red dextrose broth (Difco®), Postgate medium B, nutrient broth (Difco®) and thioglycollate medium (Difco®) used to determine most probable numbers of acid-producing bacteria (APB), SRB, general heterotrophic aerobes, and anaerobes, respectively. Dilutions were incubated for 28 d at room temperature.

Four coupons (1 horizontally and 3 vertically oriented) were removed monthly. Coupons were fixed in cedacolyte buffered 4% glutaraldehyde in seawater, rinsed in distilled water and examined using environmental scanning electron microscopy (ESEM) and energy dispersive spectroscopy (EDS) to characterize corrosion morphology, biofilm structure and corrosion product composition (Pope et al., 2000). After ESEM evaluation, coupons were cleaned with an acid solution (ASTM, 1994), weighed (Denver Instrument Company, Model TC-104, precision +/− 0.1 mg) and re-examined with ESEM. Some coupons required additional treatment in a boiling caustic solution containing 20 g NaOH and 2 g Zn in 100 ml distilled water. The open-circuit potential (Ecorr) was monitored continuously using an Agilent® HF94970A data logger and linear polarization resistance (LPR) was performed on each sample every 1–3 months. LPR was used to determine the polarization resistance (Rp) of each electrode. The inverse (1/Rp) is the instantaneous corrosion rate given in (ohms⁻¹). Acquisition time for Rp is < 1 min. Dissolved oxygen (DO) in each container was monitored continuously using a dissolved oxygen electrode (OxyGuard® DO Probe, Port Moody, British Columbia, Canada) and a MadgeTech® mini data logger (Warner, NH).

At the conclusion of the experiment (396 d), two vertically oriented samples were removed from the anaerobic chamber and exposed to air for 2 h. The samples were placed in individual containers of 500 ml of oxygenated and deoxygenated artificial seawater. The artificial seawater had been deaerated for 2 h with bubbling N₂ gas. 1/Rp − Ecorr trends were recorded over an 8-d period, using a Ag/AgCl reference electrode and a carbon rod as a counter electrode. Corrosion products were prepared for x-ray diffraction with an agate mortar and pestle under nitrogen, using acetone to prepare a slurry that was transferred to glass disks (2.54 cm diameter). A SCINTAG XDS 2000 X-ray diffractometer was used in the study. The instrument was operated at a voltage of 35 kV and 15 mA current. A step scan from 2 to 70° (2θ) was used, 0.05° increment and 8 s dwell time per step. A steady stream of nitrogen was used to flood the interior of the instrument to prevent oxidation. Data were retrieved and converted to Excel spreadsheets by Diffraction Master.

RESULTS

Changes in bulk water chemistry as a function of time for both exposure conditions are presented in Tables II (aerobic) and III (anaerobic). For the aerobic conditions, the pH decreased from 8.02 to 7.29 over the 396-d exposure. The initial pH in the anaerobic chamber was lowered to 6.23 because of CO₂ used in the deoxygenating process. The pH increased to 7.08 over the exposure period. In general, sulphide concentration in the bulk medium increased with time in both chambers. Bulk sulphide concentration in the anaerobic seawater was consistently higher.
than that of the aerobic seawater. Sulphate concentrations declined in both cases. Low concentrations of ammonia were measured in both exposure conditions. Turbidity consistently decreased with time in the aerobic water and fluctuated under anaerobic conditions. The microbial population of the bulk water varied with exposure condition. In the chamber maintained with exposure to air, all measured microbial populations (Table IV) initially decreased with time, but at the conclusion of the experiment (396 d) the populations of aerobes and anaerobes returned to their original numbers. Culturable SRB were observed at 60 d in the aerobic condition. Under anaerobic conditions (Table V) the numbers of culturable anaerobic bacteria i.e. general anaerobic heterotrophs, APB and SRB, increased with time. Populations of culturable SRB increased by five orders of magnitude over the entire experiment.

At the conclusion of the experiment, general observations were made of the condition of the water in each chamber. The bottom of the aerobic chamber was covered by large amounts of settled reddish/brown corrosion products, while the anaerobic chamber had black corrosion products at the bottom. The aerobic water had a stale smell, while the anaerobic water smelled of sulphide.

DO concentration (Figure 3) for the aerobic seawater fluctuated between 4 ppm (mg L⁻¹) and 1 ppm over the entire exposure period. The initial DO concentration of 4.3 ppm decreased to 1.6 ppm during the first 10 d and fluctuated over the next 200 d. After 200 d, DO concentration increased slowly from 3.5 to 4.5 ppm. The oxygen-stripped seawater had an initial DO concentration of < 1 ppm and quickly dropped to 0 in the first days, and remained at 0 for the 396 d of exposure.

Ecorr was monitored continuously for each of the 1020 carbon steel electrodes over the entire exposure in both the aerobic and anaerobic chambers. Figure 4 shows the average Ecorr values by row for both aerobic and anaerobic cases. Standard deviations of average Ecorr values were 1% or lower throughout the entire experiment (not shown). The Ecorr values for all samples started at approximately -0.75 V (Ag/AgCl). Over the next 80 d, the Ecorr values for the aerobic condition increased by 40 mV. In contrast, the Ecorr values in the anaerobic chamber increased by 40 mV but at approximately 45 d the Ecorr values of the different orientations (vertical, rows 1–3 and horizontal, row 4) separated. The Ecorr of row 4 coupons decreased to approximately -0.74 V (Ag/AgCl) in a few days and then slowly increased by
20 mV over the next 50 d. The $E_{\text{corr}}$ of the vertical rows decreased to $-0.74$ V (Ag/AgCl) over 20 d, but in contrast to row 4 did not increase after dropping to $-0.75$ V (Ag/AgCl). The quick drop and separation of the $E_{\text{corr}}$ values at 45 d corresponded to an increase in sulphide concentration (Table III) and culturable SRB (Table V). A notable difference between exposure conditions throughout the entire experiment was the observation of small fluctuations ($\pm 5$ mV) of the $E_{\text{corr}}$ values in the aerobic condition while the $E_{\text{corr}}$ values for coupons in the anaerobic chamber remained stable. At 80 d in the aerobic condition, the fluctuations began to increase to almost 100 mV in amplitude. At day 87, the datalogger malfunctioned and data were lost until day 115 at which time the fluctuations increased to approximately 200 mV in amplitude. Fluctuations continued until day 200 of exposure at which time the $E_{\text{corr}}$ values stabilized. Small fluctuations were still apparent. The $E_{\text{corr}}$ rose by 50 mV over the remainder of the experiment. Stabilization of the $E_{\text{corr}}$ and DO occurred at same time i.e. day 200. No appreciable difference in $E_{\text{corr}}$ was observed between the coupons as a function of row in the aerobic case. In the case of the anaerobic exposure, between 60 and 110 d the horizontal (bottom, row 4) coupon $E_{\text{corr}}$ began to increase to almost $-0.71$ V (Ag/AgCl) while the vertical (side, rows 1, 2 and 3) coupons $E_{\text{corr}}$ remained at $-0.74$ V. Simultaneously, a stratification of $E_{\text{corr}}$ values was observed between the two orientations (horizontal and vertical) in the anaerobic case. At approximately day 150, the $E_{\text{corr}}$ of row 1 separated from rows 2 and 3, both of which slowly decreased by 20 mV over the next 50 d. At day 200, the $E_{\text{corr}}$ of rows 2 and 3 separated also. Jumps in the $E_{\text{corr}}$ at days 260 and 305 indicated disturbances due to sample collection. After 305 d, all the $E_{\text{corr}}$ value for coupons in the anaerobic chamber had begun to merge to a single value around $-0.72$ V (Ag/AgCl).

Linear polarization measurements were performed on individual electrodes in both exposure conditions over the 396-d exposure. $R_p$ was calculated for each sample and $R_p$ values were averaged by row and exposure type. Standard deviations of average instantaneous corrosion rates were 9% or less for the

![FIGURE 4](image-url)  
**FIGURE 4** Average $E_{\text{corr}}$ (vs Ag/AgCl) over time values for C1020 samples in stagnant aerobic (aero) and anaerobic (anaer) conditions displayed by row (R). R1, R2, R3 = vertically orientated samples with R1 being at the top of the tank, R3 towards the bottom and R2 between the two; R4 = horizontally orientated sample at the bottom of the tank.

![FIGURE 5](image-url)  
**FIGURE 5** $1/R_p$ (instantaneous corrosion rate) over time (days) for C1020 samples in stagnant (a and b) aerobic and (b) anaerobic conditions. Aerobic conditions are included with anaerobic data (b) to indicate the much higher rates in anaerobic conditions. Early corrosion rates are shown in (c) for both aerobic and anaerobic conditions. R1, R2, R3 = vertically orientated samples with R1 being at the top of the tank, R3 towards the bottom and R2 between the two; R4 = horizontally orientated sample at the bottom of the tank. Average values are displayed.
aerobic condition, while the anaerobic condition had higher standard deviations of 18% or less throughout the entire experiment. The inverse, 1/Rp (a value proportional to the instantaneous corrosion rate) was plotted vs exposure time (Figure 5a, 5b). Standard deviation bars are not shown in Figure 5 to preserve data clarity. Between 23- and 35-days exposure, the corrosion rates for all samples were relatively low with the lowest being the anaerobic case (Figure 5c). Corrosion rates are reported in ohms⁻¹; these data were not normalized to the 2 cm² electrode area. At the same time, 1/Rp values indicated stratification within the aerobic chamber. Row 1 electrodes, closest to the air/water interface, had the highest average corrosion rate, while row 4 electrodes had the lowest. No indications of stratification were observed in the anaerobic chamber in the early exposure times. After >100 d exposure, the 1/Rp measurements indicated that the highest instantaneous corrosion rate was measured in the horizontal (bottom, row 4) coupons exposed to anaerobic seawater. This separation of bottom and side coupon corrosion rate after 23 d corresponds to the separation of Ecorr at approximately the same time. At 200 d in the aerobic condition, the corrosion rate increased for all rows, corresponding to the stabilization of Ecorr. In the anaerobic case, the corrosion rate of row 1 separated and increased from rows 2 and 3 (corresponding to an increase in the Ecorr). After 300 d, the corrosion rate of row 2 separated from row 3 and increased. Figure 5b has both anaerobic and aerobic corrosion rates plotted to facilitate the direct comparison of the instantaneous

![Graph](image_url)

**FIGURE 6** 1/Rp–Ecorr trend of anaerobic samples previously exposed to anaerobic conditions for 396 d, exposed to air for 2 h, and placed in (a) aerated artificial seawater and (b) deaerated artificial seawater.
vertically orientated samples (rows 1, 2, and 3). In general, the horizontally orientated samples had the largest corrosion rate in the anaerobic condition until 396 d exposure at which time row 1 had a significant increase in corrosion rate; while row 4 showed a decrease. This change is also seen in the $1/R_p$ data (Figure 5b). Figure 7b also indicates the weight loss corrosion rate of the two samples which were exposed to air and then returned to aerated (row 2) or deaerated seawater (row 3). The weight loss was greater for the aerobic exposure than the anaerobic exposure. Both samples had less weight loss than row 1, but more than row 4 at the end of the experiment.

The appearance of the electrodes varied with exposure condition. Observations have been documented in Figures 8 and 9. The corrosion products formed under aerobic and anaerobic seawater conditions were predictably different in appearance and composition. Under aerobic conditions, reddish brown corrosion products, identified as lepidocrocite and goethite by XRD, persisted on the surfaces of all coupons/orientations throughout the experiment (Figure 8a, b). Filamentous bacteria were associated with the oxides (Figure 8c, d), but were obscured by the oxides by the conclusion of the experiment (Figure 8e, f). The oxides were extremely tenacious and resistant to acid cleaning. The corrosion was general. Coupons exposed in anaerobic seawater were covered with black corrosion products (Figure 9a, b). Sulphur deficient iron sulphide (mackinawite) was identified in corrosion products within the first month of anaerobic seawater exposure. In later exposures, small amounts of pyrrhotite were identified in the corrosion products formed under anaerobic conditions. After day 139 the epoxy was blackened obscuring the coupons. The most conspicuous microorganisms in the sulphide corrosion products were curved rods (Figure 9c, d). The corrosion on the vertically oriented coupons was localized, deep gouging (Figure 9e) while the horizontally oriented coupon had a porous appearance with some deep pitting (Figure 9f). Pit depths were not measured.

DISCUSSION

Previous investigators demonstrated that corrosion due to the activities of SRB is more aggressive in the presence of oxygen, i.e. corrosion of mild steel by SRB under completely anaerobic conditions was negligible compared to the corrosion of mild steel by SRB in the presence of oxygen. The experiments described in this paper were directed at answering a different question: Is oxygen required for the corrosion of mild steel in natural seawater?

Several investigators (Eashwar & Subramaniam, 1990; Mansfeld & Little, 1992; Lee et al., 1993a; 1993b) have demonstrated that natural marine
biofilms form on metal surfaces, providing an anaerobic metal/biofilm interface and an environment for the growth of SRB, independent of bulk oxygen concentrations. Biofilms 75 μm thick in aerobic media can produce anaerobic conditions at the biofilm/metal interface if the aerobic respiration rate is greater than the diffusion rate of oxygen into the biofilm (Lee et al., 1993a; 1993b; Lee et al., 1995). Hamilton and his co-workers (Sanders & Hamilton, 1985; Hamilton, 1999, 2000; Hamilton & Lee, 1995) were the first to demonstrate sulphide production by SRB within anaerobic niches of biofilms in oxygenated seawater. Despite this possibility, there were no indications of anaerobic niches and sulphide production within the oxide corrosion layers formed under the aerobic experimental conditions described in the present paper. The EDS and XRD spectra indicated iron oxides with traces of phosphorus and calcium. No sulphur could be detected by EDS in the corrosion products over the 396-d exposure period, indicating the absence of sulphide corrosion products. XRD confirmed the presence of iron oxides, lepidocrocite and goethite. After acid cleaning, an adherent layer of black iron oxide remained on the surface of the coupons exposed to aerobic seawater. Removal required caustic cleaning.

Most of the previous laboratory experiments on SRB-induced corrosion of carbon steels exposed to seawater were conducted with nutrient-supplemented artificial seawater and an inoculum of 1 – 3 microbial species. Nutrients can influence the experimental outcome in several ways. Attachment of cells to surfaces is a strategy for bacterial survival in environments where the bulk water phase is nutrient limiting. Geesey (1987) stressed that many survival mechanisms are not expressed when microorganisms are subjected to the laboratory conditions used for most microbiological research.

Hydroxide, acetate and carbonate can inhibit pitting corrosion by acting as buffers. Oxyanions (e.g. SO₄²⁻, NO₃⁻, PO₄³⁻) are often present in nutrients. Molar Cl⁻/oxyanion ratios can be used to predict the likelihood of pitting or crevice corrosion (Leckie & Uhlig, 1966; Kehler et al., 2001). The
relationships between the concentration of inhibitive and aggressive anions correspond to competitive uptake of the anions by adsorption or ion exchange at a fixed number of sites on a metal surface. Webster and Newman (1994) examined the impact of media constituents on localized corrosion and concluded that Cl\textsuperscript{–} must be present in a concentration at least comparable to that of all other anions combined, otherwise corrosion was inhibited even at high H\textsubscript{2}S concentrations (up to 500 ppm). Other corrosion investigators have concluded that extracellular electron transfer by SRB. From the metal anode to the universal electron typical of microbiologically influenced corrosion produced kinetically favoured pathways of electron flow exposed under totally anaerobic conditions was included that the activities of microorganisms produce iron sulphides. The corrosion of the carbon steel electron transfer hypothesis, Hamilton (2003) concluded that each sulphide had a characteristic transformation between sulphide species depends on the state of iron. In some cases the corrosion products contained 30% sulphur, in addition to phosphorus and iron. The concentration of sulphur is especially high when taking into account the bulk water sulphide was < 1 ppm throughout the experiment (Table III). A similar observation was made by Lee et al. (2003) with 70Ni/30Cu exposed to artificial seawater inoculated with SRB. MIC of mild steel by SRB has been reviewed extensively (Sanders & Hamilton, 1984; Hamilton & Lee, 1995; Lee et al., 1995; Lewandowski et al., 1997; Nielsen et al., 1993; Hamilton, 1999, 2000). SRB within mixed species biofilms produce sulphide that reacts with iron to produce iron sulphide corrosion products that may be either protective or corrosive. King and Wakerly (1973) demonstrated that the initial sulphide film that forms in the presence of SRB is mackinawite. They further demonstrated that sulphides moderate, but do not prevent corrosion. When iron sulphides form a tightly adherent thin film, they are protective. However, iron sulphides are inherently unstable and their disruption can give rise to corrosion cells between the iron sulphide in direct electrical contact with the underlying steel (cathode) and the exposed-steel surface (anode). In their experiments, continued availability of sulphide leads to a steady thickening of the sulphide layer and a transformation of mackinawite to greigite, Fe\textsubscript{3}S\textsubscript{4} and eventually to pyrrhotite. Transformation between sulphide species depends on pH, temperature, redox potential and relative concentration of reactants. King and Wakerly (1973) determined that each sulphide had a characteristic corrosiveness but the attack was consistently pitting.

Carbon and energy flux in both individual cells and microbial ecosystem require electron transfer and metal ion oxidation/reduction. In his 'unifying electron transfer hypothesis,' Hamilton (2003) concluded that the activities of microorganisms produced kinetically favoured pathways of electron flow from the metal anode to the universal electron
acceptor, oxygen. He observed that microbial ecosystems, including soils, sediments, water columns, and biofilms, are characterized by aerobic and anaerobic zones that operate as a continuum via redox couples within the ecosystem. The interactions between oxygen and sulphate depend on redox cycling via intermediate electron carriers. The present authors observed evidence of stratification in the aerobic chamber in terms of $E_{corr}$ within 23 d (Figure 5c). Hamilton (2003) further stressed that biofilm growth is a dynamic process and the microorganisms within the biofilm are in a constant state of flux. Individual bacterial species and bacterial consortia are characterized by their primary energy source and electron donor and by the nature of the terminal electron acceptor. Oxygen is the terminal electron acceptor for aerobic species, but for anaerobic species there are alternate electron acceptors, e.g. nitrate, sulphate, ferric iron, and CO$_2$. It is possible that in the complex chemistry of seawater and biofilms there are electron acceptors other than oxygen to drive electron transfer and drive corrosion reactions. Under the experimental conditions described in this paper, corrosion of carbon steel was more aggressive in totally anaerobic conditions than in aerobic conditions. On-going experiments have been designed to evaluate the impact of alternating aerobic/anaerobic conditions in more rigorous experimental conditions.

CONCLUSIONS

In the experiments described in this paper, coupons exposed to natural aerobic seawater for 396 d developed intact, tenacious iron oxide surface deposits. In contrast, the coupons exposed anaerobically over the same period were covered with non-tenacious sulphides. Anaerobic conditions did not inhibit corrosion and oxygen was not required for aggressive localized corrosion. Once oxygen was introduced to a carbon steel coupon previously maintained under strictly anaerobic conditions, the corrosion was extremely aggressive.

Acknowledgements

This work was supported by the Office of Naval Research Program element 060153N (6.1 Research Program) and the University of Maryland. XRD data were collected at the MicroBeam Laboratory in the Department of Geology and Geophysics at the University of New Orleans, New Orleans, LA. NRL Publication Number NRL/JA/7303/2004/0006.

References


Eashwar M, Subramanian G (1990) Probing microbiologically influenced corrosion of steel during purification of seawater. CORROSION / 90, Paper No 120, NACE International


