



CARBON STEEL CORROSION IN KEY WEST AND PERSIAN GULF SEAWATERS AT VARYING OXYGEN CONCENTRATIONS

Richard I. Ray, Jason S. Lee and Brenda J. Little
Naval Research Laboratory, Stennis Space, Center, MS 39529

Edward J. Lemieux
Naval Research Laboratory, Key West, FL 33041

ABSTRACT

Corrosion of 1020 carbon steel coupons in natural Key West and Persian Gulf seawaters was directly related to exposure conditions. Exposure conditions included the following: stagnant and sloshing, oxygenated and deoxygenated seawater, in addition to, alternating immersion and drying with oxygenated and deoxygenated seawaters and atmospheres. Instantaneous corrosion rates significantly increased when oxygen was introduced into hypoxic or deoxygenated seawaters. Microbial populations in the two waters fluctuated with exposure conditions. Of all of the exposure conditions, the anaerobic stagnant Key West seawater exposure produced the highest corrosion rates and sulfide levels.

KEY WORDS: *carbon steel, seawater, ballast, deoxygenation, alternate immersion, SRB, sulfide*

INTRODUCTION

Deoxygenation of seawater has been demonstrated as an environmentally friendly ballast water treatment to control introduction of non-native aquatic species.¹ Investigators have proposed that the same treatment provides a low-cost, effective corrosion control measure for uncoated carbon steel ballast tanks based on the concept that reducing oxygen from the ballast tanks will limit oxidation.^{1, 2} Matsuda *et al.*² conducted shipboard trials by sealing a ballast tank at the deck and installing vertical pipes into the headspace. They reported that pumping pure nitrogen gas into the headspace for 1.5 hr reduced dissolved oxygen (DO) levels in the seawater to approximately 0.2 parts-per-million (ppm) and decreased the rate of uniform corrosion of carbon steel by 90% as determined by weight loss.

Hamilton³ recently proposed a model for corrosion of carbon steel due to SRB in which sulfate, an intermediate electron acceptor, is reduced to sulfide. In his model, sulfide 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.^{4, 5} Seawater typically contains 2 g l⁻¹ sulfate and 5-7 mg l⁻¹ DO. Hardy & Bown⁶ and Lee *et al.*^{7, 8} demonstrated that the most aggressive corrosion due to SRB occurs when carbon steel is exposed to alternating oxygenated/anaerobic conditions. Hardy and Bown⁶ 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.*^{7, 8} 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 desulfuricans*. Lee *et al.*^{7, 8} used electrochemical techniques to evaluate corrosion of 1018 carbon steel (polished to 600 grit) and concluded that the corrosion rate under totally anaerobic conditions was negligible compared to that under aerobic conditions. Both groups concluded that under anaerobic conditions, naturally occurring sulfate-reducing bacteria (SRB) produce sulfides, resulting in conversion of the oxide to a sulfide. The result of repeated oxygenated/deoxygenated cycles is reportedly severe localized corrosion, *i.e.*, pitting. Most reported cases of SRB induced corrosion of carbon steel in marine waters are in environments with some dissolved oxygen in the bulk medium.³ Anaerobic conditions and sulfides can form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations.⁴

Both sets of experiments⁶⁻⁸ 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 Hardy and Bown⁶ and Lee *et al.*^{7, 8} can be directly transitioned to exposures of carbon steel to natural seawater with no additives and a natural microflora. Furthermore, Hamilton's theory³ 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.^{1, 2} In this paper we describe laboratory experiments designed to test the hypothesis that oxygen is required for aggressive corrosion of carbon steel exposed to natural seawater. The effects of water stagnation vs. movement (alternate immersion, sloshing) and differing physical chemistry variables also were examined.

MATERIALS AND METHODS

Detailed descriptions of these exposure chambers have been published previously.⁹⁻¹¹ Cylindrical chambers (35.5 cm dia. and 27.9 cm ht.) were constructed from heavy gauge, chemical resistant, opaque polyethylene. Corrosion coupons were descaled, non-polished 1020 carbon steel (Table 1), 1.5 cm dia. x 0.16 cm thick with an as-mill finish. Individual insulated wires were attached to the back of each coupon and held in place using conductive silver adhesive and carbon tape. The exposure side of the coupon was coated with vacuum grease and centered face down inside a plastic mount (3.175 cm dia. x 2.54 cm ht.). Coupons were mounted in epoxy with the wire connection exposed to the epoxy. Vacuum grease prevented intrusion of epoxy between the coupon 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 coupons) and horizontally (9 coupons) in each chamber to simulate ballast tank sidewalls and bottoms, respectively, for a total of 36 coupons (Figure 1b). A heavy gauge plastic cylinder (17 cm dia. x 23 cm ht.) held the coupons in place with the vertically oriented coupons positioned inwards and the horizontally oriented coupons 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. Ag/AgCl electrodes and a platinum/niobium mesh were used as reference and counter electrodes, respectively (Figure 1a). Exposure chambers were filled (as illustrated in Figure 1b) with natural seawater collected at the Naval Research Laboratory (NRL) Corrosion Facility, Key West, FL or from the Persian Gulf off the pier in Bahrain. Natural Key West, FL seawater was deoxygenated using an in-line injection of premixed inert gases containing 0.2 ppm DO. A combination of carbon dioxide (CO₂) and nitrogen (N₂) gases was used to decrease gas bubble size, thereby increasing the bubble surface-to-volume ratio and facilitating deoxygenation. This experimental configuration is a general description of the setup used throughout the various exposure conditions detailed here. Specific variations of this setup will be addressed below.

Seawater Characterization

The following parameters were used to characterize a 20 ml portion of the seawaters: dissolved oxygen, total organic carbon, bulk pH, sulfide concentrations and salinity. Sulfide concentrations were determined in triplicate using the methylene blue method 228 C¹² and a spectrophotometer. 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: phenol red dextrose broth, Postgate medium B, nutrient broth and thioglycollate medium used to determine most probable numbers of acid-producing bacteria (APB), SRB, general heterotrophic aerobes, and anaerobes, respectively. Dilutions were incubated for 28 days at room temperature. Total organic carbon (TOC) was also measured using standard techniques.

Electrochemistry

Linear polarization resistance was used to determine the polarization resistance (R_p). The inverse ($1/R_p$) is proportional to the instantaneous corrosion rate given in (ohms⁻¹). Acquisition time for R_p is <1 min. DO in each chamber was monitored continuously using a DO probe immersed in the midsection of the chamber and a mini data logger.

Stagnant Conditions – Key West, FL Seawater

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 one-inch tube in the chamber cover. The chamber filled with deoxygenated water was maintained in an anaerobic hood with an atmosphere of 5 % CO₂, 10 % H₂ and the balance N₂.

Alternate Immersion Conditions – Key West, FL Seawater

Experiments were conducted with natural seawater at the Naval Research Corrosion Laboratory, Key West, FL. 1020 carbon steel coupons in three separate chambers were exposed to the following: (1) fill/drain cycles of alternating natural oxygenated seawater and air (aerobic/aerobic), (2) fill/drain cycles alternating deoxygenated natural seawater and air (deoxygenated/aerobic) and (3) fill/drain cycles alternating deoxygenated natural seawater and inert gas (deoxygenated/deoxygenated). Natural seawater was deoxygenated in the same manner as described above with a target DO value of 0.2 ppm. The

system was designed so that the inert gas was also used to blanket the headspace in the deoxygenated/deoxygenated exposure during the fill cycle or the entire chamber volume during the drain cycle. Whereas in the deoxygenated/aerobic exposure, no attempt was made to prevent air from entering the headspace. After draining, a thin layer of seawater remained in the bottom of all chambers (Figure 1b).

Sloshing Conditions – Persian Gulf Seawater

Two chambers were used to expose 1020 carbon steel to natural Persian Gulf seawater in aerobic and anaerobic conditions. The chambers were placed on shaker platforms that rotated at 50 rotations per minute to mimic sloshing encountered at sea. Epoxy-mounted carbon steel coupons were oriented in rows both vertically (18 coupons) and horizontally (6 coupons) for a total of 24 coupons. No coupons were placed in the row 2 position. Exposure chambers were filled with natural Persian Gulf seawater collected off the pier in Bahrain to a level equal to the row 2 position (Figure 1b). Coupons in row 1 were employed to determine the effect of salt spray on the corrosion of C1020 above the water line but will not be discussed in this paper. Natural Persian Gulf seawater was deoxygenated using a nitrogen gas. Every 7 days air was bubbled through the bottom of the water column in the aerobic chamber; nitrogen gas was used in the anaerobic condition to keep the DO level near zero (<0.3 ppm).

RESULTS

Characterization of Key West, FL and Persian Gulf Seawaters

Natural Key West, FL, seawater had salinity of 38 parts-per-thousand (ppt) and pH of 8.02 while the deoxygenated seawater had a pH of 6.23 and initial TOC concentration of 1.74 mg/L. Sulfide concentration was negligible (parts-per-billion (ppm)) in the natural and deoxygenated seawaters. Initial DO concentration was 6.5 ppm. At the time of collection (0 days exposure), the natural seawater contained culturable general aerobes, general anaerobes and APB, but no culturable SRB (Table 2 & 3).

Natural Persian Gulf seawater had a salinity of 44 ppt and pH of 7.63 at the onset (0 days exposure) of the experiment (Tables 4 & 5). The initial TOC concentration was 2.41 mg/L. Sulfide concentration was negligible and the microbial population was high for all types (aerobe, anaerobe, APB, SRB). Changes in sloshing bulk water chemistry as a function of time for both exposure conditions are also presented in Tables 4 (aerobic) and 5 (anaerobic). For the aerobic conditions, pH increased from 7.63 to 8.08 over 102-day exposure. Unlike the stagnant and alternating conditions, initial pH in the anaerobic chamber was the same as for the aerobic case, due to the lack of CO₂ in the deoxygenating process. The anaerobic pH increased to 8.28 over the exposure period. In general, sulfide concentration in the bulk medium increased with time in both chambers. Bulk sulfide concentration in the anaerobic seawater was higher than that of the aerobic seawater. The microbial population of the bulk water varied with exposure condition. In the chamber maintained with exposure to air, all measured microbial populations (Table 4) initially decreased with time. No culturable SRB were observed in the aerobic condition after the start of the experiment. Under anaerobic conditions (Table 5) the numbers of culturable bacteria (excluding SRB) decreased with time, but still contained more the aerobic case. Populations of culturable SRB initially decreased with time but maintained the highest level of culturable bacteria throughout the experiment.

Stagnant Conditions – Key West, FL Seawater

Changes in stagnant bulk water chemistry as a function of time for both exposure conditions are presented in Tables 2 (aerobic) and 3 (anaerobic). For the aerobic conditions, pH decreased from 8.02 to 7.29 over the 396-day exposure. 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, sulfide concentration in the bulk medium increased with time in both chambers. Bulk sulfide concentration in the anaerobic seawater was consistently higher than that of the aerobic seawater. The microbial population of the bulk water varied with exposure condition. In the chamber maintained with exposure to air, all measured microbial populations (Table 2) initially decreased with time, but at the conclusion of the experiment (396 days) the populations of aerobes and anaerobes returned to their original numbers. No culturable SRB were observed at any time in the aerobic condition. Under anaerobic conditions (Table 3) 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.

DO concentration (Figure 2) for the aerobic seawater fluctuated between 4 ppm (mg l⁻¹) and 1 ppm over the entire exposure period. Within the first 3 days, DO concentration decreased from the initial value of 6.5 to 4.3 (data not shown on graph). DO concentration further decreased to 1.6 ppm by day 10 and fluctuated over the next 200 days. After 200 days, DO concentration increased slowly from 3.5 to 4.5 ppm. Deoxygenated seawater had an initial DO concentration of less than 1 ppm and quickly dropped to 0 (anaerobic) in the first days, and remained anaerobic for the 396 days of exposure.

Linear polarization measurements were performed on individual coupons in both exposure conditions over the 396-day exposure. R_p was calculated for each coupon and R_p values were averaged into the categories *side* (rows 1-3) and *bottom* (row 4) for each exposure type. Standard deviations of average instantaneous corrosion rates were 9 % or less for the aerobic condition, while the anaerobic condition had higher standard deviations of 18 % or less throughout the entire experiment. The inverse, 1/R_p (a value proportional to the instantaneous corrosion rate) was plotted vs. exposure time (Figure 3). Standard deviation bars are not shown in Figure 3 to preserve data clarity. Between 23- and 35-day exposures, corrosion rates for all coupons were relatively low with the lowest being the anaerobic case. Corrosion rates are reported in ohms⁻¹, these data were not normalized to the 2 cm² coupon area. After 70 days exposure, instantaneous corrosion rate for the bottom horizontal row 4 coupons began to increase dramatically, in contrast to the side anaerobic rates, which didn't increase significantly until 300 days. Figure 3 has both anaerobic and aerobic corrosion rates plotted to facilitate the direct comparison of the instantaneous corrosion rates. In general, instantaneous corrosion rates for the anaerobic condition were two orders of magnitude higher than the aerobic condition.

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 sulfide.

Alternate Immersion Conditions – Key West, FL Seawater

Water was analyzed after a 14 day wet cycle during the exposure period of 74 – 98 days (Table 6). The pH fluctuated within narrow ranges from the original values. Bulk sulfide concentrations in all chambers increased (Table 6). SRB were cultured from both aerobic/aerobic and deoxygenated/deoxygenated chambers.

DO concentrations in the deoxygenated water and atmosphere were consistently higher than the design value of 0.2 ppm (Figure 4). Draining water from the chambers had a profound influence on DO measurements.

Instantaneous corrosion rates ($1/R_p$ reported in units of ohms^{-1}) were measured using the LPR technique every 30 – 90 days and are reported as average values in Figures 5. $1/R_p$ data for the aerobic/aerobic chamber indicated side rows corroded at rates 1.5 – 3 times faster than bottom row 4 over the first 170 days. Corrosion rates for side row coupons were very dynamic in comparison to the stable rates for bottom row coupons. The side rows showed the largest range (0.0015 – 0.01 ohms^{-1}) of rates over the experimental period time, while those of the bottom row had a much smaller range of (0.0015 – 0.006 ohms^{-1}).

$1/R_p$ data for the deoxygenate/aerobic chamber indicated that initially, side row coupons corroded faster than bottom row coupons. However, at 98 days the bottom row began to corrode slightly faster than the side rows. At 137 days, the corrosion rate for the side rows increased to 0.022 ohms^{-1} while the corrosion rate for the bottom row was around 0.005 ohms^{-1} . This jump in corrosion rates for side row coupons corresponded to measurements taken immediately after a long (~47 days) empty cycle with 7 ppm oxygen in the atmosphere (Figure 4). Corrosion rates for side row coupons during this period were twice as high as the largest corrosion rate measured for any row in the aerobic/aerobic chamber for the entire exposure. For the remainder of the experiment, the bottom row corroded at twice the rate of the side rows. At 395 days, bottom row corrosion rate increased to the high rate (0.022 ohms^{-1}), observed at 137 days for the side rows.

$1/R_p$ data for the deoxygenated/deoxygenated chamber followed the same trends for first 170 days as that of deoxygenated/aerobic chamber, including a jump (0.012 ohms^{-1}) in corrosion rates for side row coupons at 137 days. At 170 days, all rows had the same low corrosion rate of 0.001 ohms^{-1} . However, at 207 days, corrosion rates of all rows increased to between 0.007 – 0.01 ohms^{-1} with row 4 having the lowest rate. This rate increase corresponded to a measurement taken after a 46-day exposure to 5 ppm atmospheric oxygen. Interestingly, coupons in the aerobic/aerobic and deoxygenated/aerobic chambers were exposed to higher concentrations of atmospheric oxygen (7 ppm) over the same exposure period but did not exhibit the same increase in corrosion rates as side row coupons in the deoxygenated/deoxygenated chamber. After 207 days, corrosion rates of the side rows remained low at 0.001 ohms^{-1} while the bottom row corroded at twice the rate but were still low in comparison to the deoxygenated/aerobic chamber.

Corrosion rates were highest for side row coupons in the deoxygenated/aerobic chamber. Corrosion rates for side rows in the aerobic/aerobic chamber were unaffected by long periods of exposure to atmospheric oxygen whereas, side rows in the other two chambers were strongly affected in the first 150 days, after which, only the deoxygenated/aerobic chamber was consistently affected by atmospheric oxygen levels. $1/R_p$ values for row 4 of all chambers were low initially. The instantaneous corrosion rate for row 4 of the aerobic/aerobic chamber remained stable throughout the experiment as did those in the deoxygenated/deoxygenated chamber. At the conclusion of the experiment, coupons in row 4 of the deoxygenated/aerobic chamber were corroding at the highest rate of any of the rows in any of the chambers. Coupons in the deoxygenated/oxygenated chamber row 4 had the highest corrosion rates over the experiment, while the side rows in the aerobic/aerobic chamber and all coupons in the deoxygenated/deoxygenated chamber had the lowest.

Sloshing Conditions – Persian Gulf Seawater

DO concentration (Figure 6) for the aerobic sloshing seawater fluctuated between 6.2 ppm and 8 ppm over the entire exposure period. Spikes in DO concentration correspond to the injection of air. Deoxygenated sloshing seawater had a DO concentration range between 0 and 0.3 ppm. Dips in DO concentration correspond to the injection of nitrogen gas. Generally, DO concentration for the sloshing anaerobic seawater increased after nitrogen gas injection. The large spikes in DO concentration at 35 and 94 days exposure for the anaerobic condition represent inadvertent air leaks that were open for 24 hrs.

Linear polarization measurements were performed on individual coupons in both exposure conditions. R_p was calculated for each coupon and R_p values were averaged into the categories *side* and *bottom* for each exposure type. $1/R_p$ was plotted vs. exposure time (Figure 7). Standard deviation bars are not shown in Figure 7 to preserve data clarity. Aerobic bottom coupons had a steadily corrosion rate of about 0.002 ohms^{-1} , while the side coupons corroded slightly slower at 0.0015 ohms^{-1} . Instantaneous corrosion rates for the anaerobic condition (both side and bottom coupons) were two orders of magnitude smaller than the aerobic condition. No significant difference between side and bottom rates was observed in the anaerobic case. In Figure 7, note the spikes in instantaneous corrosion rates of the anaerobic condition at 35 and 94 days exposure, corresponding to the influx of oxygen into the system by way of the air leaks.

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. Also, 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. The experiments described in this paper were directed at answering different questions: What effect does differing physical chemistries between different geographical seawaters have on corrosion? What affect does stagnation have on corrosion severity? What effect does dissolved oxygen concentration have on the corrosion of mild steel in natural seawater?

The major differences between Persian Gulf seawater and Key West seawater at the time of collection include the following: salinity, temperature, and microbial concentrations. Temperature and salinity can increase the corrosivity of seawater directly. The numbers and types of microorganisms one is able to culture depends on the storage conditions, *i.e.*, whether the seawater is aerobic or anaerobic. The total microbial population is limited by nutrients. In the case of Persian Gulf seawater, salinity, temperature and initial microbial population values were all higher than the corresponding Key West values. Given these higher values one would expect Persian Gulf water to be a more corrosive environment than Key West seawater. In these experiments, this was not shown to be true. All deoxygenated and anaerobic waters maintained high levels of culturable SRB. Alternating deoxygenated/deoxygenated Key West seawater and sloshing anaerobic Persian Gulf seawater produced sulfides levels of approximately 0.2 ppm, while stagnant anaerobic Key West seawater had the highest values in the excess of 0.6 ppm. The stagnant anaerobic Key West seawater also maintained the highest total microbial populations, even aerobes were found in abundance. Therefore, stagnation of seawater may play a vital role in increasing sulfide and microbial population values. In the methylene blue standard method for sulfide concentration determination¹², it is stated that excess shaking of the test ampoules can result in lower sulfide measurements due H_2S gas coming out of solution due to agitation.

Sloshing and repeated filling and emptying (alternate immersion) of seawater could result in lower dissolved sulfide concentrations, resulting in a less corrosive environment. This notion is supported by the stagnant Key West anaerobic exposure having the highest corrosion rates with the lowest rates being found in the sloshing anaerobic Persian Gulf water. However, differences in seawater nutrient concentrations may also have influenced the experimental outcome. TOC levels were higher for Persian Gulf seawater (2.41 mg/L) when compared to Key West levels (1.74 mg/L). Attachment of cells to surfaces is a strategy for bacterial survival in environments where the bulk water phase is nutrient limiting. Therefore, more cells may have attached to the carbon steel surfaces in the Key West stagnant water than in the sloshing Persian Gulf seawater. A more mature and denser Key West seawater biofilm may have formed, producing higher sulfide levels at the microbe/metal interface and thereby increasing corrosion severity in the stagnant case. Geesey¹³ stressed that many survival mechanisms are not expressed when microorganisms are subjected to the laboratory conditions used for most microbiological research. The effect of biofilm shear stresses due to water movement may also have played a role.

Dissolved oxygen levels were decreased to hypoxic levels by direct treatment of natural seawater with an inert gas mixture or nitrogen gas and dissolved oxygen levels were measured within the water column itself. The concentration of DO in the seawater was a direct function of the performance of the gaskets and seals. When the seals held it was possible to maintain decreased oxygen levels in the water. In a similar shipboard experiments, Matsuda *et al.*² indicated that controlling the oxygen concentration was the most difficult aspect of their deoxygenation experiment. The oxygen data from the alternate immersion exposure reported in this paper (Figure 4) demonstrate that difficulty. In the initial stages of the experiment, it is extremely easy to reduce the oxygen concentration in the bulk seawater to below 1 ppm. However, aerobic respiration and abiotic corrosion reactions consume oxygen readily and drive the DO concentration to zero within days in all chambers resulting in anaerobic conditions. When seals failed (*e.g.*, 100 and 180 days), oxygen diffused into the chambers immediately. Hence, we can assess the corrosion of carbon steel resulting from ingress of oxygen into hypoxic environments. Peaks in the instantaneous corrosion rates at 137 and 207 days (Figure 5) followed periods of exposure to atmospheric oxygen (Figure 4). Corrosion rates of side row coupons of the two exposure conditions with deoxygenated seawater (deoxygenated/aerobic and deoxygenated/deoxygenated) were affected. Bottom rows were less affected because residual water prevented desiccation. Hypoxic conditions in the deoxygenated/deoxygenated chamber produced less corrosion as measured by LPR. However, introduction of oxygen caused an immediate increase in the corrosion rate. This same phenomenon was also seen in the sloshing Persian Gulf anaerobic exposure. Introduction of oxygen at 35 and 94 days (Figure 7) resulted in increased corrosion rates, but not to the same magnitude as the alternate immersion conditions (Figure 5). These results confirm the experiments of Hardy and Bown⁶ and Lee *et al.*^{7,8}

CONCLUSIONS

- Stagnant Key West seawater produced the highest corrosion rates and highest sulfide concentrations in these experiments.
- Refilling and water movement may have contributed to lower sulfide levels in alternate immersion and sloshing conditions.
- Introduction of oxygen into an anaerobic/hypoxic system resulted in an increase in corrosion rate and severity.

ACKNOWLEDGEMENTS

This work was supported by the Office of Naval Research Program element 0601153N (6.1 Research Program). NRL Publication Number NRL/PP/7303-05-5317.

REFERENCES

1. M. N. Tamburri, K. Wasson, M. Matsuda, "Ballast water deoxygenation can prevent aquatic introductions while reducing ship corrosion," *Biol Conserv* 103, 3 (2002) p. 331-341.
2. M. Matsuda, S. Kobayashi, H. Miyuki, S. Yosida, "An anticorrosion method for ballast tanks using nitrogen gas," Report of Research and Development to the Ship and Ocean Foundation (Japan), October, 1999.
3. W. A. Hamilton, "Microbiologically influenced corrosion as a model system for the study of metal microbe interactions: a unifying electron transfer hypothesis," *Biofouling* 19, 1 (2003) p. 65-76.
4. W. A. Hamilton, S. Maxwell, "Biological and corrosion activities of sulphate reducing bacteria within natural biofilms," in *Biologically Induced Corrosion*, ed. S. C. Dexter (Houston, TX: NACE International, 1986), p. 131-136.
5. P. F. Sanders, W. A. Hamilton, "Biological and corrosion activities of sulphate-reducing bacteria in industrial process plant," in *Biologically Induced Corrosion*, ed. S. C. Dexter (Houston, TX: NACE International, 1986), p. 47-68.
6. J. A. Hardy, J. L. Bown, "The corrosion of mild steel by biogenic sulfide films exposed to air," *Corrosion* 42, 12 (1984) p. 650-654.
7. W. C. Lee, Z. Lewandowski, S. Okabe, W. G. Characklis, R. Avci, "Corrosion of mild steel underneath aerobic biofilms containing sulfate-reducing bacteria - Part I: At low dissolved oxygen concentration," *Biofouling* 7 (1993) p. 197-216.
8. W. C. Lee, Z. Lewandowski, M. Morrison, W. G. Characklis, R. Avci, P. H. Nielsen, "Corrosion of mild steel underneath aerobic biofilms containing sulfate-reducing bacteria - Part II: At high dissolved oxygen concentration," *Biofouling* 7 (1993) p. 217-239.
9. J. S. Lee, R. I. Ray, B. J. Little, E. J. Lemieux, "Evaluation of deoxygenation as a corrosion control measure for ballast tanks," *CORROSION / 2005*, Paper no. 05217 (Houston, TX: NACE International, 2005).

10. J. S. Lee, R. I. Ray, E. J. Lemieux, B. J. Little, "An evaluation of carbon steel corrosion under stagnant seawater conditions," CORROSION / 2004, Paper no. 04595 (Houston, TX: NACE International, 2004).

11. J. S. Lee, R. I. Ray, E. J. Lemieux, A. U. Falster, B. J. Little, "An evaluation of carbon steel corrosion under stagnant seawater conditions," Biofouling 20, 4/5 (2004) p. 237-247.

12. "Methylene blue method 228 C," Standard Methods for the Examination of Water and Wastewater, 13th Ed, Vol.(Washington, D.C.: American Water Works Association, 1971), p. 558.

13. G. G. Geesey, "Survival of microorganisms in low nutrient waters," in Biological Fouling of Industrial Water Systems: A Problem Solving Approach, eds. M. W. Mittelman and G. G. Geesey (San Diego: Water Micro Associates, 1987), p. 1-23.

TABLES

Table 1. Chemical composition of carbon steel 1020.

AISI-SAE designation	C	Mn	P max	S max	Fe
1020	0.17-0.23	0.3-0.6	0.04	0.05	balance

Table 2. Water chemistry and bacterial counts in stagnant aerobic Key West seawater.

Days Exposure	pH	Sulfide (ppm)	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
0	8.02	<0.01	4	3	4	0
60	7.33	<0.01	1	1	1	1
258	7.23	0.13	2	-	1	-
396	7.29	0.30	4	3	1	0

Table 3. Water chemistry and bacterial counts in stagnant anaerobic Key West seawater.

Days Exposure	pH	Sulfide (ppm)	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
0	6.23	<0.01	4	3	4	0
48	6.79	0.52	3	5	5	3
246	7.07	0.65	2	3	2	4
396	7.08	0.50	3	4	4	5

Table 4. Water chemistry and bacterial counts in sloshing aerobic Persian Gulf seawater.

Days Exposure	pH	Sulfide (ppm)	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
0	7.63	<0.07	7	8	8	7
56	-	-	3	3	3	0
102	8.08	0.14	3	0	0	0
144	-	-	3	0	0	0

Table 5. Water chemistry and bacterial counts in sloshing anaerobic Persian Gulf seawater.

Days Exposure	pH	Sulfide (ppm)	Aerobes (10) ^x	Anaerobes (10) ^x	APB (10) ^x	SRB (10) ^x
0	7.63	<0.07	7	8	8	7
56	-	-	3	3	3	4
102	8.28	0.21	3	3	1	5
144	-	-	3	1	1	5

Table 6. Water chemistry and bacteria counts after 14 day fill cycle for all chambers in the alternating immersion exposure of Key West seawater (collected on exposure day 98).

Exposure (Fill/Drain Cycle)	pH	Sulfide (ppm)	Aerobes (10)^x	Anaerobes (10)^x	APB (10)^x	SRB (10)^x
<i>Natural Seawater</i>	8.02	<0.03	4	3	4	0
Aerobic/Aerobic	7.42	0.12	1	2	2	5
Deoxy/Aerobic	7.29	0.18	3	3	3	0
Deoxy/Deoxy	6.57	0.20	3	1	2	3

FIGURES

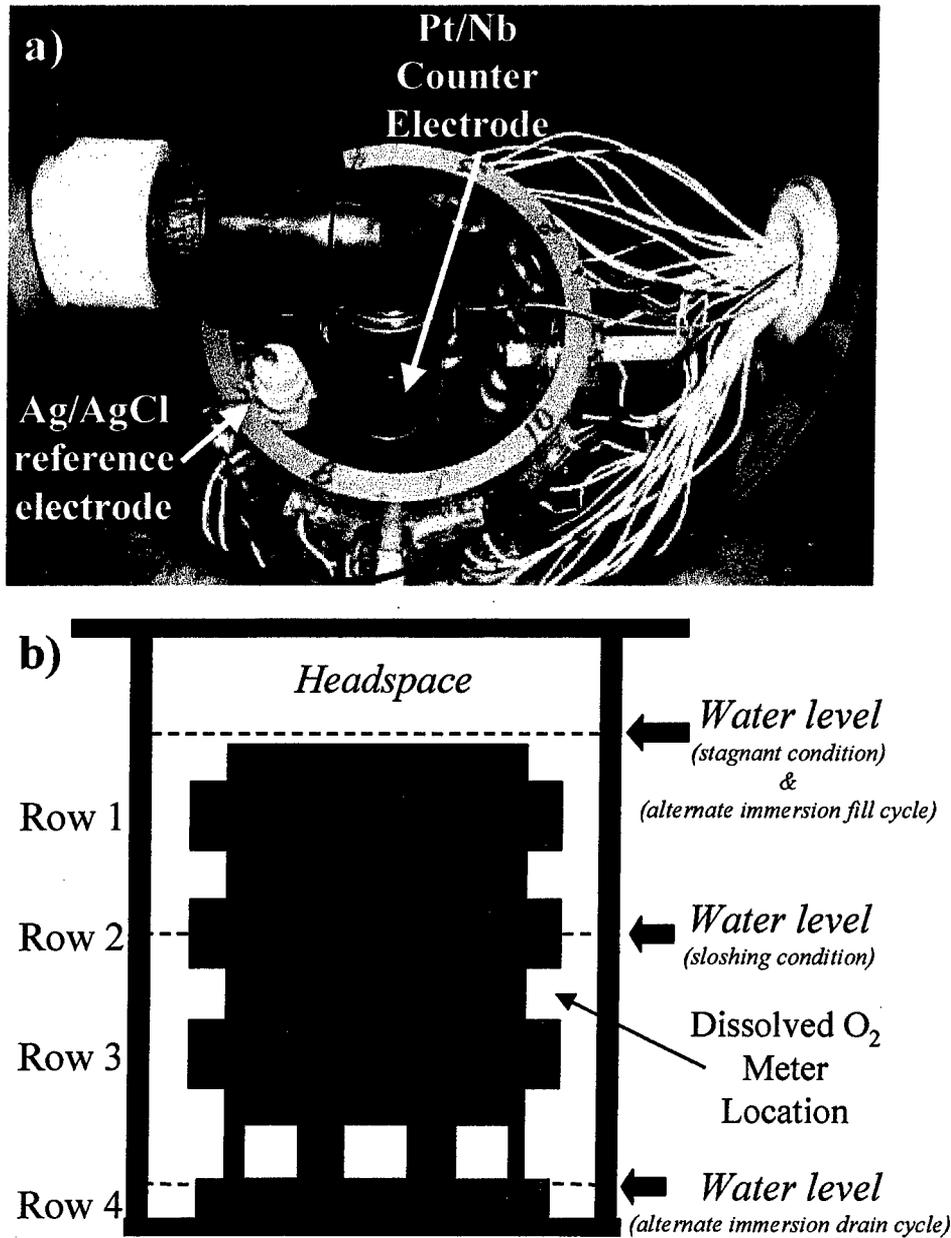


Figure 1. a) Experimental chamber used to examine rates and mechanism of corrosion. b) Schematic of coupon holder and individual side rows 1 – 3 and bottom row 4.

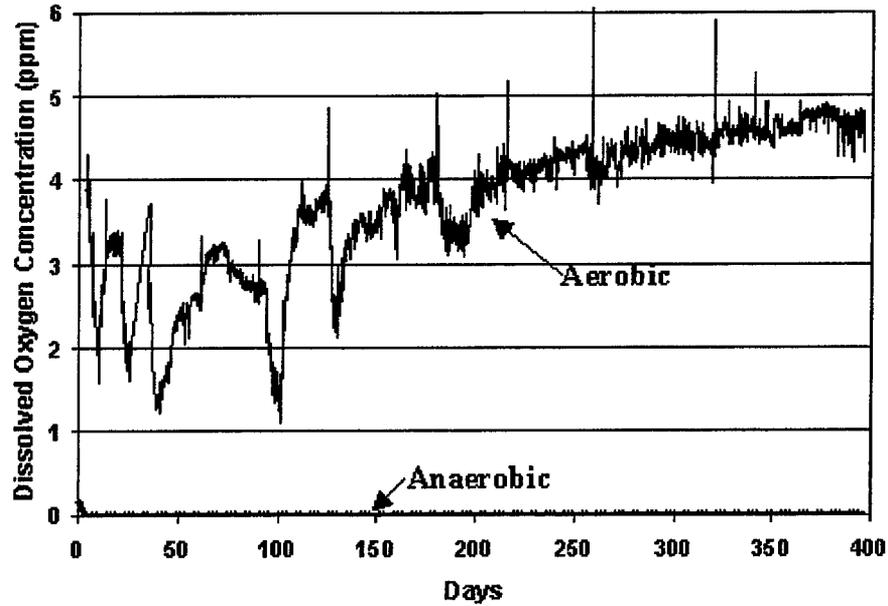


Figure 2. Dissolved oxygen concentration (ppm) over time for both aerobic and anaerobic stagnant conditions in Key West seawater. Periodic upward spikes in the aerobic data indicate coupon removal.

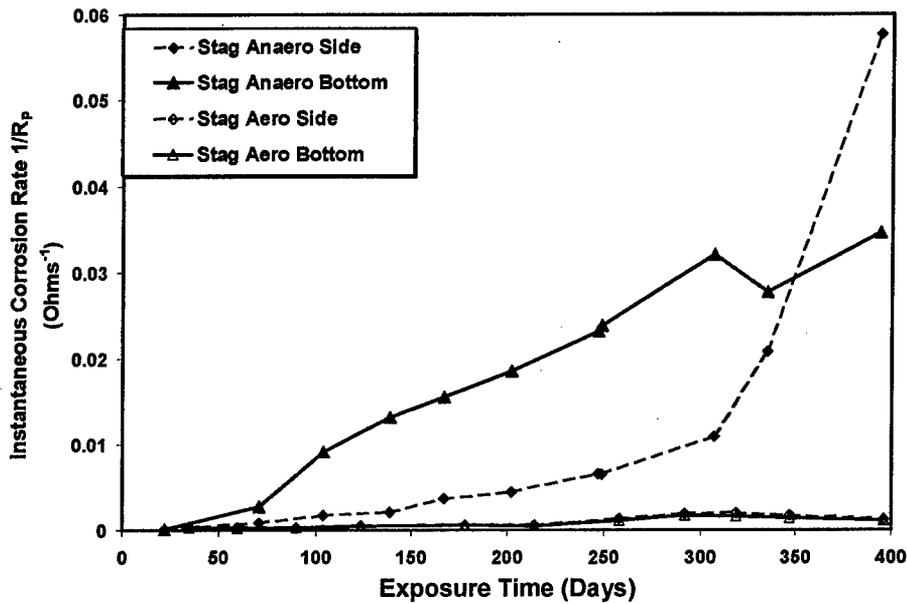


Figure 3. $1/R_p$ (instantaneous corrosion rate) over time (days) for C1020 coupons in stagnant aerobic and anaerobic Key West seawater. Aerobic conditions are included with anaerobic data (b) to indicate the much higher rates in anaerobic conditions. Average values displayed.

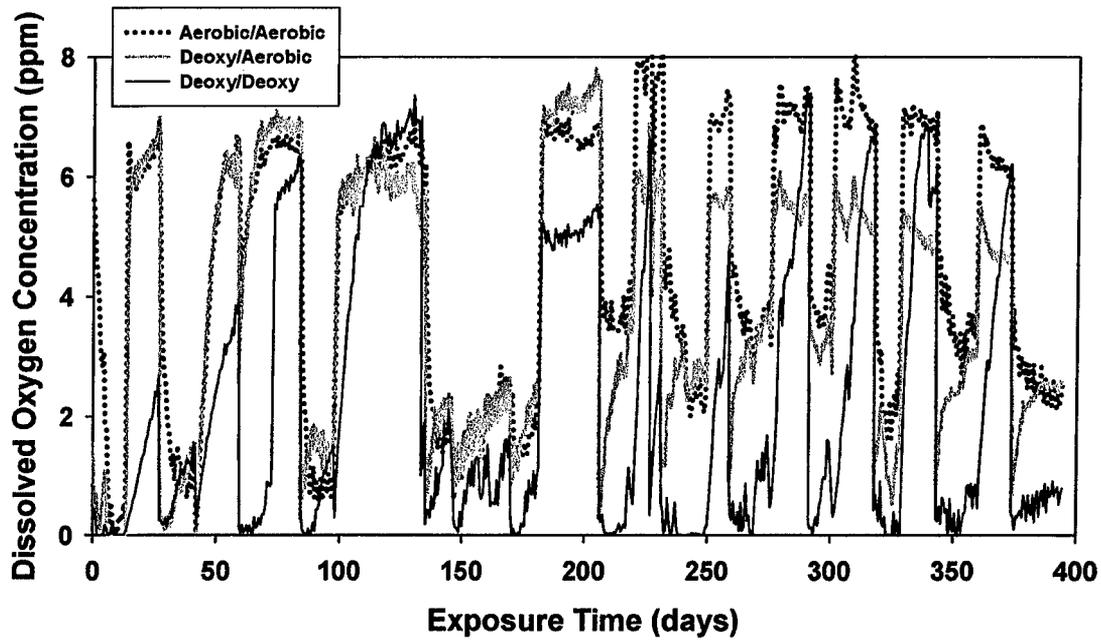


Figure 4. Key West seawater dissolved oxygen (ppm) measured in the three different alternate immersion exposures.

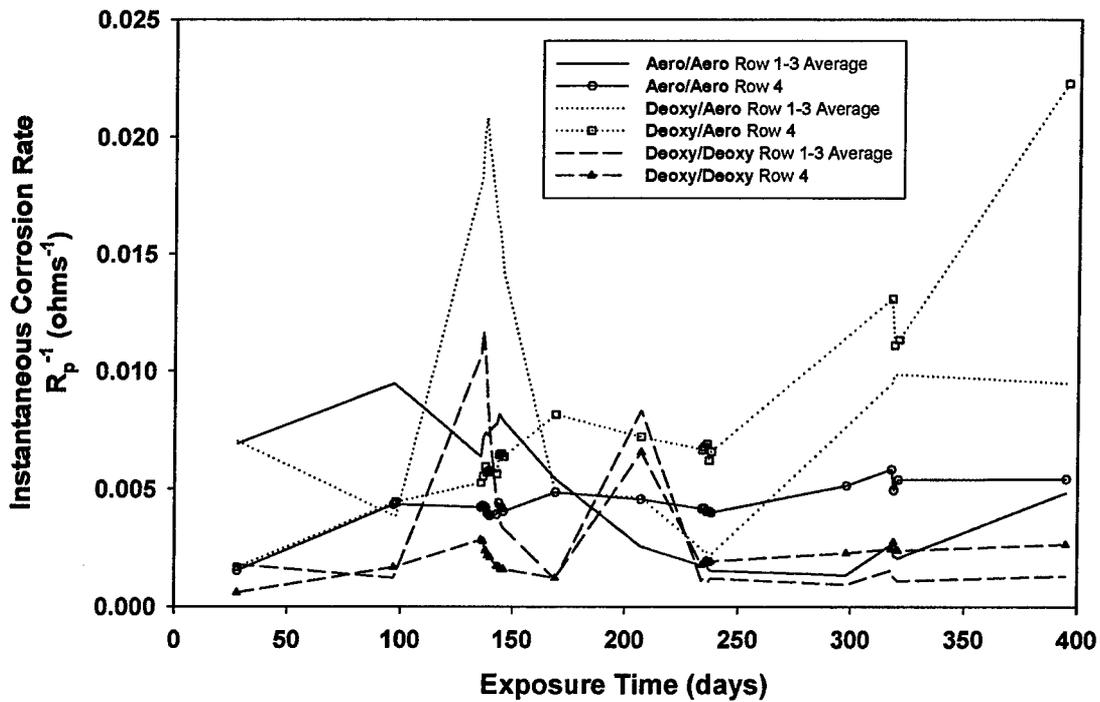


Figure 5. Instantaneous corrosion rates ($1/R_p$, ohms⁻¹) of side (average of rows 1, 2, and 3) and bottom row 4 coupons for the three alternate immersion conditions in Key West seawater. Shaded areas indicating drain cycle periods.

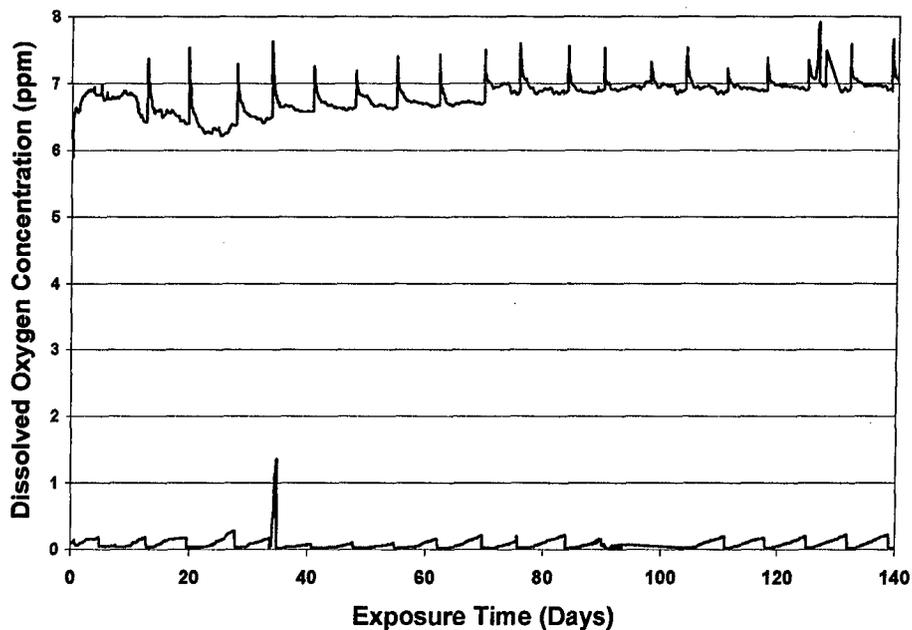


Figure 6. Dissolved oxygen concentration (ppm) over time for both aerobic and anaerobic sloshing conditions in Key West seawater.

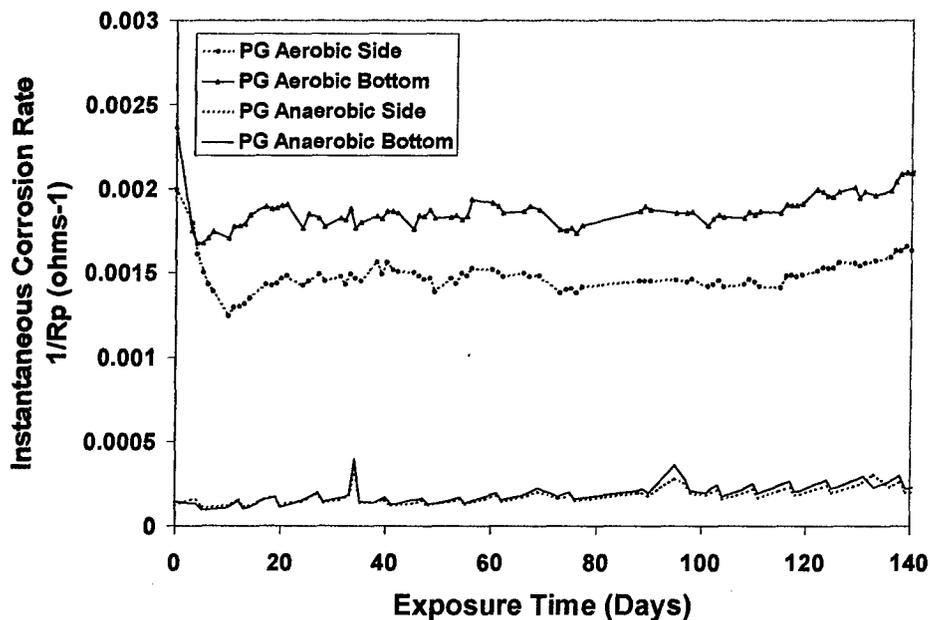


Figure 7. Instantaneous corrosion rates ($1/R_p$ ohms⁻¹) of side (average of rows 1, 2, and 3) and bottom row 4 coupons for aerobic and anaerobic sloshing Persian Gulf seawater exposure. Shaded areas indicating drain cycle periods.

REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0188*

The public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing the burden, to the Department of Defense, Executive Services and Communications Directorate (0704-0188). Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number.

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE (DD-MM-YYYY) 07-06-2006		2. REPORT TYPE Conference Proceedings (not refereed)		3. DATES COVERED (From - To)	
4. TITLE AND SUBTITLE Carbon Steel Corrosion in Key West and Persian Gulf Seawaters at Varying Oxygen Concentrations				5a. CONTRACT NUMBER	
				5b. GRANT NUMBER	
				5c. PROGRAM ELEMENT NUMBER PE0601153N	
6. AUTHOR(S) Richard I. Ray, Jason S. Lee, Brenda J. Little, Edward J. Lemieux				5d. PROJECT NUMBER	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER 73-5052-15	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Naval Research Laboratory Oceanography Division Stennis Space Center, MS 39529-5004				8. PERFORMING ORGANIZATION REPORT NUMBER NRL/PP/7303-05-5317	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Office of Naval Research 800 N. Quincy St. Arlington, VA 22217-5660				10. SPONSOR/MONITOR'S ACRONYM(S) ONR	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S)	
12. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release, distribution is unlimited.					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT Corrosion of 1020 carbon steel coupons in natural Key West and Persian Gulf seawaters was directly related to exposure conditions. Exposure conditions included the following: stagnant and sloshing, oxygenated and deoxygenated seawater, in addition to, alternating immersion and drying with oxygenated and deoxygenated seawaters. Microbial populations in the two waters fluctuated with exposure conditions. Of all of the exposure conditions, the anaerobic stagnant Key West seawater exposure produced the highest corrosion rates and sulfide levels.					
15. SUBJECT TERMS Carbon steel; seawater; ballast; deoxygenation; alternate immersion; SRB; sulfide					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UL	18. NUMBER OF PAGES 16	19a. NAME OF RESPONSIBLE PERSON Jason S. Lee
a. REPORT Unclassified	b. ABSTRACT Unclassified	c. THIS PAGE Unclassified			19b. TELEPHONE NUMBER (Include area code) (228) 688-4494