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DETERIORATION OF STRUCTURAL INTEGRITY DUE TO CHEMICAL TREATMENT OF BALLAST WATER

FINAL REPORT

May 2005

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REPORT/PROPOSAL: Deterioration of Structural Integrity due to Chemical Treatment of Ballast Water

DATE: May 2005

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EXECUTIVE SUMMARY

BMT Fleet Technology Limited was tasked by Transport Canada under Solicitation No. T8275-020463/001/SS on behalf of the Ship Structures Committee, to evaluate the "Deterioration of Structural Integrity due to Chemical Treatment of Ballast Water Techniques." A significant amount of research and development has been conducted worldwide into the efficacy of various types of ballast water treatment methodologies from a biological effectiveness stand point and in February of 2004, IMO agreed on the first international ballast water management convention which contains biological efficacy standards. While there has been concern expressed over the global strength issues of deep water ballast exchange endangering the safe operations of ships, none of the research to date has examined the long term integrity aspects of structures exposure to ballast water treatment technologies specifically chemical agents.

The project had been divided into several tasks starting with an extensive literature review. The review looked at the corrosion of steel in fresh and salt water, the effect of pH and temperature on corrosion and the role of oxygen. The review indicated that the corrosion rates for steels exposed to sea water vary from 0.02 to 0.37mm/year with the average rate of approximately 0.1mm/year. The corrosion rate in an open natural system is controlled by the diffusion rate of oxygen from the bulk solution to the steel surface and the composition of the carbon steel that is being attacked has no effect on rates. Initially the corrosion rates are higher and are at least 2.5 times the subsequent steady state rate that begins earlier than one month following exposure according to some studies.

The effect of pH on corrosion rates was also reviewed and for soft tap water with NAOH or HCl as it was observed that between pH 4 and 10, there is no effect on corrosion rate; however, with a combination of additives, the corrosion rates can vary dramatically in the pH range of 4 and 10. Corrosion rates are also observed to increase with temperature. When corrosion is controlled by diffusion of oxygen, the corrosion rate at a given O_2 concentration doubles between 0 and 30°C. Other factors that accelerate bulk diffusion, such as agitation and wetting and drying cycles that afford atmospheric oxygen better access through the meniscus in the drying stage, also accelerate corrosion. These factors account for the enhanced attack observed at the waterline and splash zone in marine environments. Studies indicate that the corrosion rate also increases with the salinity and reaches a maximum with salt concentration of around 1 ppt, however, after that the corrosion rate decreases with salt concentration and this has been linked to the reduction of dissolved oxygen in water after the salt concentration exceeds 1 ppt.

The information on the microbiologically-influenced corrosion (MIC) has also been presented in the literature review with more focus on the anaerobic corrosion. The issues such as the mechanisms involved in anaerobic microbial corrosion and more importantly, the role of oxygen, has been discussed along with different experimental programs that have been carried out to study MIC. De-oxygenation is one of the techniques being proposed to prevent biofilm production and thus reduce microbiological-induced corrosion. However, there is a general agreement that alternating conditions of de-oxygenation and oxygenation resulting from emptying and filling up of the ballast tanks may result in much higher corrosion rates.

Information on the effects of the candidate agents likely to be added to combat invasive species on the corrosion of steels was compiled. In general, these agents can be grouped into two groups; oxidizing agents and non-oxidizing agents. The chemicals in the oxidizing group include hypochlorite, peroxide and ozone. Chemicals in the non-oxidizing group may include Gluteraldehyde that is non-oxidizing like formaldehyde. SeaKleen™ (a trade name for a chemical biocide) is a quinone and quinones are inert. It has been suggested that one of the bi-products produced (in very small amounts) is hydrogen peroxide, an oxidant.

The effect of hypochlorite on the corrosion of steels has been studied for both the fresh and salt water environment and there seems to be no difference in the corrosion rates in both environments. However, differences have been observed in the case of ozone in fresh and salt water environments primarily because ozone reacts with the chemical constituents of the sea water and thus its half life is short. Today, as environmental concerns grow about the use of chlorine for industrial oxidizing applications, other alternatives such as hydrogen peroxide are being explored and tested.

From the literature review and discussions with the research community, two potential agents, SeaKleen™ and PERACLEAN® OCEAN, were selected for further investigation. An experimental protocol was developed for the testing program. The effect of SeaKleen™ and PERACLEAN® OCEAN on the pH of fresh water and salt water was examined. The corrosion testing with each agent was carried out for 30 days using tap water and salt water of 15 ppt and 35 ppt salinity. Bare steel and coated steel with scribe marks to simulate defects in coatings as per ASTM D1654 were tested. Four ballast tank conditions, submerged, humid, buried and splash zones were also simulated in the present corrosion testing program.

Testing demonstrated the potential for increased corrosion from oxidising agents. It is recommended that corrosion tests be carried out for longer periods than the 30-day tests used for the present program and the testing should also be carried out for different time intervals to determine the corrosion rates.

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1. INTRODUCTION

The introduction of Aquatic Nuisance Species (ANS) via ships' ballast water is becoming an increasingly detrimental ecological issue. Numerous mechanical, physical and chemical treatments that may reduce ANS introductions through ballast water medium are presently being investigated.

The principal direction of research and development conducted world wide has been into the biological effectiveness of various type of ballast water treatment methodologies. In February of 2004, IMO agreed on the first international ballast water management convention[1] and this convention introduced biological efficacy standards. At this time, there are no known single technologies which can effectively meet all aspects of the IMO convention standards and it is generally agreed that a multi-stage methodology will be the most effective against all taxa ranging from multi-celled organisms, including resting stages, through to single cell bacteria and viruses. In many cases, the secondary stage of these technologies is chemical agent based. While there has been concern expressed over the global strength issues of deep water ballast exchange endangering the safe operations of ships, none of the research to date has examined the long term integrity aspects of structures exposure to ballast water treatment technologies, specifically chemical agents.

SeaKleen™ and PERACLEAN® OCEAN are possible solutions to the ANS issue. However, as there was concern they may have damaging effects on the integrity of ship structures, this study was conducted. This study investigates the effects of SeaKleen™and PERACLEAN® OCEAN on the coating systems and the degree of corrosion imparted on ships' bare steel and demonstrates the integrity of ships' structures in a simulated environment.

Aqueous corrosion of steels in natural waters depends entirely upon the availability of oxygen [1]. The rate of corrosion can be increased by many factors including the presence of oxidants. Moreover, corrosion in a ballast tank environment is a function of temperature, agitation of the liquid, the wetting and drying cycles and structural strain. These factors account for enhanced attack observed at the waterline and splash zone in marine environments. Oxidizing agents added to oxygenated water have varying influences on the corrosion rates of steel. Anions, such as chromate or permanganates, are effective in inhibiting the rate of corrosion. The effects of SeaKleen™ and PERACLEAN® OCEAN on corrosion rates are not known at the typical exposure rates and environments of a ballast tank situation. This project examines the effect of SeaKleen™ and PERACLEAN® OCEAN in a fresh water ballast tank environment.

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[1] International Convention for the Control and Management of Ships' Ballast Water and Sediments requires discharges of ballast water to contain less than 10 viable organism greater than 50 microns per cubic meter, less than 10 viable organism between 10 and 50 microns per millilitre and carry less than 1 Vibrio Colerea, 250 E-coli and Enterococci colony forming unit per 100 millilitre.

2. LITERATURE REVIEW

2.1 Corrosion of Steels in Natural Waters

Aqueous corrosion of steels in natural waters depends entirely on the availability of oxygen [1]. When the source of oxygen is air in an open natural system, the rate of attack has been observed to average approximately 0.1mm/year (0.004 inches/year or 4mpy) at ambient temperatures [2] and this rate is controlled by the diffusion rate of oxygen from the bulk solution to the steel surface. Consequently, the composition of the carbon steel that is being attacked has no effect on rates. In short term exposures, the rate tends to be higher on clean bare surfaces but the rate decreases with longer exposures as surface scales build up. This trend is clearly shown in the recent compilation of data by Matsushima [3] reproduced below, Figure 2.1, for steels exposed to seawater for up to 40 years. Matsushima points out that the rates vary from 0.02 to 0.37mm/year with the average rate of approximately 0.1mm/year.

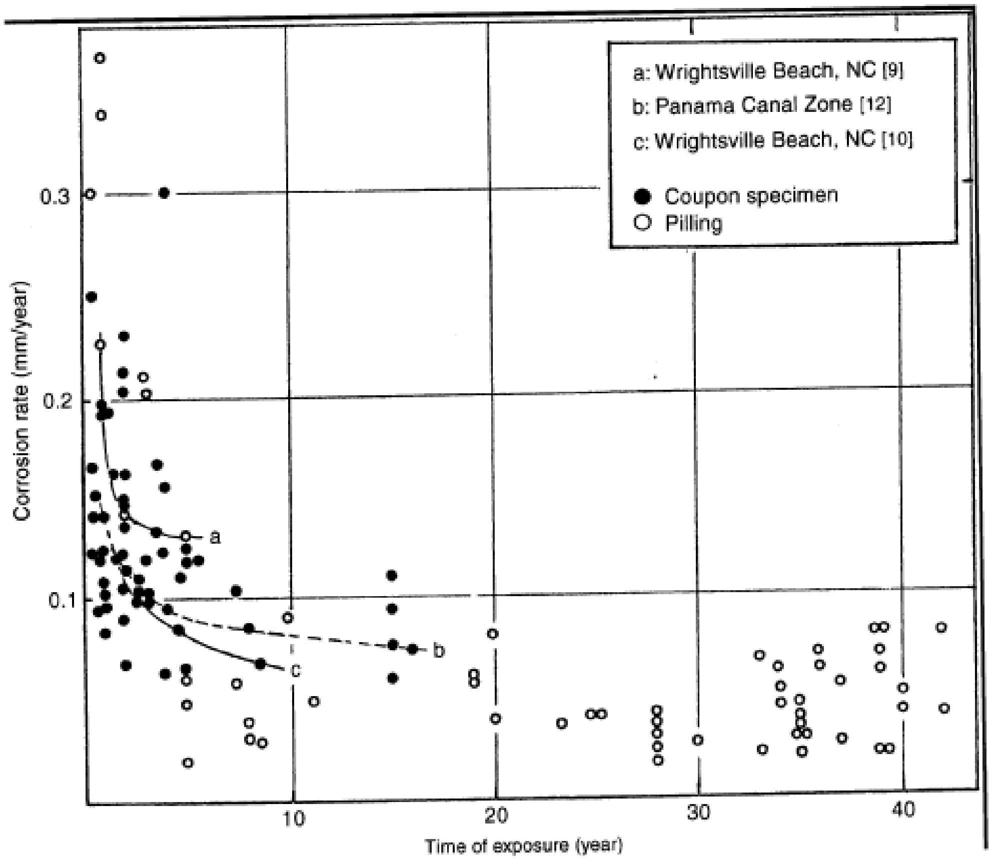

Figure 2.1: Compilation of Data by Matsushima [3] for Steels Exposed to Sea Water for up to 40 Years

In laboratory tests, to compare experimental variables in a controlled way, much shorter exposures are usually employed with the duration of the test only sufficient to give a measurable weight change with the apparatus available. In these cases, initial rates may be very high, but it is generally not clear when the transition to linear kinetics begins.

For example, Uhlig [4] suggests that the high initial rate diminishes over a period of days to the steady-state value, while Larrabee and Mathay [5] indicate that the steady state for air saturated raw city water (pH 6.2) at high temperature (150°F) was reached in 15 minutes. Recent seawater exposure data of Jeffrey and Melchers [6] for two trials (Trial 1 commencing in winter and Trial 2 in summer) are reproduced in the following graph, Figure 2.2. When adjusted for temperature, these results suggest that the steady-state rate begins earlier than one month and that the initial rate is at least 2.5 times the subsequent steady-state rate.

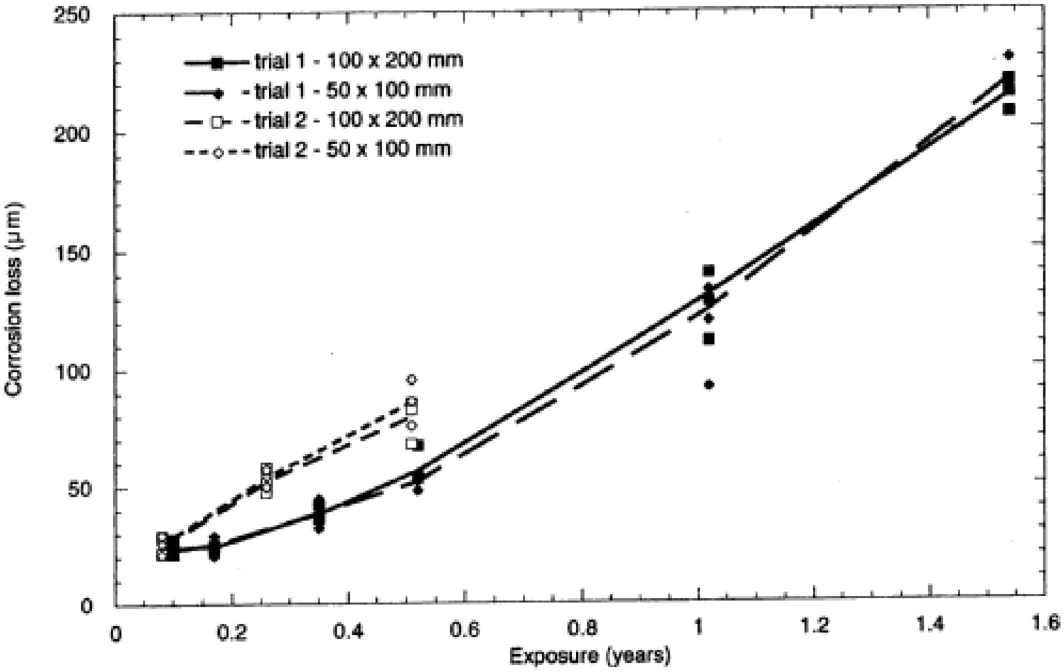

Figure 2.2: Sea Water Exposure Data of Jeffrey and Melchers [6] for Two Trials (Trial 1 Commencing in Winter and Trial 2 in Summer)

2.2 Effects Related to pH

The effect of pH on corrosion rates in aerated waters is well known in the case of laboratory tests using high purity water or soft natural water. Between pH 4 and 10, there is no effect on corrosion rate. However, Matsushima [7] has reviewed the effect of pH in fresh water environments of various water qualities. His results are reproduced below, Figure 2.3, where:

a = soft tap water with NaOH or HCl additions

b = aerated water + 2.5mmol/L $NaHCO_3$/2.5mmol/L $NaOH/CO_2$ - 16 days

c = aerated water + 2.5mmol/L $NaHCO_3$/0.5mmol/L $NaOH/CO_2$ - 16 days

d = $NaHCO_3/CO_2$ - 3 days

e = soft water + $NaOH/CO_2$

It should be noted that the waters for curves b, c and d contain no calcium, unlike natural waters, but the magnitude and direction of the trends for curves b to e are counterintuitive since higher pH values are expected to stabilize protective layers.

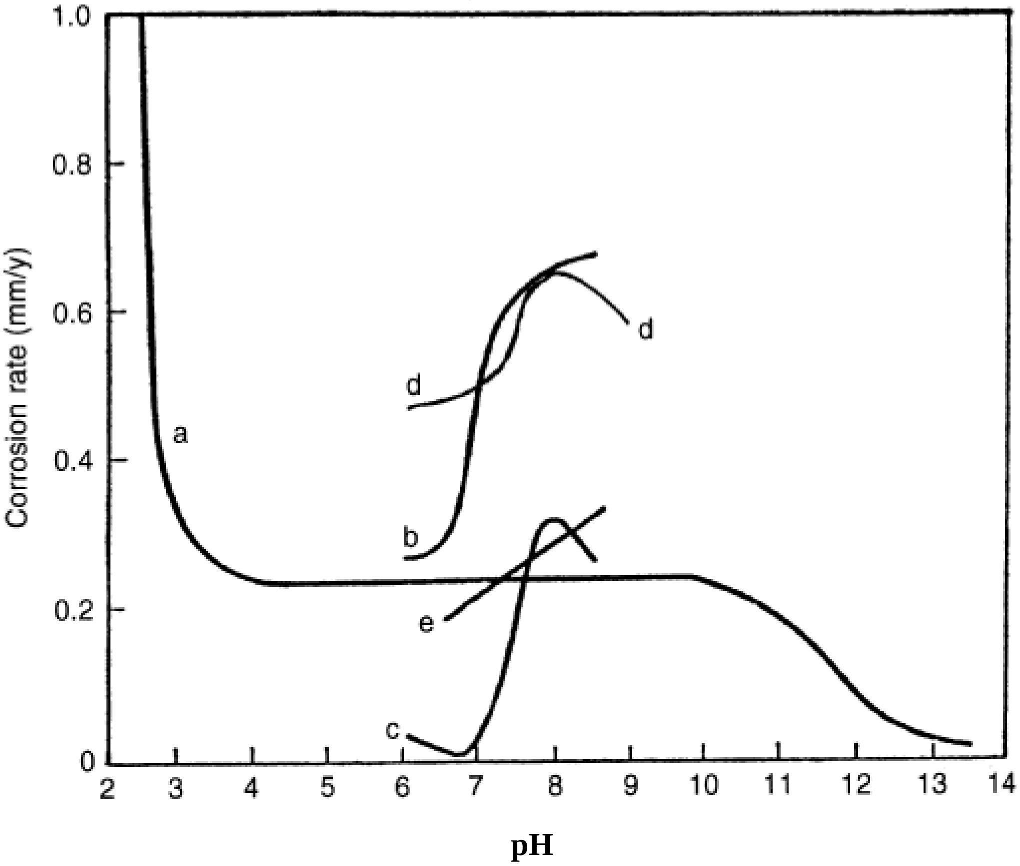

Figure 2.3: Matsushima's [7] Results of the Effect of pH in Fresh Water Environments of Various Water Quality

2.3 Effects of Temperature

When corrosion is controlled by diffusion of oxygen, the corrosion rate at a given O_2 concentration doubles between 0 and 30°C [8] because diffusion rates increase with temperature, as in Figure 2.4. In an open vessel, allowing dissolved oxygen to escape, the rate increases linearly to about 80^{o}C and then falls to a low value at the boiling point.

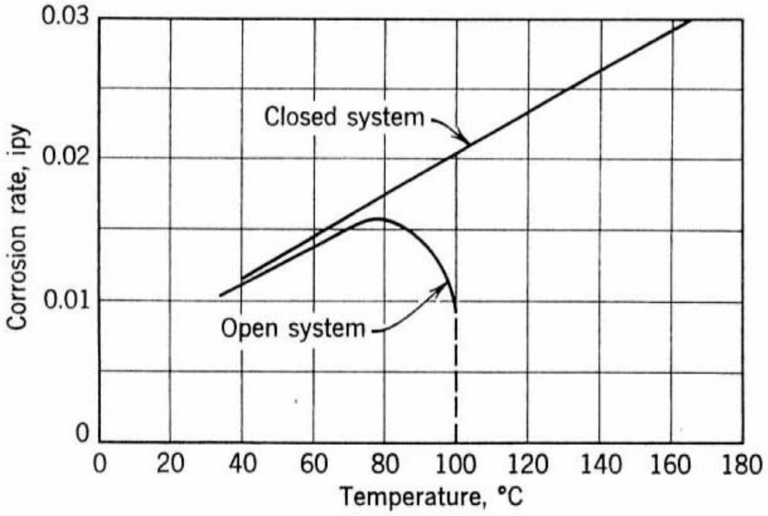

Figure 2.4: Effect of Temperature on Corrosion of Iron in Water Containing Dissolved Oxygen

Agitation of the liquid reduces the thickness of the boundary layer and wetting and drying cycles can afford atmospheric oxygen better access through the meniscus in the drying stage to accelerate bulk diffusion of oxygen and corrosion. These factors account for the enhanced attack observed at the waterline and splash zone in marine environments.

2.4 Effect of Salinity

Corrosion rate increases with salinity [7b] however, as mentioned earlier the aqueous corrosion of steels in natural waters depends entirely on the availability of oxygen [1]. Figure 2.5 shows a plot of corrosion rate and dissolved oxygen versus salinity [7b]. Initially the corrosion rate increases with the increasing salinity until it reaches a peak at about 1 ppt (parts per thousand) with dissolved oxygen remaining constant at about 9 mg/litre. However, the corrosion rate decreases thereafter with the increase in salinity. This decrease in corrosion rate has been attributed to the decrease in the concentration of dissolved oxygen which reduces to about 1 mg/l at about 30 ppt salinity. This graph also illustrates that fresh water and seawater may not be as aggressive as brackish waters containing 0.1 percent chloride ion concentration.

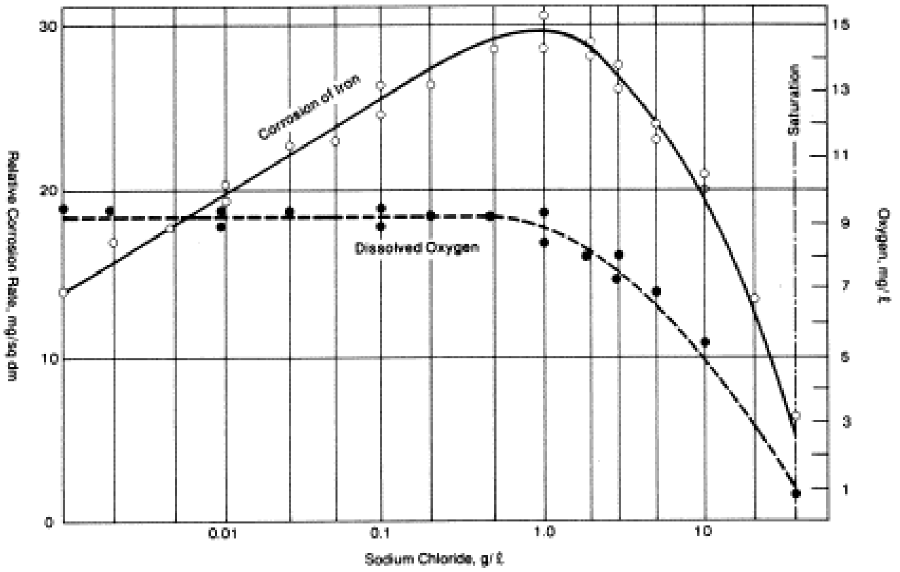

Figure 2.5: Variation in Corrosion of Iron as a Function of Salinity and Dissolved Oxygen

2.5 Effects of Additives

Oxidizing agents added to oxygenated water may have positive or negative effects on corrosion rates of steels. Some anions, such as chromates or permanganates, are effective inhibitors and result in corrosion rates approaching zero. Others such as Chlorine are known to accelerate corrosion; however, other conditions dictate the extent of this acceleration. The effects of hypochlorite (Chlorine), cupric ions and ozone tend to be positive on corrosion rates and are being studied at present by BMT Fleet Technology Limited of Kanata, Ontario [9] to simulate ballast tank corrosion. Other researchers have examined the effects of various agents on corrosion rates; however, few have been directed to the conditions found in a ship's ballast tank.

In general, the candidate agents that are likely to be added to combat invasive species can be grouped into two groups; oxidizing agents and non-oxidizing agents. The most common chemicals in the oxidizing group include chlorine and chlorine dioxide used extensively in the pulp and paper industry and researched extensively in high concentrations. Chloramine (produced by combining chlorine and ammonia) is also an oxidizing agent but is reported to be more stable than chlorine and therefore longer lasting.

In a ballast tank situation, chloramine should behave like other oxidizing biocides although the decay rate may affect the overall exposure time. Today, as environmental concerns grow about the use of chlorine for industrial oxidizing applications, hydrogen peroxide, with its harmless by-products, may provide an attractive alternative,

Chemicals in the non-oxidizing group may include Gluteraldehyde, a first cousin to formaldehyde. It is non-oxidizing like formaldehyde and inert.

SeaKleen™ (a trade name for a chemical biocide) is a quinone and quinones are inert and appear to be organic chemicals consisting of a benzene ring with attached reactive oxygen. It has been suggested that one of the by-products produced (in very small amounts) is hydrogen peroxide, an oxidant. The potential for accelerated corrosion is the same as with hypochlorite or ozone.

2.5.1 Hypochlorite

Hypochlorite ion has no inhibiting effect and, to the contrary, acts as an additional oxidizing agent to accelerate the corrosion of steel. Because it is a common chemical used in many applications where steel pipes are used, there is much literature devoted to the effects of corrosion in the presence of Hypochlorite. A prime example of the application and focus of research is in the pulp and paper industry. Because hypochlorite solutions are unstable at neutral and lower pHs, they normally contain excess alkali, however, a typical environment where hypochlorite is found in a bleach plant washer at a concentration of 30ppm and 40°C [5], the pH was reported to be 9. It is not clear, based on other limited data from the pulp and paper industry, what degree of acceleration can be expected but Bennett [12] states that in acidic and neutral solutions, corrosion increases with time of wetness, temperature, acidity and oxidizing power and rates as high as 0.625 mm/yr can be experienced in a worse case scenario.

When used as a biocide at room temperature and pH 8.5, Franklin et al [13] found that hypochlorite at two parts per million (ppm or μg/l) had little effect on the corrosion rate of carbon steel because the biofilm was not disturbed, but at 16ppm a marked increase in corrosion was noted.

However, in applications more akin to the ballast water treatment case, less data is available with less dramatic results found, for example, when hypochlorite (of unknown concentration) was used as a biocide in completely de-aerated seawater for injection at Prudhoe Bay, a residual corrosion rate of 0.07mm/yr [8] was attributable to the hypochlorite after corrosion associated with microbial action had been eliminated. Moreover, work by this proponent [9] demonstrated that corrosion in the presence of low concentrations of hypochlorite was observed only in the aggressive conditions of the ballast tank splash zones; in other areas no significant increase was observed.

Laboratory studies of corrosion rates as a function of pH and temperature have been carried out on carbon steels at high concentrations of calcium hypochlorite by Maradov [15]. The results are listed below for two steels with different carbon contents and show no distinction between steel compositions.

Table 2.1: Corrosion Rates of Carbon Steel St10 (0.105%C) and St45 (0.46%C)

Active Chlorine %	pH	Temperature °C	Rate mm/yr St10	Rate mm/yr St45
42	7	20	0.186	0.230
42	7	40	0.208	0.573
40	9	20	0.438	0.345
40	9	60	0.924	1.457
44	9	20	0.422	0.281
44	9	60	1.624	0.378

It is interesting to note that even in very concentrated solutions corrosion rates at room temperature are not excessive compared to the 0.1mm/yr expected in natural waters

The decomposition products of hypochlorites at pH above approximately 7.5 are described by the following equation [10] and the reaction products remain in solution.

$$2ClO^- \rightarrow O_2 + 2Cl^-$$

2.5.2 Peroxide

Peroxide is a strong oxidizer, with a standard electrode potential of 0.682 V (vs. standard hydrogen electrode [SHE]) compared to ozone at 2.07 V (vs. SHE) and chlorine at 1.36 V (vs. SHE) [4]. Hydrogen peroxide can be formed by the oxidation of water according to the reaction $2H_2O \rightarrow H_2O_2 + 2H+ + 2e$ at noble potentials or by the reduction of oxygen dissolved in the solution according to the reaction $O_2 + 2H+ + 2e \rightarrow H_2O_2$ at more active potentials. Hydrogen peroxide therefore appears to be unstable and reducible to water in one potential range and unstable and oxidizable to oxygen in another. It has been found that these two potential ranges have a common area in which hydrogen peroxide is doubly unstable and can decompose into water and oxygen according to the reactions:

$$\begin{array}{ll} H_2O_2 + 2H^+ + 2e & \rightarrow 2H_2O \\ H_2O_2 & \rightarrow O_2 + 2H^+ + 2e \\ \hline \end{array}$$

$$2H_2O_2 \rightarrow 2H_2O + O_2$$

In the domain of double instability, and only in this domain, hydrogen peroxide can decompose chemically into water and oxygen.

Consequently, if a solution of hydrogen peroxide is in contact with a metallic surface whose electrode potential is situated in the domain of double instability, the hydrogen peroxide can decompose spontaneously into water and oxygen. Conversely, if hydrogen peroxide decomposes into water and oxygen on a metallic surface, then this surface must necessarily exert an electrode potential in the domain of double instability.

While the corrosion behaviour of highly alloyed corrosion resistant stainless steels used in bleach plants in the pulp and paper industry has been studied extensively, the amount of literature on the corrosion of carbon steels exposed to solutions containing peroxide is both limited and conflicting.

For example, Pourbaix [18] investigated the action of hydrogen peroxide at two concentrations (300 and 3000ppm) in pure water on high carbon steel. After several hours in the diluted peroxide solution, the potential ($E = -0.2V$) and pH (5.7) fell in the domain where the corrosion of iron and the reduction of hydrogen peroxide occurred. Therefore, corrosion of the steel without evolution of gas took place according to the following reactions:

$$Fe \rightarrow Fe^{++} + 2e$$

$$H_2O_2 + 2H^+ + 2e \rightarrow 2H_2O$$

$$Fe + H_2O_2 + 2H^+ \rightarrow Fe^{++} + 2H_2O$$

For the more concentrated hydrogen peroxide solution, the potential and pH ($E = 0.72V$ and pH = 3.4) initially fell in the domain of iron passivity and double instability of hydrogen peroxide. Consequently, the iron passivated with essentially zero corrosion rate and gaseous oxygen evolved on the surface according to the reaction $2H_2O_2 \rightarrow 2H_2O + O_2$.

As a result of the decomposition of peroxide by this reaction, the concentration of peroxide eventually fell below the critical value required to maintain the domain of iron passivity and the system reverted to the domain of iron corrosion typical of that observed with the lower initial peroxide concentration. Consequently, Pourbaix's results show that hydrogen peroxide at any concentration in pure water will eventually lead to accelerated corrosion of iron.

More recently, to make up for a lack of quantitative corrosion data, Mathiyarasu et al [19] exposed mild steel coupons polished with 4/0 emery paper in natural pond water containing three levels of sodium peroxide for seven (7) days. The pond water had the following composition:

pH	6.8
Dissolved oxygen	6.2 mg/l
Chloride	160ppm
Sulphate	67ppm
Calcium	130ppm
Magnesium	86ppm

Total hardness	216ppm
Dissolved solids	539 mg/l
Suspended solids	197 mg/l
Total Solids	736 mg/l
Total alkalinity	250

Using a weight loss methodology, corrosion rates of 2.74, 1.29 and 0.61mpy were measured at sodium peroxide concentrations of 300, 400 and 500ppm, respectively. The authors propose the reaction $Na_2O_2 + H_2O \rightarrow 2H_2O_2 + 2NaOH$ to account for the increase in pH which they believe was responsible for the observed decrease in corrosion rate with increasing sodium peroxide concentration.

These authors also observed that the biocide efficiency of Na_2O_2 reached 100% only at the highest concentration of 500ppm.

2.5.3 Ozone

Ozone is a strong oxidizer, with a standard electrode potential of 2.07 V (vs. standard hydrogen electrode [SHE]). It is an even stronger oxidizer than chlorine that has a standard electrode potential of only 1.36 V (vs. SHE) [23]. Depending upon the pH of the solution in which it is dissolved, molecular ozone will either react directly with components in solution or decompose into hydroxyl free radicals, oxygen and hydroxides as seen below:

$$20_3+H_2O+e^- \rightarrow OH^\bullet + 5/2\ O_2+OH^-$$

The hydroxyl free radical is a more powerful oxidizer than ozone, with a potential of 2.80 V (vs. SHE) [24]. At pH values above 7.5, much of the ozone will decompose into hydroxyl radicals that will react rapidly with water contaminants. Below this pH, molecular ozone is stabilized and only a small fraction of the ozone will be converted into hydroxyl free radicals. Care must be taken when using ozone at elevated pH levels due to the rapid reactions that can occur between the hydroxyl free radicals and water contaminants, with no beneficial effects of disinfection or oxidation occurring.

2.5.3.1 Ozone Production

Ozone is produced directly from molecular oxygen, either through ultraviolet radiation or from corona discharge. Ultraviolet radiation uses UV wavelengths of either 254 nm or 186 nm. If air is used as a source of molecular oxygen, these wavelengths produce either 0.01% ozone by weight in air or 0.1%, respectively [24]. Corona discharge is by far the most popular method of ozone production, but the most inefficient. It utilizes either dry air or oxygen that is subjected to a high voltage between two electrodes. Only about 10% of the energy supplied is used to make ozone, while the remainder is lost as heat [25]. The amount of ozone produced in this system is regulated by the amount of power supplied to the system, as well as the feed gas used. Using air, 1 to 3.5% ozone by weight can be produced, while 6 to 12% can be produced using oxygen [24].

If air is used to produce the ozone, nitrogen oxides are formed during the discharge process. In the presence of water, hydrolysis of the nitrogen compounds results in the formation of nitric acid in minute amounts (0.003-0.005% by weight of the input gas). This reaction results in a reduction in pH when the ozonated gas is dissolved in aqueous solutions. The reduction in pH is so small, however, that in bulk solutions it will probably not affect the corrosivity of the solutions.

2.5.3.2 Ozone Solubility

The solubility of ozone in a solution depends on several factors:

- the concentration of ozone exiting the gas generator;
- the temperature of the solution;
- the ozone demand in the solution; and
- the pH of the solution.

The theoretical concentration of ozone in solution can be found using the concentration of ozone exiting the generator and Henry's Law [24]:

$$Y = [H][X]$$

Y = Concentration of gas in solution

X = Mole fraction of ozone in gas phase

H = Henrys Law constant

Using Henry's Law, ozone has a theoretical solubility of 10 times that of oxygen in pure water but in solutions other than pure water, it has been recorded more on the order of 1 to 1.5 times that of oxygen. This discrepancy between theory and practice is due to ozone depleting impurities in real solutions, which are not accounted for in Henry's Law, as well as the low partial pressure of ozone [25, 26].

The amount of ozone-demanding impurities in a solution affects the decomposition of ozone, with more impurities greatly decreasing the half-life. For pure water, the half-life of ozone is on the order of hours, while in normal water, the half-life is from 5 to 20 minutes. Impurities that can decrease the half-life include soluble iron, magnesia, and bromide, as well as microorganisms [24].

As was mentioned earlier, ozone will decompose into hydroxyl radicals at pH levels above 7.5. Increasing the pH above this value will cause the half-life of ozone to decrease significantly. At pH 10 the decomposition of ozone is so rapid that no residual ozone can be measured [24].

2.5.4 Corrosion Behaviour of Steel in Ozonated Waters

The amount of literature on the corrosion of steels exposed to ozonated solutions is both limited and conflicting. The main source of conflict is that the corrosion data is based on cooling tower water environments utilizing different environmental conditions and few scientific controls. At ozone concentrations of less than 0.3 mg/L, no significant difference has been reported for the steady state corrosion potentials of mild steel in aerated as opposed to ozonated solutions [27-30]. Above concentrations of 1 mg/L, ozone shifts the corrosion potential noble to the aerated corrosion potential [27, 29, 30, 31]. The literature values for the corrosion of mild steels in ozonated and aerated water are summarized in Table 2.2.

For cooling water environments, where temperatures range from 38-49^{o}C, there have been reports of reduced corrosion rates of mild steels when exposed to ozone [32, 33]. In a pilot cooling tower, Meier found that the corrosion rates of mild steel decreased from 0.71 mm/y when chlorine was used alone as a biocide to 0.11 mm/y when ozone alone was used [33]. This decrease in corrosion rate is most likely due to the deposit of scale and corrosion product on the metal surface that was noted in the presence of ozone. There have also been reports of ozone increasing corrosion rates in cooling water environments [27, 28, 35]. Lawson, in an 18-month trial, found that the addition of 0.1 mg/L ozone caused the corrosion rates of mild steel to range from 0.076 to 0.250 mm/y, a factor of four (4) times higher than corrosion rates reported for a traditional molybdate-based water treatment program [34]. Once again, severe fouling and scaling were evident when ozone was used. In laboratory studies using ozone treated cooling water and flow rates of 0.33 m/s, Strittmatter [27] and Yang [28] together found that low ozone concentrations of 0.1 mg/L had no effect on the corrosion rate of mild steel, while the addition of 1 mg/L increased the corrosion rates by a factor of seven.

There have also been reports of a neutral effect of ozone on the corrosion rates of mild steel in cooling water environments [23, 27, 28, 35]. Bird has reported ozone to be neutral in the protection of mild steel for open evaporation cooling systems, suggesting that conventional corrosion inhibitors such as sodium nitrate are more effective [35]. Hettiarachchi, adding 24 ppm Mg^{2+}, 195 ppm Cl^{-}, 345 ppm SO_4^{2-}, and 88 ppm Cu^{2+} to water to simulate cooling water, found that ozone concentrations of 1.5 to 3 mg/L had no effect on mild steel [23].

In their research, Strittmatter, Yang, and Hettiarachchi have all come to the conclusion that the corrosion rates of mild steel in cooling waters have little dependence on ozone, but are dominated by the water chemistry of the system [23, 27, 28].

In de-ionized and fresh water at 30^{o}C respectively, both Matsudaira [31] and Kaiga [36] found that ozone levels between 0.2 and 2.1 mg/L increased the corrosion rates of mild steels by a factor of 2 to 3. The work by Kaiga compared the ratio of the corrosion rates in aerated and 0.3-1.0 mg/L ozonated solutions at different flow velocities. At velocities below 1 m/s, the presence of ozone was found to increase the corrosion rate of mild steel, while the corrosion rate of cast iron was unaffected [36]. At 1 m/s, however, the corrosion rate of mild steel was found to decrease, possibly due to formation of a passive film. Matsudaira's results for mild steel at solution velocities of 0.05-0.1 m/s and a concentration of 2.1 mg/L ozone echoed those of Kaiga, showing an increase in corrosion rate compared to aerated solutions [31]. At a solution velocity of 1.7 m/s, however, ozone had no effect on the corrosion rate of mild steel compared to aerated solutions. In contrast to these studies, Walton found the corrosion rate of mild steel to decrease when exposed to 2 mg/L of ozone [37].

Table 2.2: Summary of Mild Steel Corrosion Measured in Ozonated Water

Environment	Ozone Concentration (mg/L)	Ozonated Corrosion Rate (mm/y x 100)	Aerated Corrosion Rate (mm/y x 100)
Cooling Tower Water*	0.1	7.6-25(17)	2.5-18 (17)
	.1	1.8(10, 11)	11(13)
	0.3	17(13)	
	0.1-0.5	8.3(20)	
	0.5	12-16(16)	
	0.95	2.0-5.3(21)	
	1.0	13 (l0, 11)	
	2.0	17 (19)	
Water	0.2-1.0	36-221(*9)	28 (*9)
	2.1	18(14)	7.4(14)
Simulated Cooling Water	0.1	11 (*10)	13(12)
	1.0	18(*10)	51 (*10)
	3.0	18 (12)	

*= Indicates that corrosion rates were measured in flowing solution.

2.6 Micro-biologically Influenced Corrosion

In aquatic environments, microbial cells attach to solids. Immobilized cells grow and reproduce, and produce extra cellular polymers that provide structure to the assemblage termed a biofilm. Figure 2.6 shows a conceptual model of stratified biofilm [41].

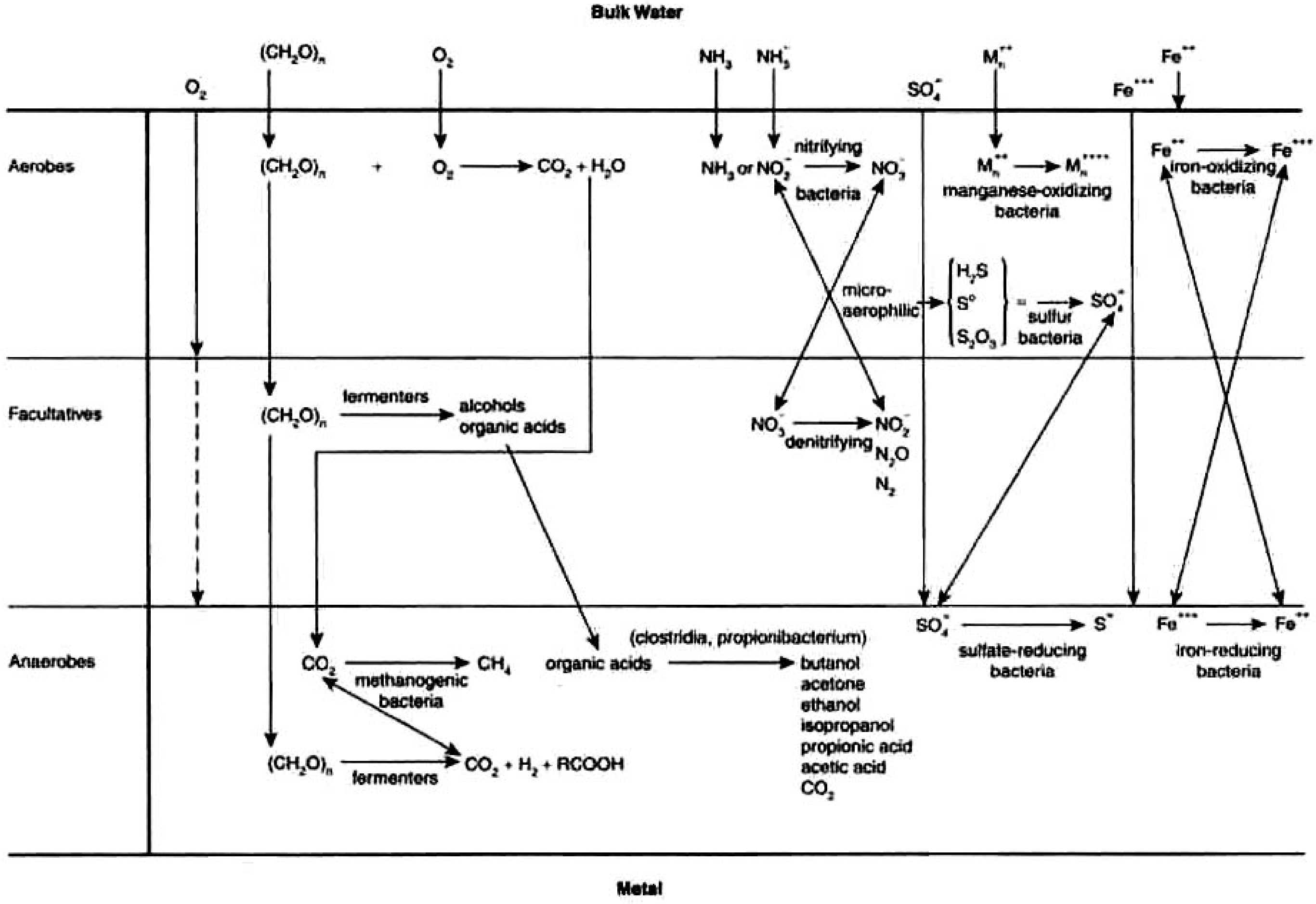

Figure 2.6: Conceptual Model of Stratified Biofilm [1]

When the presence of a biofilm influences the corrosion process, it is known as a biocorrosion phenomenon. This is more commonly termed microbiologically-influenced corrosion (MIC) [42]. Microorganisms can be categorized according to oxygen tolerance as follows [43]:

- strict (or obligate) anaerobes, that will not function in the presence of oxygen;
- aerobes, that require oxygen in their metabolism;
- facultative anaerobes, that can function both in the absence or presence of oxygen; and
- microaerophiles that use oxygen but prefer low levels.

2.6.1 Bacterial Corrosion in the Absence of Oxygen

Electrochemical considerations suggest that, in an environment of approximately neutral reaction and with the exclusion of oxygen, corrosion of iron would be negligible or absent. However, severe corrosion has been reported in mild steel pipes buried in clay soil, under the above-mentioned circumstances, where a perforation of a ¼-inch thick wall has occurred in as little as four years [44]. The corrosion is often localized and is generally characterized by a black corrosion product and a strong smell of hydrogen sulphide. In the 1930s, Kuhr indicated that the conditions in which this phenomenon occurred were precisely those best suited to the growth and proliferation of sulphate reducing bacteria (SRB) and proposed the following overall mechanism for the corrosion [44]. However, since then, several other different mechanisms have been reported.

$$4\,Fe + SO_4^{2-} + 4H_2O \rightarrow FeS + 3Fe(OH)_2 + 2OH^-$$

Beech et al reported a case where a pitting and perforation of the 12 mm steel hull plate at the bottom of the ballast tank was found and that it had probably occurred within a nine-month period when the vessel had undergone construction work [45]. Figure 2.7 shows a photograph of the cross-section of the corroded hull plate. The analysis revealed the presence of high levels of SRB in mud samples and significant sulphide ion and iron sulphide formation in pitted regions. Figure 2.8 shows a schematic to indicate the corrosion cells that can form inside the pits [45]. The damage was primarily attributed to MIC mainly due to the presence of SRB action. It was discovered that the harbour berth used for the construction work was located close to a discharge from a fish processing plant that could have provided a high level of nutrient rich material during ballasting operation.

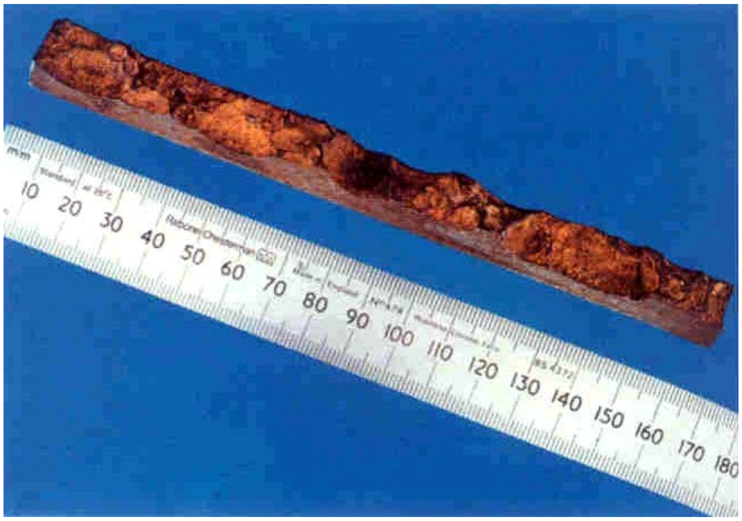

Figure 2.7: Cross-section of the Hull Plate, Showing the Reduction in Normal Thickness (12mm) [5]

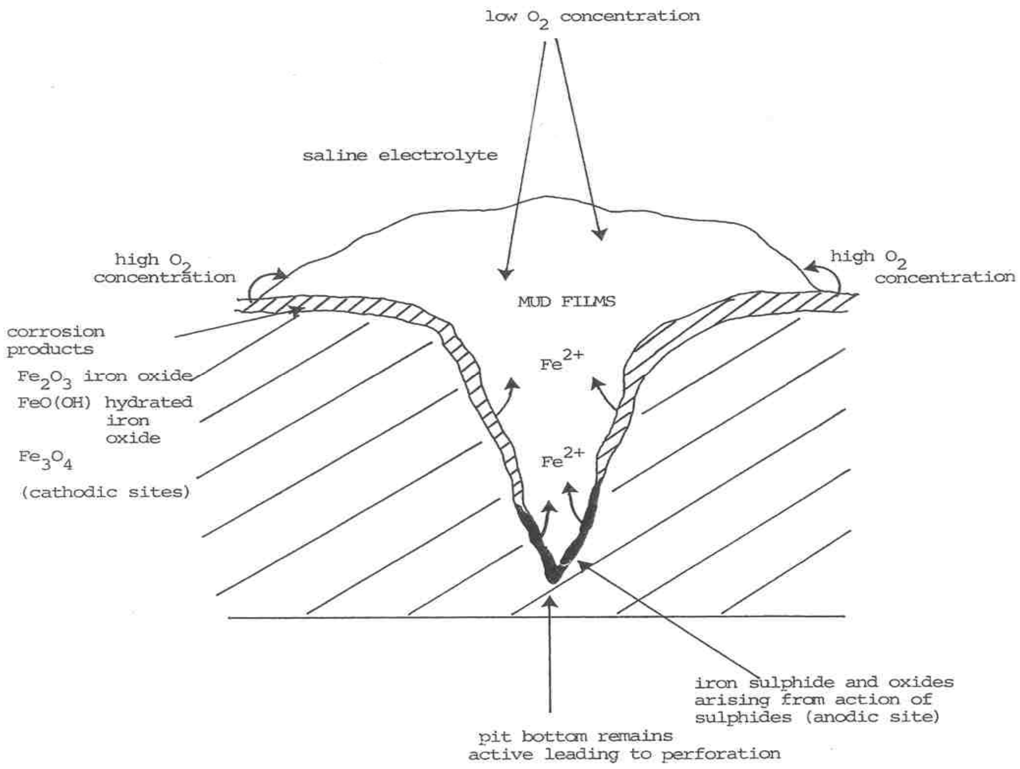

Figure 2.8: Corrosion Cells that Can Arise under Mud Films and in the Presence of Biofilms [5]

2.6.2 Sulfate Reducing Bacteria

SRB's are a diverse group of obligate anaerobes implicated in 95% of cases of biocorrosion [42]. In the UK, the cost of such fouling has been estimated at UK ₤0.6-1.0 billion per annum (1976 estimate) and the annual loss to the US Navy has been estimated at $5 billion due to corrosion related failures (1991 estimate) [42].

All SRB's are anaerobes and for the most part they will require a complete absence of oxygen and a highly reduced environment to function efficiently. However, they circulate in aerated waters including those treated with chlorine and other oxidizers until they find a suitable site [43]. SRB's reduce sulfate to sulfide, which usually forms hydrogen sulfide or, if iron is available, as black ferrous sulfide [3]. In the absence of sulfate, some strains can function as fermenters and use organic compounds such as pyruvate to produce acetate, hydrogen and carbon dioxide. Many SRB strains also contain hydrogenase enzymes, which allow them to consume hydrogen [43].

Most common strains of SRB grow best in the temperature range of 25-35°C. However, a few strains capable of functioning efficiently at more than 60°C have been reported. Most of the micro-organisms function within a narrow temperature band. However, certain SRBs grow well at high temperatures (~100°C) under high pressure (2500 -4500 psi), but can also grow at temperatures closer to 35°C at atmospheric pressure [43]. Bulk water pH can have a significant effect on the micro-organisms. Growth of common strains of SRBs slows above pH 11 and is completely stifled at pH 12.5 [43].

2.6.3 Role of Oxygen

There is a great debate over the exact mechanisms involved in anaerobic microbial corrosion and importantly the role of oxygen. In the field, it has been seen that the most dramatic instances of SRB corrosion are generally associated with access to oxygen [46].

Experiments were carried out where a sheet of mild steel was exposed to a growing culture of SRB under controlled conditions of anoxia. A non-homogenous film was observed on the surface and a slow corrosion rate was recorded. After completion of the growth phase, the mild steel sheet was subjected to short pulses of air and during this phase the corrosion rate accelerated 90 fold to a value of 0.65mm/year [46]. The nature of corrosion was pitting. The above experiment thus ruled out the role of oxygen having an impact on biofilm development or growth of SRB and the accumulation of ferrous sulfide corrosion products. It is the further modification of these sulfide products that is crucially affected by the sudden ingress of oxygen [46]. This finding has been confirmed by others and was observed that there was no correlation between SRB numbers or activity and the rate or extent of corrosion [46]. Nielsen et al carried out experiments where under alternating periods (12 hours) of oxic and anoxic conditions for 35 days, high rates of corrosion up to 4 mm/year were recorded [46]. Due to the complexity of the process of biologically influenced corrosion, Hamilton et al have raised the issue of the “What is the exact role of oxygen in stimulating SRB corrosion? Is it causal or casual?” [46].

Lee et al carried out other experimental work under different dissolved oxygen (DO) concentrations [46]. They reported that under low DO (1.5 $mg.l^{-1}$) during the first fifteen days, the measured corrosion declined as well as DO concentration decreased to levels of 0.6-1 mg/l. The data was interpreted as decreasing aerobic corrosion resulting from the lowered oxygen levels due to microbial activity within the developing biofilm. During the same period, there was a considerable build up of SRB in the biofilm. During the next three weeks of the experiment, DO of the bulk phase dropped further to $0.4 mg.l^{-1}$ and zero oxygen was recorded at the base of the biofilm and corrosion increased. This phase of the corrosion was due to SRB activity and was characterized by a high incidence of pitting. This result seems contradictory to the results reported in the above paragraph where no direct correlation was observed between SRB numbers or activity and the rate of corrosion.

Examination of the surface revealed that no evidence of pitting in the initial two weeks of exposure and the surface film consisted of iron oxides. During the final three-week period when pits became evident, sulfur, iron and oxygen signals were detected from the steel surface. Sulphur was present at pit depths down to 3600 angstroms and oxygen at the areas immediately around the pits [46].

From a ballast tank perspective, if the environment is completely deoxygenated, in all probability, the SRB corrosion rate may not be as extensive and the aqueous corrosion will be reduced. On the other hand however, the deoxygenated conditions raise other issues:

How does the SRB-related corrosion rate quantitatively compare with the corrosion rates under oxygenated conditions, i.e., the total observed corrosion is the sum of SRB related and aqueous corrosion, but in what proportions?

Secondly, if there is an ingress of oxygen in the previously deoxygenated ballast tank, and thus a condition of high levels of SRB's, is there a resulting acceleration of total corrosion?

Normally, aqueous corrosion alone may not corrode the steel as fast as cited in the above examples (hole in a 6.25 mm pipe in four years or perforations in a 12 mm ballast water steel pipe in nine months). In both these cases, SRB's were implicated. However, the general conditions in both circumstances were not completely deoxygenated. It could very well be a combination of the SRBs and the ingress of oxygen. Since the presence of SRB and oxygen is likely in the ballast water tank environment, will extremely high corrosion rates occur frequently? This then raises the issue: is the combination of SRB's and oxygen ingress alone responsible for such high corrosion rates or are other factors involved?

A member of the Technical Committee provided additional information and comments about the microbiological induced corrosion and these are reproduced in Appendix A.

2.7 Protective Coatings

Hare [16] reviewed the topic of corrosion control of steel by organic barrier and sacrificial coatings. He points out that the fundamental requirements of the barrier system are that the coating should be: (a) impermeable to damaging ionic species and, if possible, to oxygen; and (b) that it should maintain adhesion to the steel under wet conditions. Hare emphasizes that sufficient impermeability to water is not possible except in very thick films (>20 dry mils which is a low value for ships epoxy application) and that the ingress of water leads to de-adhesion. However, all barrier film systems on engineering structures contain defects or "holidays" and the size and distribution of these defects determines the effectiveness of the paint system. Surface preparation of the steel substrate to remove contamination is the key to a successful system. In addition, localized mechanical damage may occur.

Because defects are inevitable, sacrificial coatings in the form of zinc-rich primers have been developed to delay the corrosion process. Although zinc is more reactive than iron (one measure of this reactivity is the Standard Oxidation Potential, E°, where E° for Zn/Zn^{++} is -0.763 volts and E° for Fe/Fe^{++} is -0.440 volts), pure zinc corrodes at a slower rate than iron in near-neutral aqueous solutions because of the formation of a partially protective film of corrosion products. For example, in sea water zinc coatings on steel are reported to corrode at ~0.025mm/yr [17] while bare steel corrodes at ~0.1mm/yr as discussed above.

This inherent corrosion resistance of zinc is important only with intact coatings where attack occurs through the topcoat and the zinc-rich layer before reaching the underlying steel. At defects which extend through the coating however, the aqueous environment is in immediate contact with the zinc-rich layer and the underlying steel and the sacrificial role of zinc is most important. When iron and zinc are coupled together electrically, electrons can flow from the zinc to the iron driven by the 0.3 volt greater electronegativity of the zinc. These excess electrons flowing to the iron suppress corrosion of the iron at the expense of additional corrosion of the zinc.

In discussing coatings for corrosion control in bleach plants, Bennett (12) states that zinc-rich primers with chemical resistant topcoat such as polyamide epoxies are most widely used, but these usually do not provide sufficient resistance to bleach plant environments. Amine-cured epoxy, vinyl and polyurethane were claimed to give better protection.

2.7.1 Presence of Oxidizing Agents

DnV [39] conducted a limited number of experiments on coated samples of steel subjected to exposure to ozonated water and found that there was an increase in the delaminating of coating. BMT [40] also conducted experiments in ozonated water and found that there was no significant increase in delamination but a dramatic deterioration of coating stability was observed, i.e., the epoxy paint was chemically attacked. The former was conducted in seawater where the presence of ozone is short lived due to the reaction salts and the latter in fresh water where the ozone levels could be maintained.

BMT [9] conducted a series of experiments using the ASTM Standard “Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D1654-92” with standard ship tank coating systems and varying exposures to hypochlorite. Over the 15-day exposure tests, some increase in coating damage was observed. This work was reviewed by the Michigan Environmental Sciences Board and longer-term testing was recommended. These tests are currently underway. A further comment on this work by the MESB was that incubation periods for paint de-lamination could be several months and thus not revealed by simple damage acceleration tests such as the ASTM scratch methods used. Therefore, a series of comparative permeability tests were conducted in this follow-on work. The results have not yet been published; however, basic results are presented in the Figure 2.9 that shows no increase in coating permeability with exposure to hypochlorite.

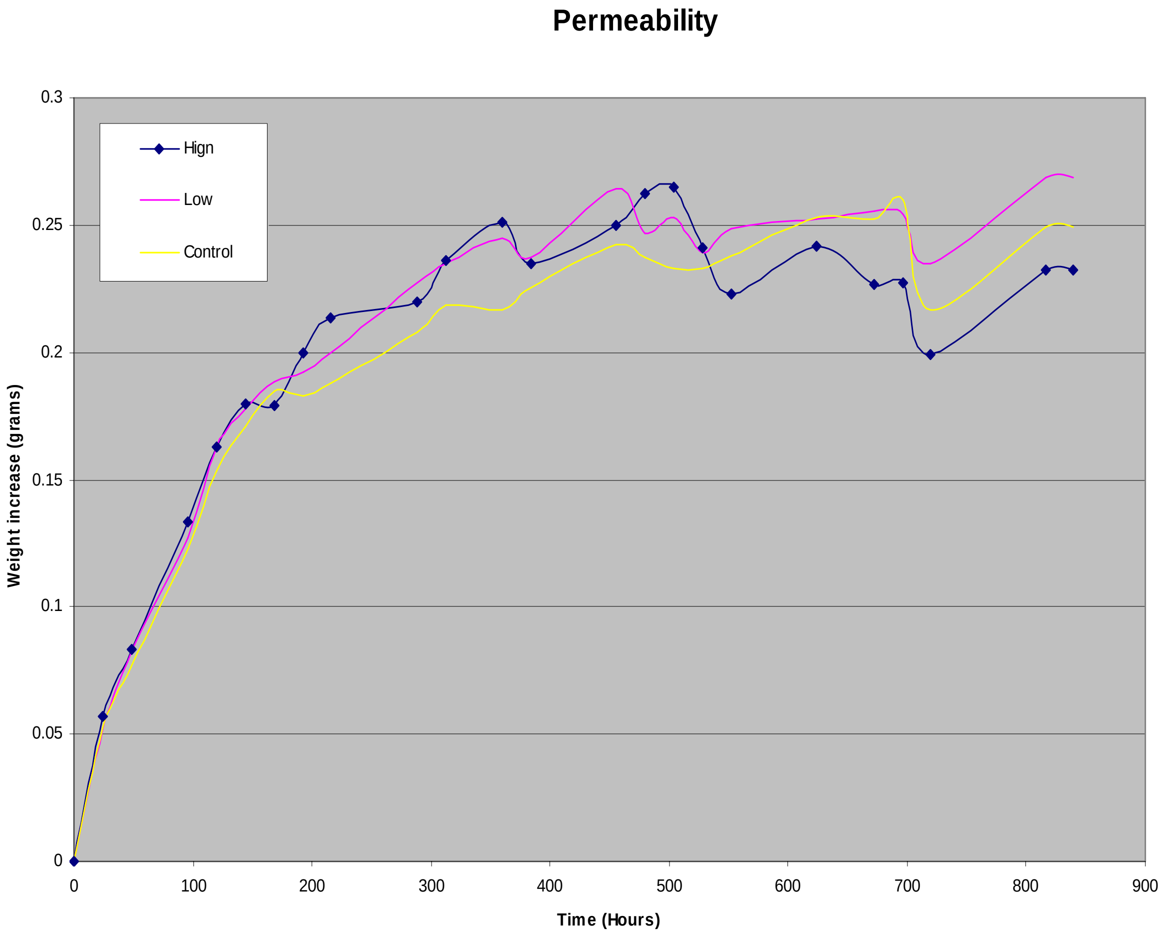

Figure 2.9: Water Take-up Increase over Time Varying Exposure to Hypochlorite

2.8 Ship Structures

The Tanker Structure Cooperative Forum [17] publish the most extensive publicly available database of “at ship” measured corrosion thickness diminution rates. In tanker ship ballast tanks designed solely for the carriage of ballast water, corrosion rates have been measured at between 0.1 mm/yr (0.004 inches/y) to 1.2 mm/y (0.047 inches/y). This order of magnitude difference is attributed to location in the tank. This reference also examines coating conditions and notes high levels of coating deterioration across all tank locations primarily related to age of coating and provides a measure as a % of coverage. All coating damage observed is attributed to localized disbonding and subsequent steel corrosion.

Paik (x) developed a time dependent corrosion wastage model for tankers and FPO’s in which corrosion loss is calculated from the following equation:

$$t_r = C_1 \left(T - T_c - T_t\right)^{C_2}$$

where the thick of the steel t_r at time **T** after construction is dependent on the time to coating break down $\mathbf{T_c}$ and a transition time $\mathbf{T_t}$ and coefficients C_1 and C_2. Paik investigated 34 different components within the typical ship structure and from a statistical review found thickness over time of up to 32 years. He concluded that the variance in data was best approximated by setting C_2 to 1 and that both $\mathbf{T_c}$ and $\mathbf{T_t}$ were indeterminable with a best fit to data available at around 7.5 years. This model reflects mean corrosion rates in FPO structures at between 0.026 mm/year and 0.24 mm/year with maxima in the order of three times greater, again dependent on the environment in which the particular structural member resides. These rates are consistent with, but slightly lower than, the rates published by the tanker forum.

2.8.1 Ship Structure Related Biocide Studies

DnV [39] conducted a series of experiments in ozonated seawater. In short term tests (minutes to hours), corrosion was measured using redox potential techniques that showed corrosion rates could accelerate 500% with the introduction of ozone. DnV stated the high life of ozone in seawater to be 5.3 seconds and that the reaction products include chlorine and bromine compounds with the former causing the increased oxidization. Over longer term ballast tank simulation tests during which the structure was either left in ozonated water, subjected to a cyclic exposure or held in the air space above water, the results were less dramatic and indeed showed that in the constant submergence zone, corrosion rates doubled but in the cyclic section there was a reduction in corrosion rates in the presence of ozone. It was also noted that corrosion rates did not achieve steady state over the 80 to 90 days of the test period, which probably indicates higher than normal corrosion rates. The sample size is small, however, and no treatment of statistical significance is present. The DnV experiments also examined paint systems and concluded that, in the presence of ozone, the disbonding of epoxy paint is increased.

Stocks [40] conducted a series of experiments with ozone in fresh water. This series of tests, conducted in environments made to represent the extremes of conditions in a ballast tank, showed that ozone accelerated corrosion only in the most aggressive environment where corrosion products are being constantly disturbed. Statistical review of other environments such as those fully submerged or in damp space showed no increase in corrosion rates.

Paint deterioration was also examined using standard ASTM testing procedures and showed that no significant increase in paint damage could be detected, however, there was significant deterioration in the paint surface and a reaction occurred which reduced the paint thickness.

Stocks [9] also conducted a series of similar experiments to examine the effects of exposure to chlorine using sodium hypochlorite dosages in fresh and seawater. These tests were run over 15-day exposures and although the acceleration of corrosion in the aggressive environments was identified, there was insufficient data to quantify the rates. Additional, longer term exposure tests are currently underway.

The Australian Government Department of Agriculture and Fisheries web site http://www.affa.gov.au/content/output.cfm?&OBJECTID=F6B5C3B3-93A5-4952-98A50B604F0EDE78 provides a review of available chemical treatment systems. The following Table 2.3 is taken from that web site and summaries where corrosion is considered to be a problem:

Table 2.3: Summary of Current Status of a Range of Chemicals for Ballast Water Treatment

Chemical	**Observed results**	**Comments**	**References**
Chlorine	Bleaching of brown cyst walls of *Gymnodinium. catenatum*. Zero germination only at >500ppm free chlorine. 10% cyst germination at 100ppm	Used extensively for potable water disinfection. Effective for removal of bacterial spores and some viruses. Bacterial spores, mycobacteria and protozoa require high doses. Limited studies in seawater. Toxic byproducts and residual chlorine require post treatment. High concentrations required for dinoflagellate cysts. **Safety and corrosive effects on steel are of concern.** Inappropriate for large-scale shipboard use.	Korich et al., 1990; Sobsey, 1989; Oemcke, 1999; Bolch and Hallegraeff, 1993; Rigby et al., 1993.

Table 2.3: Summary of Current Status of a Range of Chemicals for Ballast Water Treatment (continued)

Chemical	Observed results	Comments	References
Chlorine dioxide	70% mortality of *Dreissena polymorpha* veligers in flow-through cooling water systems at 5mg/L	Effective sporicide and cysticide for potable water and for control of bacteria and viruses. Harmful byproducts. Higher costs than for chlorine treatment. **Corrosive effects on steel are of concern** Toxic residuals from side reactions. No test work with ballast water.	Van Benschoten et al., 1993a, 1993b; Oemcke, 1999.
Hydrogen peroxide	100% destruction of *G. catenatum* cysts at 10,000 ppm, 98% At 5,000 ppm, 75% at 2,500 ppm. *Alexandrium catenella* cysts killed with100 mg/l (96 h). Motile cells of *Gymnodinium nagasakiense* required 3-6 mg/L (15-30 min) and *Chattonella marina* required 15 mg/L (30 min). Newly germinated cells of *Gyrodinium* spp. did not germinate after treatment at 6 mg/L (48 hours). No germination of *Chattonella* spp. cysts at 90 mg/L*;* *Alexandrium* spp., *Scrippsiella* spp. and *Protoperidinium* spp. at 150 mg/L	**Strong oxidant. Onboard safety and corrosion a concern**. Additional quantity required to oxidize other organic material, residual chemical decomposes to oxygen and water. Very high costs.	Bolch and Hallegraeff, 1993; Rigby et al, 1993; Montani et al., 1995; Ichikawa et al 1992.

Table 2.3: Summary of Current Status of a Range of Chemicals for Ballast Water Treatment (continued)

Chemical	Observed results	Comments	References
Ozone	Used for control of bacteria and viruses in seawater.	Widely used as disinfectant in fresh water for control of difficult organisms. Can be generated on-site. Reacts with dissolved organics and other impurities (especially iron compounds), necessitating high doses. Very expensive. **Corrosion a concern.** Not considered suitable for large-scale ballast water treatment. Toxic byproducts in salt water applications.	Oemcke and van Leeuwen, 1998; Sugita et al, 1992b.
Glutaraldehyde	500mg/L required for viruses and up to 20,000 mg/L for bacterial spores. No work with target organisms. Concentrations needed to eradicate ballast water organisms will depend on whether it is used as a primary or secondary treatment option-suggested will likely be in the range of 15 to 150 ppm. Pre-treatment filtration step may be required to minimize excessive chemical use.	Widely used as a disinfectant and fixative. **Corrosive in concentrated form but OK in diluted form**. Personal safety is a major issue. Cost prohibitive for full tanks and large ships. Possible use for treatment of residual sediments.	Lubomudrov et al., 1998; Sagripanti and Bonifacino, 1996; Bailly et al.

Table 2.3: Summary of Current Status of a Range of Chemicals for Ballast Water Treatment (continued)

Chemical	Observed results	Comments	References
Copper and Silver systems	Neither bacterial nor phytoplankton viability appeared to be affected. Some influence on viability of zooplankton and dinoflagellate cysts. Effects may have resulted from inordinately high copper concentrations.	Electrically generated Cu and Ag ions are successfully used in treatment of fresh water and found to be superior to chlorination for various bacterial strains. Lloyd's predict that this option is unlikely to find a useful application in ballast water treatment as a result of the reported ineffectiveness.	Lloyds Register, 1995; Landeen et al., 1989.

2.9 Experimental Design and Selection of Biocides for Corrosion Study

The gaps in literature available are predominantly related to how additives or systems might affect the steel corrosion rates and paint deterioration in a ballast tank environment, i.e., basic chemicals and their reaction to steel is documented in research related to high concentration of chemicals in other industries; little is available in the ballast tank condition. Actual corrosion rates observed in ship structures are cover a wide range and depend on many uncharacterized variables, but can generally be grouped into structural members subject to various degrees of cyclic water immersion/exposure.

Other factors that accelerate bulk diffusion such as agitation in the liquid that reduces the thickness of the boundary layer and wetting and drying cycles which afford atmospheric oxygen better access through the meniscus in the drying stage, also accelerate corrosion. These factors account for the enhanced attack observed at the waterline and splash zone in marine environments.

Based on the available information cited above, a number of factors must be kept in mind when evaluating the effects of biocides on coated steel ballast tanks:

- **Rate:** At ambient temperature, available oxygen will be the dominant factor, but strong oxidizing agents can be expected to make an additional contribution to corrosion.

- **Aeration:** Ballast water will vary in degree of saturation with air depending on the source of the water but, to eliminate this variable and establish stable long-term reproducible experimental conditions, it is necessary to aerate the test solutions. Air saturated water will reproduce the worst-case to be found naturally and provide a baseline to quantify the effect of agent additions.
- **Steel:** Mild steels in the composition range used for shipbuilding have no effect on corrosion rates so data using one steel will provide representative results.
- **Location:** Steel exposed in conditions of total immersion; at the waterline and in the humid air spaces above the ballast water will be exposed in varying degrees to the oxidizing agents present and will corrode at different rates.
- **Environment:** Steel exposed to conditions where the corrosion products or scale are removed, such as the splash zones of ballast tanks, will exhibit higher rates of corrosion.
- **Coating Condition:** The amount of deterioration attributable to coating defects (holidays) is much greater than through coating migration, thus effort should be concentrated on acceleration of defect extent.

Taking into account the range of chemicals available for the ballast water treatment, potential agents/biocides/treatment options for which the corrosion data is already available, as well as different factors involved in the corrosion process of ballast water tanks, an experimental protocol was developed and is discussed in detail in the next chapter. Two agents that were identified for testing purposes were SeaKleen™ and PERACLEAN® OCEAN. More information about these agents can be found in Appendix B and Appendix C respectively. The information contained in these two appendices has been obtained either from their respective manufacturer/distributors and/or from their websites.

3. EXPERIMENTAL PROTOCOL

The experimental protocol is outlined in the following sections. It was developed and discussed with the Project Technical Committee to address the project objectives.

Deoxygenation as a potential biocide was also discussed with the Technical Committee. Deoxygenation should reduce aqueous corrosion but it is not clear if deoxygenation will promote anaerobic microbial corrosion. Moreover, as pointed out in the literature review, the most dramatic instances of sulphate reducing bacteria (SRB) corrosion are generally associated with intermittent access to oxygen. Therefore, it would be necessary to maintain the deoxygenated conditions in the ballast tanks and not expose it to alternating oxygenated/deoxygenated conditions.

3.1 Agent Identification and the Dosage

The two agents identified for testing purposes were:

1. SeaKleen™
2. PERACLEAN® OCEAN

Extensive discussions were held with the suppliers of the above-mentioned agents. The SeaKleen™ supplier had indicated the dosage of 2 ppm as adequate. For PERACLEAN® OCEAN, the suppliers recommended 150 ppm dosage. For 35,000 tons of ballast water the amount of PERACLEAN® OCEAN required would be 4560 liters (considering density of 1.15g/ml).

In the present program, two different dosages were tested as follows:

1. Dosage indicated by supplier;
2. Double the dosage indicated by the supplier.

3.1.1 Test Medium

The testing was carried out in fresh water and salt water of 15 ppt and 35 ppt salinity. Aquarium quality sea salt was used.

During fresh water tests, the water in the tanks was changed every 48 hours and fresh solutions were prepared. This schedule was adequate for SeaKleen™ testing as the half life of SeaKleen™ is approximately 48 hours. However, the half life of PERACLEAN® OCEAN in tap water as indicated by the suppliers is 12 hours. Therefore, 50% of the PERACLEAN® OCEAN dosage originally added will be added every 12 hours to maintain the required dosage, and the water in the tanks changed every 48 hours.

The water was changed every 10 days for salt water tests. The half Life of SeaKleen™ is reportedly the same for fresh and salt water, i.e., 48 hours. Fifty percent of SeaKleen™ dosage originally added was added every 48 hours and fresh solutions were prepared every 10 days. The half life of PERACLEAN® OCEAN varies with the salinity. The half life of PERACLEAN® OCEAN is six (6) hours in 15 ppt salinity and four (4) hours in 35 ppt salinity. Therefore, 50% of the original dosage of PERACLEAN® OCEAN was added every four or six hours depending upon the salinity. Similar to the SeaKleen™ experiments, fresh solutions were prepared after 10 days.

This dosing routine ensured that plates were exposed to at least half strength of the agents during the accelerated corrosion test. However, in reality, a single dose of the agent would be required for every ballast water exchange.

3.2 Coating Tests

Bare steels were first coated with the Zn primer and two different coatings, based on coal tar epoxy and modified epoxy, were used.

3.3 Corrosion Principles Applied to Ballast Tanks

A number of factors must be kept in mind when evaluating the corrosion of steel in ballast tanks.

3.3.1 Aeration

Ballast water will vary in degree of saturation with air depending on the source of the water but to eliminate this variable and establish stable long-term reproducible experimental conditions, it was necessary to aerate the test solutions. Air saturated water reproduces the worst-case found naturally and provided a baseline to clarify the effect of biocide additions.

3.3.2 Steel

Mild steels in the composition range used for shipbuilding have no effect on the corrosion rate so only one steel material was used.

3.3.3 Location

In a ballast tank steel is totally immersed, is exposed to splash zone at the waterline, is exposed to the humid air space above the ballast water and exposed to varying degrees of the oxidizing agents which could lead to different corrosion rates. In addition, steel could be buried under debris at the bottom of the ballast tank and would be expected to experience lower oxidizing conditions and correspondingly lower corrosion rates.

3.3.4 Sample Size

Large samples are preferable because they minimize edge effects but smaller samples are easier to prepare, expose and evaluate. A sample size of approximately 75 mm x 125 mm is usually considered to be a practical compromise. The exposure of triplicate samples gives an indication of the variability of the corrosion processes.

3.3.5 Bare Steel Samples

Bare samples are useful to determine the corrosivity of different environments and the results are readily quantified by measuring weight loss with an analytical balance.

3.3.6 Coated and Scribed Samples

Coatings applied in the laboratory tend to be of higher quality than those applied in the field and contain fewer smaller defects. Scribing the samples as recommended in ASTM D1654 introduces gross reproducible defects that clarify the role of the damaged coating in protecting the underlying steel.

3.4 Experimental Approach

To address the important parameters discussed previously, an experimental approach was developed to quantify the corrosion rate of representative bare and coated steel samples in a simulated ballast tank environment treated with biocide. It is anticipated that the results obtained will provide relative durability data but the experimental nature of the approach precludes extrapolation to long exposure times in service.

3.4.1 Equipment and Materials

3.4.1.1 Apparatus

The corrosion study was be carried out in a simplified version of a rotating wheel apparatus, Figure 3.1, with which BMT Fleet Technology has developed extensive expertise in the study of weld-zone corrosion of icebreaking ships. A rectangular plastic vessel with dimensions approximately 1200 mm x 600 mm x 800 mm was partially filled with the test solution to a depth of approximately 500 mm and a second identical vessel was inverted above the first. At the plane where the two vessels touch, a wooden frame was inserted to act as the bearing mount for a plastic shaft running across the narrow dimension of the vessels at the mid-point. On the plastic shaft a circular plastic disc 800 mm in diameter was mounted and turned by a fractional horsepower motor at approximately 15 rpm. The test coupons were bolted to this rotating disk (pitch circle radius 380 mm) and subjected to repeated complete immersions throughout the test corresponding to the splash action at the waterline of a ballast tank. A second set of corrosion coupons were hung with plastic hooks from the wooden frame separating the upper and lower rectangular plastic vessels to experience the high humidity environment expected in the upper unfilled part of a ballast tank. The upper and lower rectangular plastic vessels were held together tightly so that high humidity would result in the vapour phase but a vent was provided because air was bubbled into the test solution continuously with an aquarium air pump to ensure that the test solution remained air saturated. A third set of coupons were suspended on plastic racks in the lower rectangular plastic vessel. They were fully immersed throughout the corrosion test. Bare coupons were also buried in aquarium quality inert sand and placed in a small plastic container at the bottom of the lower rectangular plastic vessel to simulate the effect of debris on steel at the bottom of a ballast tank.

Figure 3.1: Accelerated Corrosion Testing Apparatus

3.4.1.2 Steel

Steel conforming to the broad guidelines of ABS Grade A (~0.2% C, <1.1% Mn, 0.04% S max, 0.035% P max) in sheet form was used for the test coupons. The sheet was sheared into rectangles of approximately 75 mm x 125 mm size and a hole approximately 8 mm in diameter was punched in the top centre of each coupon to facilitate mounting. Bare coupons were stamped with an identification number while the coated coupons were identified on the back, unpainted surface with a vibrating scriber. A four-level identification system was used to ensure that samples were classified and recorded appropriately (see Table 3.1).

Table 3.1: Sample Identification Classification

		C	B	L	S
Coating	None	1			
	Man1	2			
	Man 2	3			
Biocide	None		1		
	Agent 1 Level 1		2		
	Agent 1 Level 2		3		
Location	wheel			1	
	submerged			2	
	humid			3	
	buried			4	
Sample	a				1
	b				2
	c				3

3.4.1.3 Surface Preparation

The coated coupons were grit blasted to a white metal finish on one side immediately before the application of the primer. The bare coupons were abraded to remove foreign material on both surfaces, degreased in acetone and blown dry.

3.4.1.4 Primer

Zinc-rich primer was applied to the grit blasted surface of the steel coupons. The application specifications of the manufacturer were followed.

3.4.1.5 Top Coats

Both a tar epoxy system and a modified epoxy system typically used for new building and coating repair were applied over the zinc-rich primer. Products from two manufacturers were used and the application was carried out according to their specifications.

3.5 Storage

Bare coupons were cleaned by sand blasting and weighed immediately before the test began. Coated samples were scribed and stored in a desicator until the start of the corrosion test.

3.6 Test Procedures

3.6.1 Sample Sets

The following combination of samples constitute one set:

1. bare steel;
2. coated and scribed (Supplier #1); and
3. coated and scribed (Supplier # 2).

3.6.2 Scribing

Samples were scribed with a straight-shank tungsten carbide tip lathe cutting tool as recommended in ASTM D1654.

3.6.3 Replicate Samples

Each set was exposed in triplicate on the rotating wheel, in the humid air above the solution and submersed in the test solution. In addition, triplicate bare coupons were buried in inert sand and submersed.

3.6.4 Solutions

The corrosion experiments were carried out in tap water and salt water of two different salinity levels, 15 ppt and 35 ppt.

3.6.5 Duration

The corrosion test lasted between 28 to 30 days.

3.7 Test Observations and Measurements

After the corrosion tests were complete, bare steel coupons were immersed in an inhibited 50/50 HCl/H_2O mixture to remove corrosion products, rinsed, blown dry and weighed. The weight change in milligrams was converted to millimeters per year. Coated and scribed coupons were evaluated as outlined in ASTM D1654 Procedure A, Method 2. A scraper was used to dislodge undercut coatings and the width of undercutting from the scribe was the basis for quantification. The results of the triplicate samples were averaged and reported.

4. EXPERIMENTAL RESULTS AND DISCUSSION

An experiment was devised based on the methodology successfully used to examine ship structural integrity in ballast tanks in the presence of biocides as explained in the previous section.

4.1 Apparatus

4.1.1 Fresh Water Tests

The equipment was set up in a climate-controlled trailer at the BMT Fleet Technology Limited facility in Kanata, Ontario, Figure 4.1.

Figure 4.1: Test Trailer at BMT Fleet Technology Limited

The apparatus consists of three-600 litre horizontally split polytuff containers each filled with 295 litres of tap water, Figure 4.2. Each container is connected by a shaft turning each of the three 800 mm, diameter, wheels upon which corrosion specimens are attached. Rotation is supplied via an electrical motor at approximately 15 rpm. The three tanks represent a control tank (tank 1), a low concentration (tank 2), and a high concentration dosing (tank 3).

Figure 4.2: Corrosion Tanks

The three tanks are fed fresh air via two aquarium pumps. Tank 2 and Tank 3, low concentration and high concentration respectively, are supplied fresh air by a single pump, while the control tank had its own aquarium pump, Figure 4.3.

Figure 4.3: Tank with Fresh Air Supply Hose

4.1.2 Salt Water Tests

The 15 ppt and 35 ppt salt water tests were carried out simultaneously in the test facility at BMT Fleet Technology Limited in Kanata, Ontario**.** The arrangement was similar to the fresh water tests, however, instead of three tanks, six tanks were used, Figure 4.4. The six tanks represent two sets, one with 15 ppt salinity and the other with 35 ppt salinity. Tanks 1, 2 and 3 were filled with 15 ppt salt water and tanks 4, 5 and 6 were filled with 35 ppt salt water. Tanks 1 and 4 represented control tanks for 15 and 35 ppt salinity respectively, tanks 2 and 5 represented low concentration for 15 and 35 ppt respectively and tanks 4 and 6 represented high concentration for 15 and 35 ppt respectively.

Figure 4.4: Six Test Tank Arrangement for Salt Water Corrosion Testing

4.2 Test Coupon Preparation

The plates were cut from sheet metal corresponding to the standard Grade “A”, shipbuilding steel as per classification society standards, i.e., American Bureau of Shipping (ABS) defined Grade A steel. These plates, (127mm X 76mm), were drilled for mounting to the apparatus. The specimens were then sand blasted to remove any mill scale, corrosion products or grease.

Bare metal specimens made identifiable with 1, 2, or 3 notches for each of the four test environments and were weighed using a Denver Instruments digital balance, Figure 4.5**.**

Figure 4.5: Denver Instruments Digital Balance

Two different paints are used in the experiment, Coal Tar Epoxy and Modified Epoxy, from two manufacturers, International Marine Coatings, and Jotun Paints Inc. The details of the coatings are provided in Appendix D. Each test coupon was first coated with a zinc rich primer. The coatings were applied on the specimens in two coats in accordance with manufacturers' specifications. The paint thickness prescribed by the manufacturer was randomly checked by the micrometer thickness gauge. The coated specimens were marked with a scribe line in the paint system in accordance with American Society for Testing Materials (ASTM), Standard "Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92".

Four sets of test specimens were subjected to simulated ballast tank environment conditions. These conditions were:

- -High humidity
- -Fully immersed
- -Buried
- -Splash zone

High Humidity – Specimens were suspended on a cord with each plate separated by plastic spacers. To ease removal of the plates, they were secured at the mid-span. The cord was hung in the upper vapour-filled region of the tank.

Submerged – Specimens were suspended in a similar fashion as the high humidity plates. These test specimens, however, were hung in the lower, water filled portion of the tank. These specimens remained fully immersed throughout the corrosion test.

Buried – Specimens were placed in small plastic containers filled with inert sand. Each tank had two plastic containers wherein one contained two plates which were layered in the sand and the other contained three plates layered in the sand. The containers were placed on the bottom of the tanks to simulate the effects of debris on the bottom of the ballast tank.

Splash zone - Specimens were attached to the rotating wheel with a radius of 380mm, by means of plastic nuts and bolts.

For consistency, the face of each plate that was painted was arranged in the same direction for all four simulated environments.

4.3 Testing

Temperature was measured once a day and adjusted so that temperature variation was within 5-6^{o}C. Immediately following completion of the test, the specimens were removed from the test apparatus and bagged to prevent drying effects as well as ensuring no plates were misplaced during post experimental analysis. Bags were labelled according to the simulated environment and the tank they were contained in.

The bare metal samples were cleaned under running water with a light brushing followed by submergence in a hydrochloric acid solution used to strip the unpainted plates of corrosion products. The solution comprised of 500 mL of distilled water, 500 mL of hydrochloric acid and 2-3 ml of an inhibitor, Rodine. After approximately five minutes, the plates were removed from the solution, washed under warm water and dried with a heat gun. To ensure the drying was complete, a small amount of methanol was placed on the plate and then dried again with a heat gun. Figure 4.6(a) and Figure 4.6(b) shows the photographs of samples of the bare steel before and after cleaning.

The painted plates were rinsed using a gentle stream of warm water. The plates were then vigorously scraped by a spatula, moving it back and forth across the scribe mark to remove the coating that was undercut and suffered loss of adhesion. This was performed in accordance with American Society for Testing Materials (ASTM) Standards, "Test Methods for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments D 1654-92". Figures 4.7(a) and Figure 4.7(b) show the painted coupons after cleaning.

Figure 4.6(a): Post Experiment Uncleaned Bare Steel Plate

Figure 4.6(b): Post Experiment, Cleaned, Bare Steel Plates

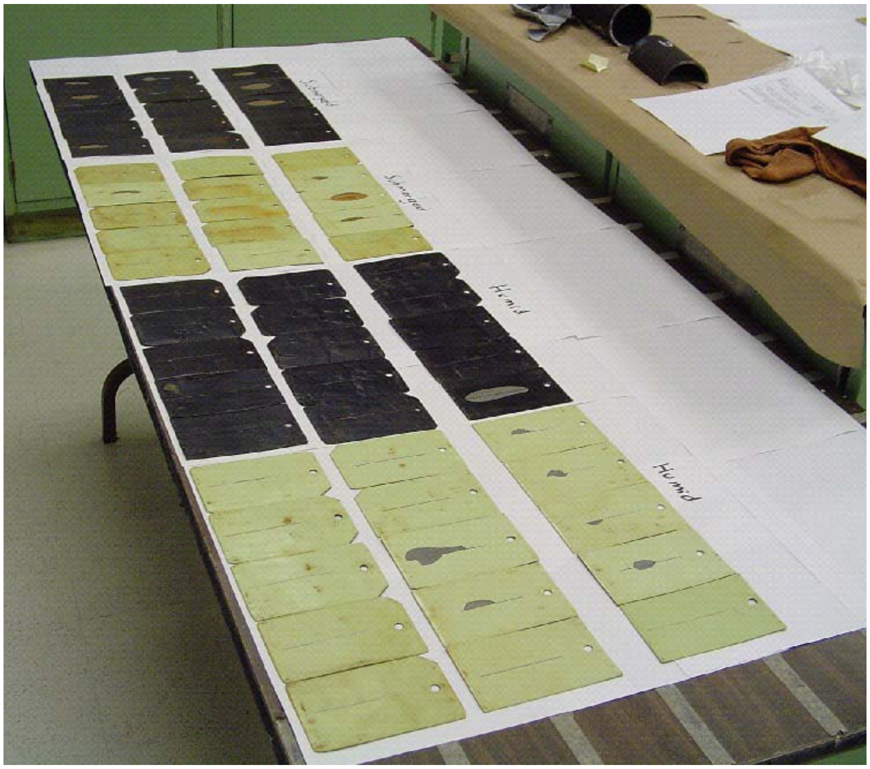

Figure 4.7(a): Post Experiment Cleaned Coated Steel Plates

Figure 4.7(b): Creepage in Coated Plates

4.4 SeaKleen™

4.4.1 Bulk Solution pH Measurements

SeaKleen™ was mixed in 1 litre of water in a beaker and the effect of concentration of SeaKleen™ on pH values of fresh water as well as simulated salt water (15 and 35 ppt salinity) was determined as shown in Figures 4.8(a), 4.8(b) and 4.8(c). pH readings of both the fresh as well as the simulated salt water did not change with the increase in the concentration of SeaKleen™. If corrosion was controlled by pH alone then the relative corrosion rates in fresh water and salt water dosed with SeaKleen™ should be the same regardless of the dosage amount.

A further set of experiments was carried out to determine whether there is any change in pH values of SeaKleen™ treated fresh and simulated salt water over time. SeaKleen™ concentration/dosage was kept at 2 ppm. The pH measurements were carried out over 55 hours and the results are shown in Figures 4.9(a) and 4.9(b). The pH values of fresh water dosed with SeaKleen™ dropped from pH 8.1 to pH 7.5 in the first 24 hours and remained relatively unchanged after that. However, in the case of SeaKleen™ dosed salt water (35 ppt salinity), the pH values increased from pH 7.35 to pH 7.7. Most of the increase in the pH values took place in the first hour.

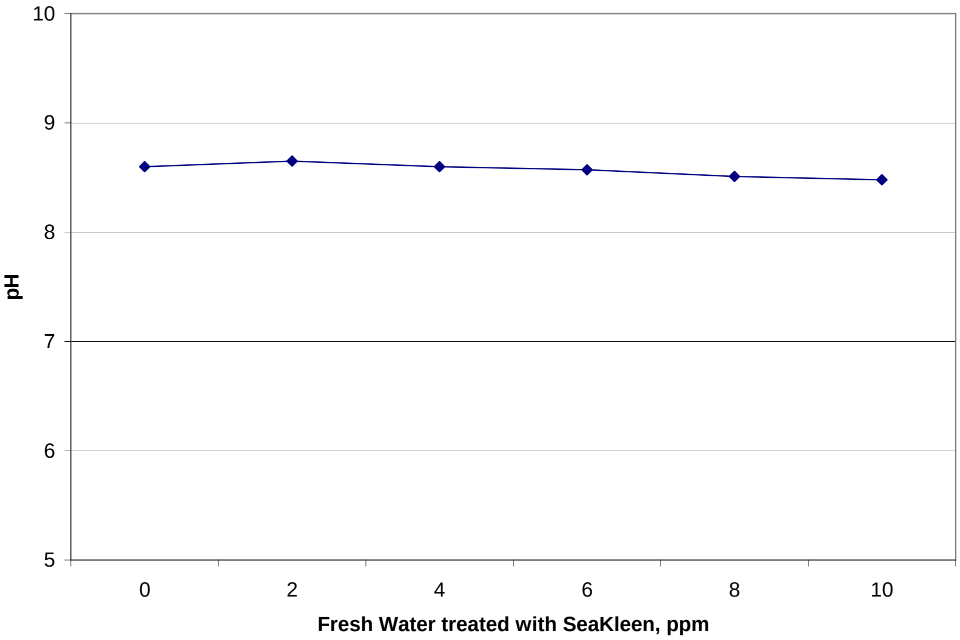

Figure 4.8(a): Effect of SeaKleen™ Concentration on pH of Fresh Water

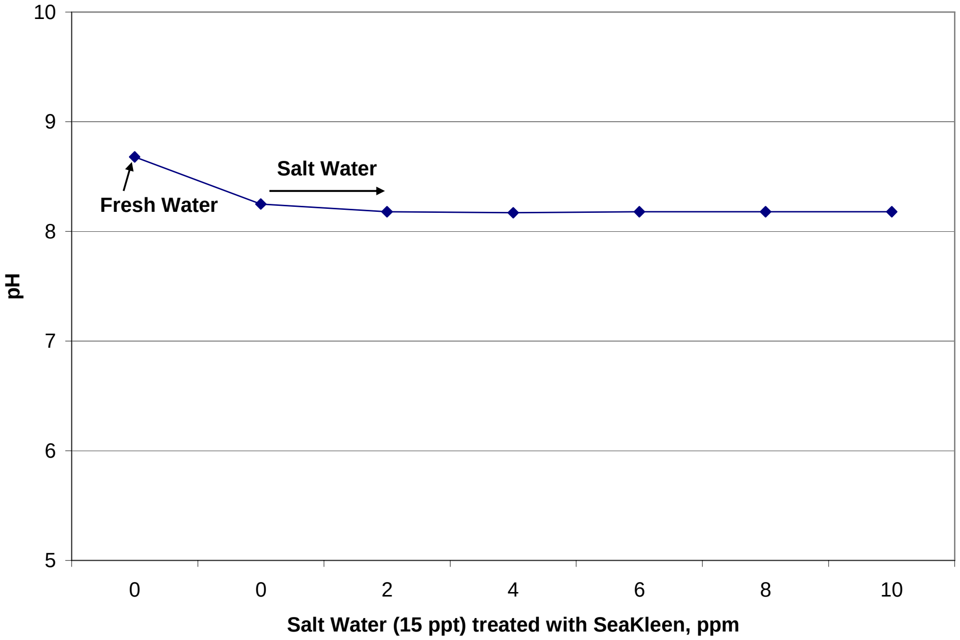

Figure 4.8(b): Effect of SeaKleen™ Concentration on pH of Salt Water (15ppt salinity)

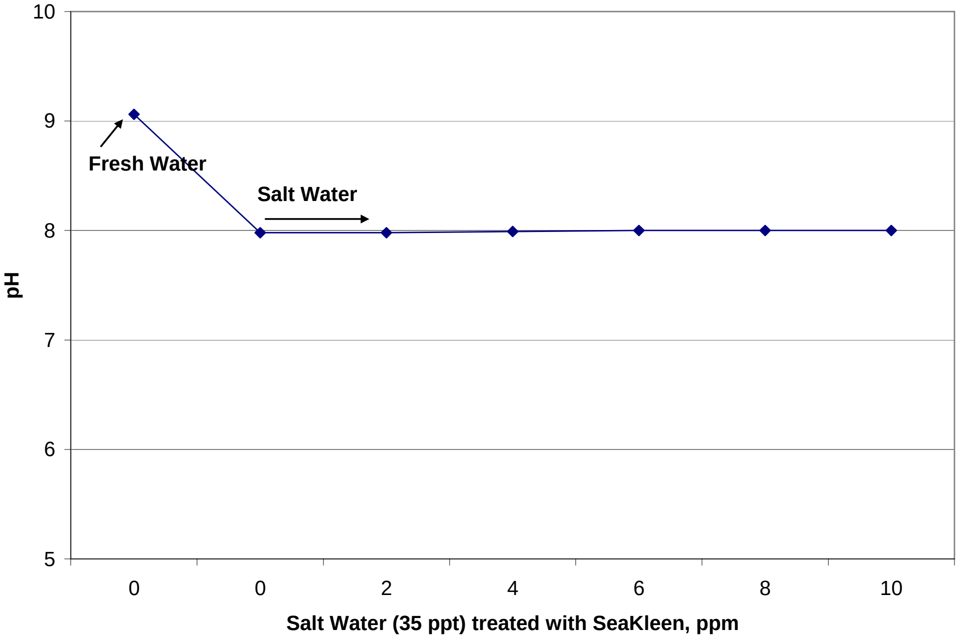

Figure 4.8(c): Effect of SeaKleen™ Concentration on pH of Salt Water (35 ppt salinity)

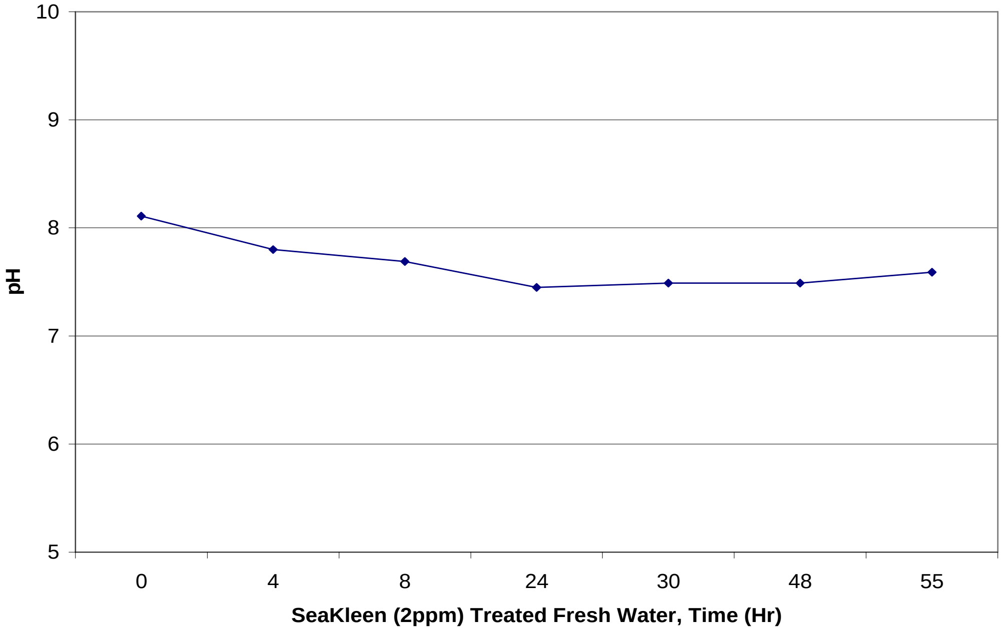

Figure 4.9(a): pH vs. Time for SeaKleen™ (2ppm) Treated Fresh Water

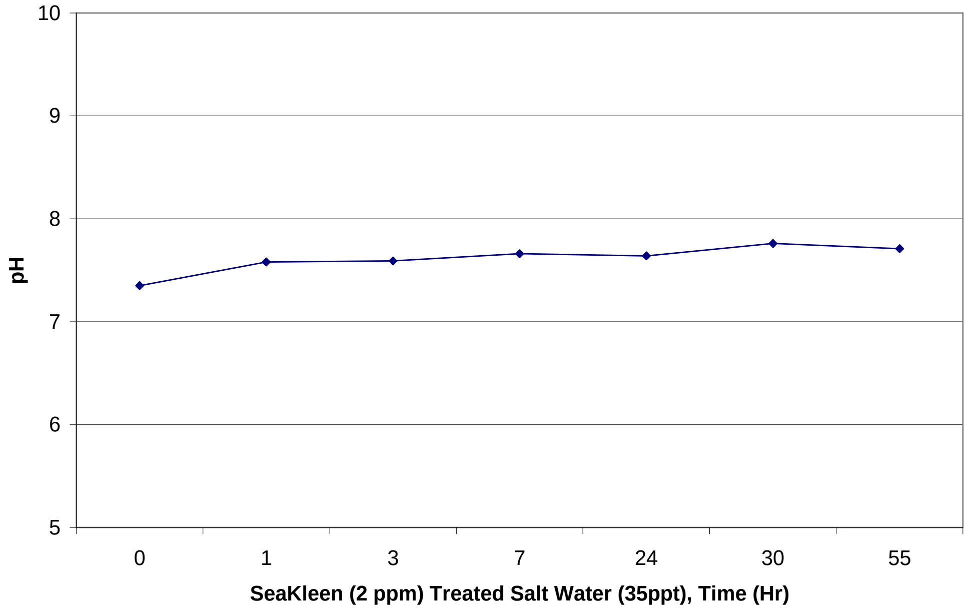

Figure 4.9(b): pH vs. Time for SeaKleen™ (2ppm) Treated Salt Water (35ppt salinity)

4.4.2 Corrosion of Bare Steel

SeaKleen™ came in a powdered form. A concentrated solution of SeaKleen™ was prepared in graduated cylinders and then mixed into Tanks 2 and 3. The SeaKleen™ came in two different batches and the two batches had different active components of 66% and 85%. Therefore the quantities were adjusted to have the adequate dosage, e.g., for 66% active component batch, a dosage of 3mg/litre was added to obtain the recommended dosage of 2mg/litre, i.e., 2 ppm.

During fresh water corrosion tests, the water in the three tanks was drained every 48 hours and refilled with fresh tap water and the appropriate dosage (0.9g in Tank 2 and 1.8g in Tank 3) of SeaKleen™ added. The ambient temperature was measured routinely and was within ±3°C, Figure 4.10(a). The test was allowed to progress with little outside involvement.

The testing was carried out simultaneously for 15 and 35 ppt salinity. Figure 4.10(b) shows the temperature during the 28 days of the testing with salt water. Figures 4.11(a) and 4.11(b) show the bulk solution pH measurements carried out on the tanks 1-3 and tanks 4-6 respectively during the salt water test program. The pH measurements remain relatively constant during the test duration and were similar to the results obtained earlier as shown in Figure 4.9(b). Half life of SeaKleen™ was indicated as 48 hours, therefore, every 48 hours 50% of the original dosage of SeaKleen™ was added to ensure that the plates were exposed to at least a half strength SeaKleen™ dosed solution. Every 10 days, fresh solution was prepared and the testing continued.

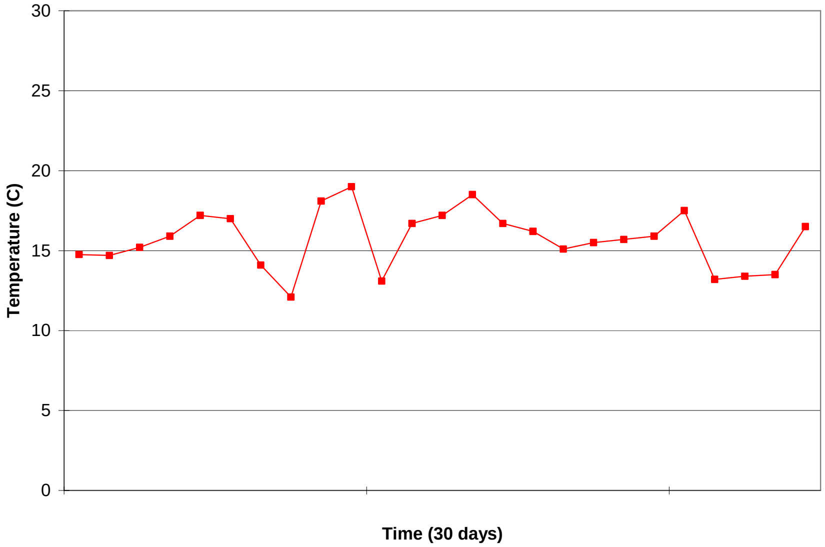

Figure 4.10(a): Test Temperature for the Duration of the Fresh Water Corrosion Test

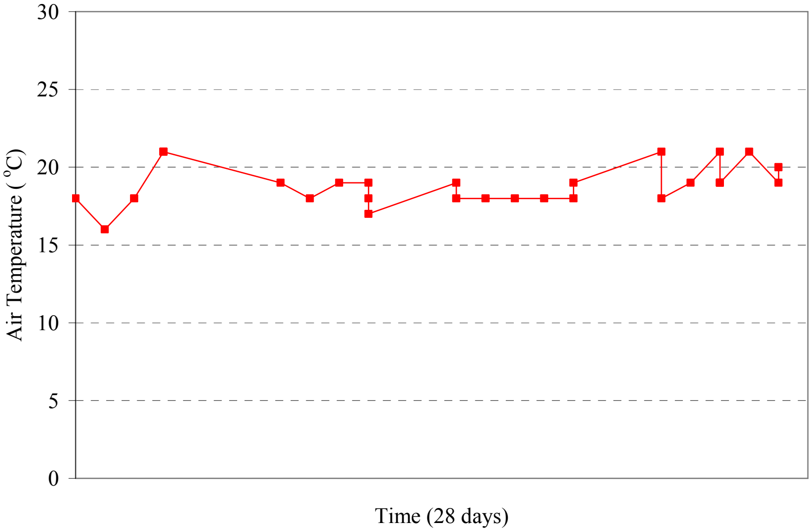

Figure 4.10(b): Test Temperature for the Duration of the Salt Water Corrosion Test

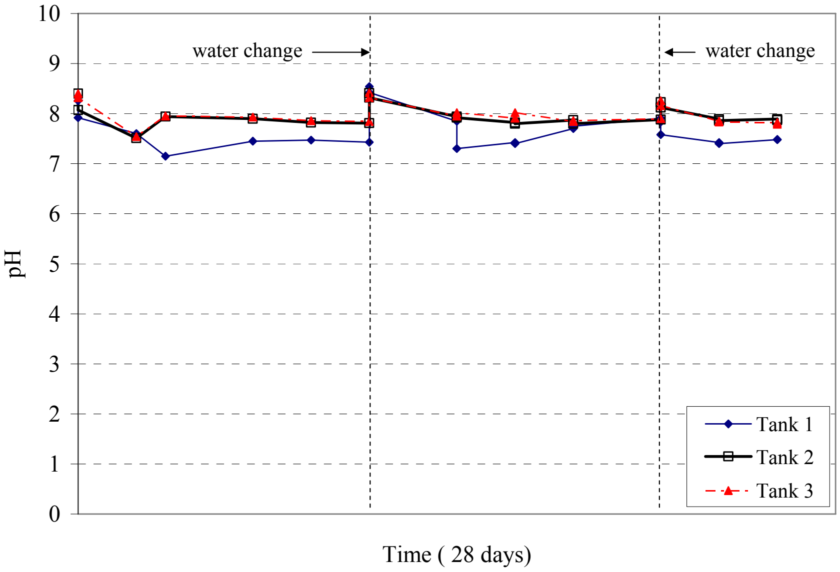

Figure 4.11(a): Bulk Solution pH Measurements for Tanks 1, 2 and 3 for the Duration of the Salt Water Corrosion Test

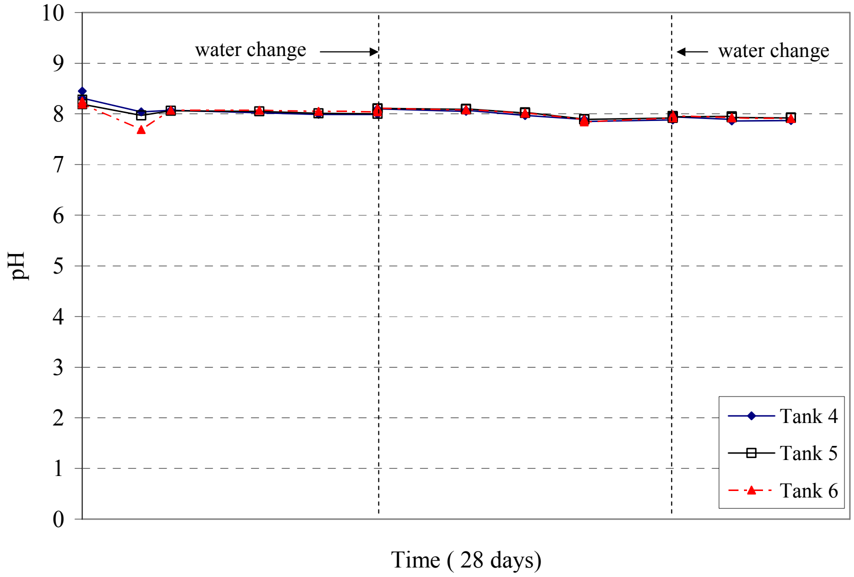

Figure 4.11(b): Bulk Solution pH Measurements for Tanks 4, 5 and 6 for the Duration of the Salt Water Corrosion Test

4.4.2.1 Fresh Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with fresh water are summarized in Table 4.1. The data was then converted to annualized thickness loss and the results are shown in Figure 4.12.

Table 4.1: Average Corrosion Weight Loss (gm) in Fresh Water Tests

Control			
Buried	Humid	Submerged	Wheel
0.44	0.42	4.80	6.12
Low Concentration			
Buried	Humid	Submerged	Wheel
0.81	0.34	4.05	7.09
High Concentration			
Buried	Humid	Submerged	Wheel
0.52	0.35	4.00	7.90

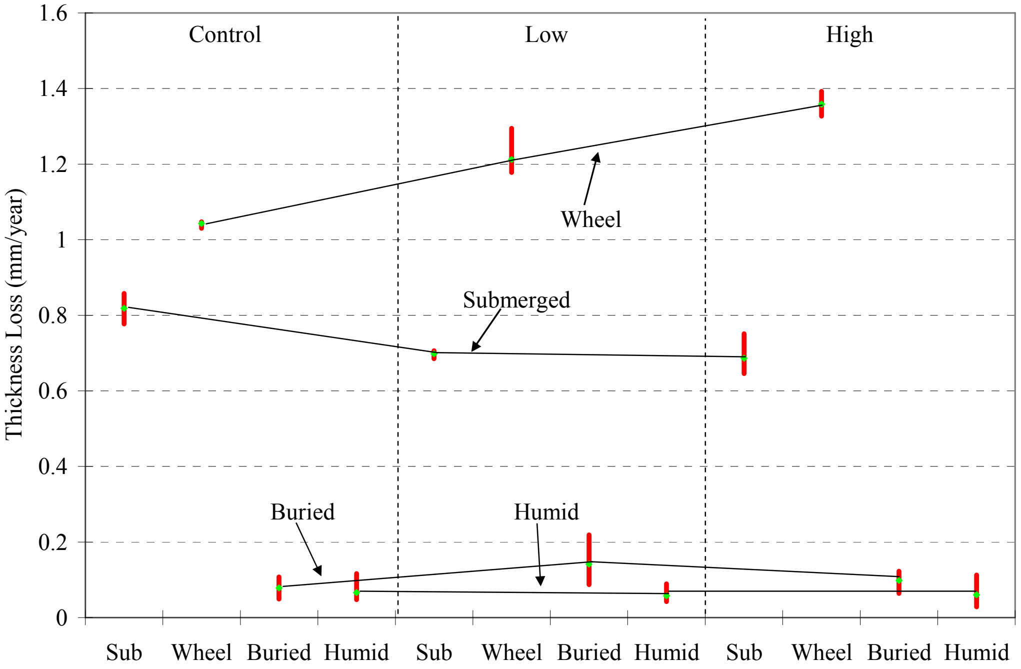

Figure 4.12: Loss of Thickness in Corrosion Tank, Fresh Water

The results for fresh water tests, Figure 4.12, demonstrate that as the aggressiveness of the environment increases so does the corrosion rate, i.e., those samples subject to constant submergence experience more corrosion than those in the humid environment and those samples on the wheel experience maximum corrosion. This is typical of the results from other experiments and reflects the variability in recorded material loss. Published data on ship ballast tank corrosion rates show that rates can vary from 0.1 mm per year to a high of 1.2 mm per year in the splash zones. The corrosion data in the control test is also within the same range.

The added corrosion effects, if any, caused by the presence of SeaKleen™ can be seen in the results of the wheel testing environment. A single parameter ANOVA analysis using the MS Excel Utility shows that there is statistical difference in the data in the wheel environment. However, there is no statistical difference in the submerged, humid and buried environments between the control tank and SeaKleen™ treated tanks. The higher rate of corrosion observed in the submerged condition in the control tank cannot be explained. The increase in the corrosion rate due to the increase in the concentration of SeaKleen™ in the wheel testing environment cannot be explained on the basis of the bulk solution pH measurements, since no change in pH measurements of fresh water was observed due to the increase in the dosage of SeaKleen™ as shown in Figure 4.8(a).

4.4.2.2 15 ppt Salt Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with 15 ppt salt water are summarized in Table 4.2. The data was similarly converted to annualized thickness loss and the results are shown in Figure 4.13.

Table 4.2: Average Corrosion Weight Loss (gm) in 15 ppt Salt Water Tests

Control			
Buried	Humid	Submerged	Wheel
0.61	0.51	4.15	5.43
Low Concentration			
Buried	Humid	Submerged	Wheel
0.53	0.55	3.04	5.27
High Concentration			
Buried	Humid	Submerged	Wheel
0.53	0.87	3.06	5.27

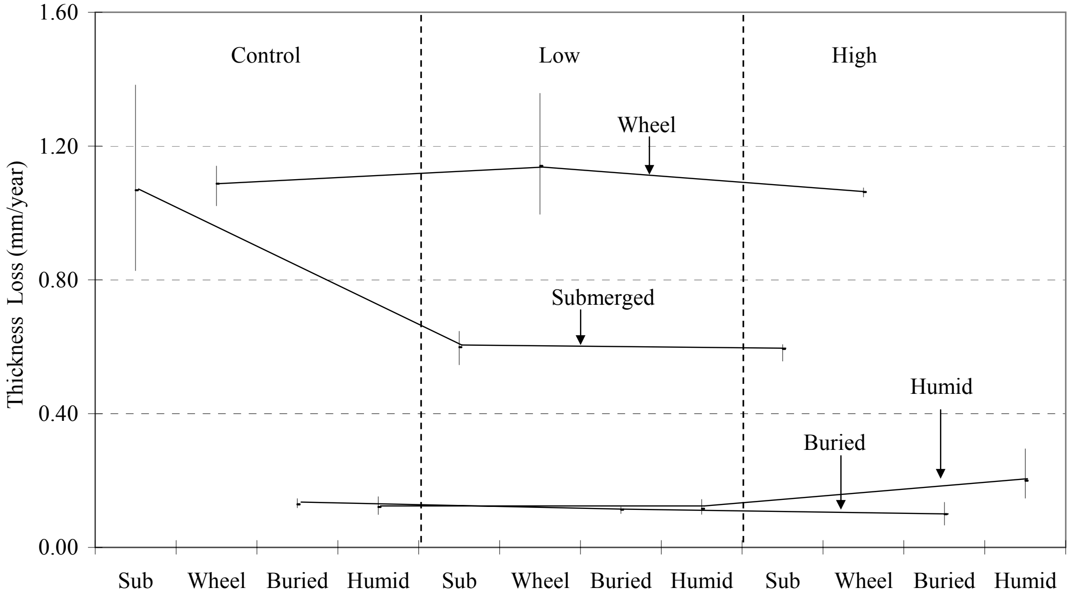

Figure 4.13: Loss of Thickness in Corrosion Tank, 15 ppt Salt Water

For 15 ppt salt water tests, Figure 4.13, corrosion rates of coupons subjected to buried and humid environment were similar irrespective of the environment, i.e., control, low dosage and high dosage. For the coupons subjected to constantly submerged environment, the results were similar to fresh water tests. In both cases, the coupons exposed to control conditions saw higher corrosion rates compared to low and high dosage SeaKleen™ concentration and there was no difference in corrosion rates exposed to single dosage and double dosage concentration. However, the corrosion results for coupons exposed to splash zone environment, i.e., the coupons mounted on the wheel, were different for 15 ppt salt water compared to fresh water results. In the case of 15 ppt salt water, no increase in corrosion rates was observed between control, low and high dosage SeaKleen™ concentration and corrosion rates were similar irrespective of the SeaKleen™ dosage. In the case of 15 ppt salt water, SeaKleen™ did not seem to increase the corrosion rates for the coupons subjected to the four different environments.

4.4.2.3 35 ppt Salt Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with 35 ppt salt water are summarized in Table 4.3. The data was similarly converted to annualized thickness loss and the results are shown in Figure 4.14.

Table 4.3: Average Corrosion Weight Loss (gm) in 35 ppt Salt Water Tests

Control			
Buried	Humid	Submerged	Wheel
0.62	2.19	2.43	4.27
Low Concentration			
Buried	Humid	Submerged	Wheel
0.56	3.12	2.48	4.66
High Concentration			
Buried	Humid	Submerged	Wheel
0.53	2.24	2.75	4.63

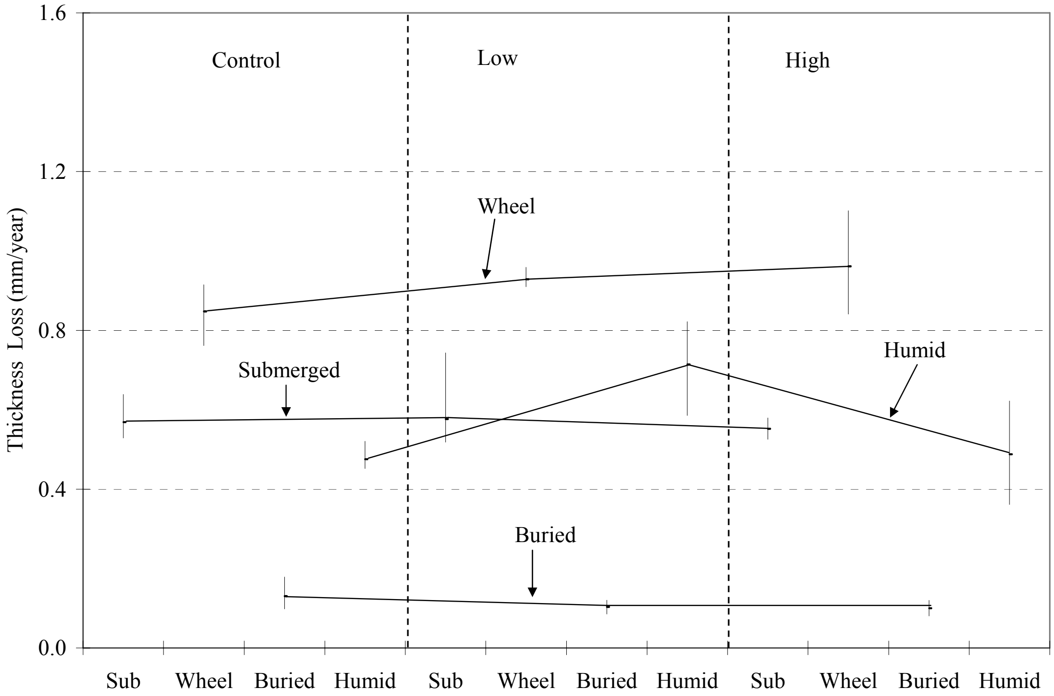

Figure 4.14: Loss of Thickness in Corrosion Tank, 35 ppt Salt Water

The corrosion results for 35 ppt salt water, Figure 4.14, show that there is not much difference in corrosion rates for all the coupons subjected to either control or low dosage and high dosage SeaKleen™ concentration. Similar to fresh water tests, a minor increasing trend in corrosion rates with increasing dosage of SeaKleen™ may be evident in the case of the coupons being subjected to splash zone environment, but it is not statistically significant. Longer term testing would be required to ascertain whether there is an increase in corrosion rates in coupons subjected to splash zone environment with increasing dosage of SeaKleen™.

4.4.2.4 Comparison of Fresh Water and Salt Water Corrosion Data

Figure 4.15(a) and Figure 4.15(b) show the comparison of the fresh water, 15 ppt salt water and 35 ppt salt water corrosion tests for the coupons subjected to constant submergence and splash zone environment for low dosage and high dosage of SeaKleen™ respectively. For both the cases of low and high dosage, the corrosion rates seem to be higher for fresh water tests compared to salt water tests. The photographs of the steel plates from salt water tests and exposed to splash zone and submerged environment are provided in Appendix E.

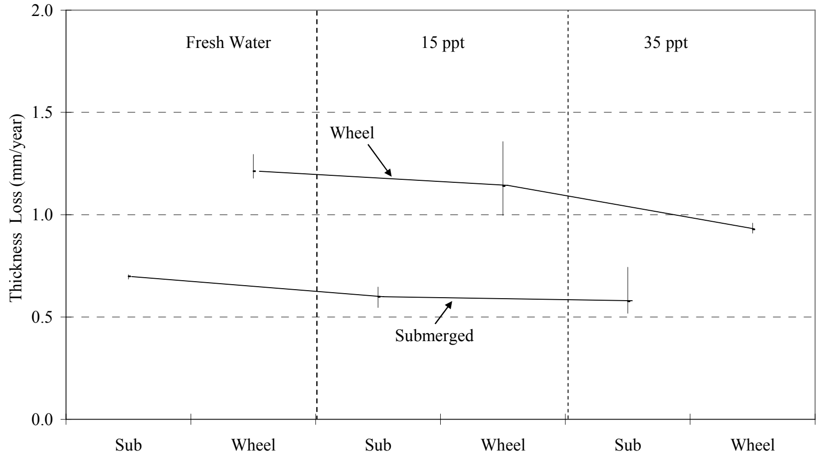

Figure 4.15(a): Comparison of Corrosion Rates in Fresh Water, 15 ppt Salt Water and 35 ppt Salt Water for Wheel and Submerged Coupons exposed to Low Dosage SeaKleen™ Concentration

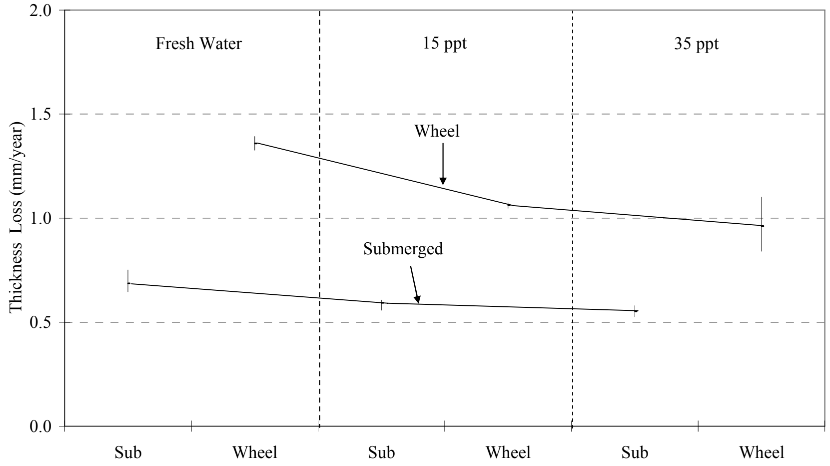

Figure 4.15(b): Comparison of Corrosion Rates in Fresh Water, 15 ppt Salt Water and 35 ppt Salt Water for Wheel and Submerged Coupons exposed to High Dosage SeaKleen™ Concentration

4.4.3 Integrity of Coating Systems

The standard used to assess the potential for coating damage is the ASTM Standard, "Test Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environment D 1654-92". In this standard, coated samples are scribed down to bare metal and exposed to the corrosive environment. The observed coating deterioration (i.e., creepage) for a distance away from the scribe lines is in accordance with **Table 4.4**.

Table 4.4: ASTM D 1654-92 Deterioration Rating

Representative Mean Creepage from Scribe	
Millimeters	Rating
0	10
0 to 0.5	9
0.5 to 1	8
1 to 2	7
2 to 3	6
3 to 5	5
5 to 7	4
7 to 10	3
10 to 13	2
13 to 16	1
Over 16	0

The results of the ASTM scribe test did not reveal any statistically valid differences in paint damage rates caused by the presence of SeaKleen™. Figures 4.16(a), 4.16(b) and 4.16(c) show the presentation of ASTM scores and creepage for different locations and exposures for fresh water tests. Similar data for 15 ppt salt water and 35 ppt salt water is presented in Figures 4.17(a), 4.17(b), 4.17(c) and 4.18(a), 4.18(b) and 4.18(c) respectively.

There was significant variation in the results from painted plates. When comparing deterioration ratings to tank concentrations few correlation can be made. It appears that creepage is not influenced by concentrations of SeaKleen™ but rather the aggressiveness of the environment is more influential in causing creepage. Furthermore, from observing the results of the study, it appears that the modified epoxy coating was much better than the coal tar epoxy coating. When comparing coating type and environment (Wheel, Submerged, and Humid), the modified epoxy coating appeared to be the superior coating in the aggressive environment induced by the wheel. There was no creepage observed in both the coatings in the humid environment. The individual results of the coatings vis-à-vis tanks are provided in Appendix F.

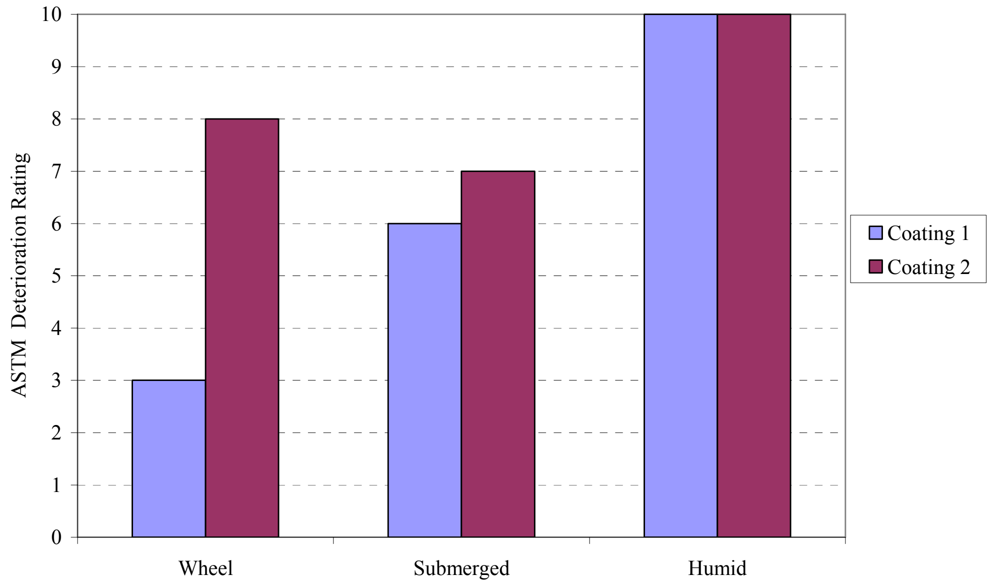

Figure 4.16(a): ASTM Score vs. Location in Tanks, Fresh Water (Average across Control and SeaKleen™ Treated Tanks)

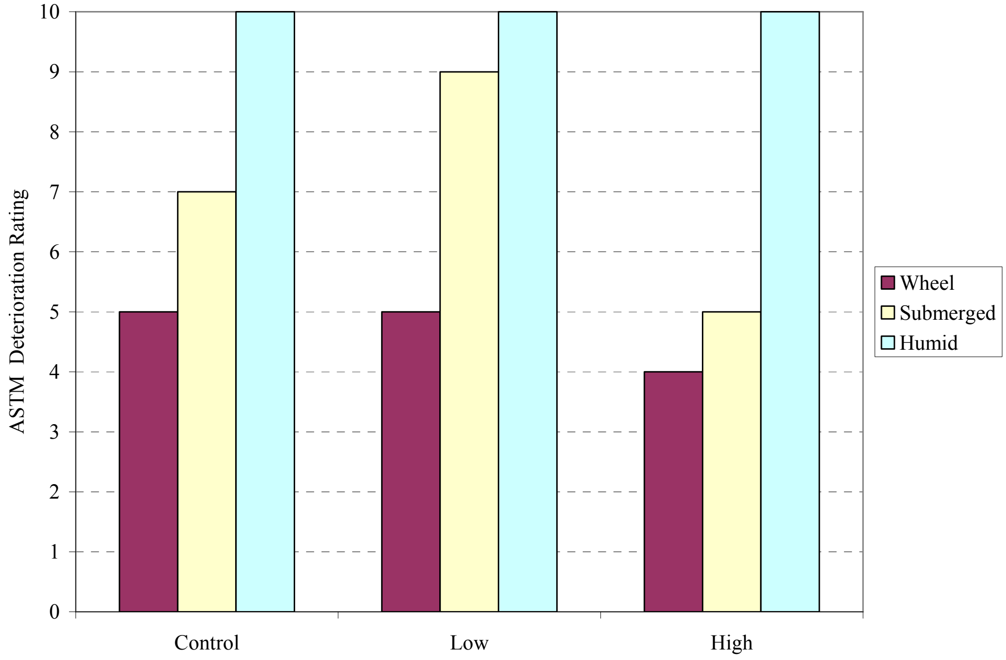

Figure 4.16(b): ASTM Score vs. Exposure (Average across all Coatings), Fresh Water

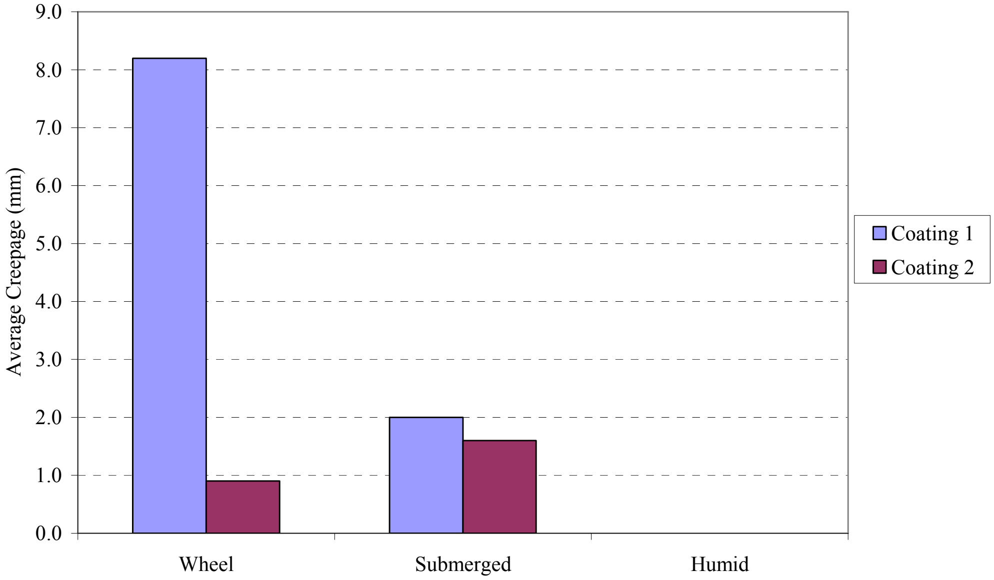

Figure 4.16(c): Average Creepage vs. Location in Tank, Fresh Water

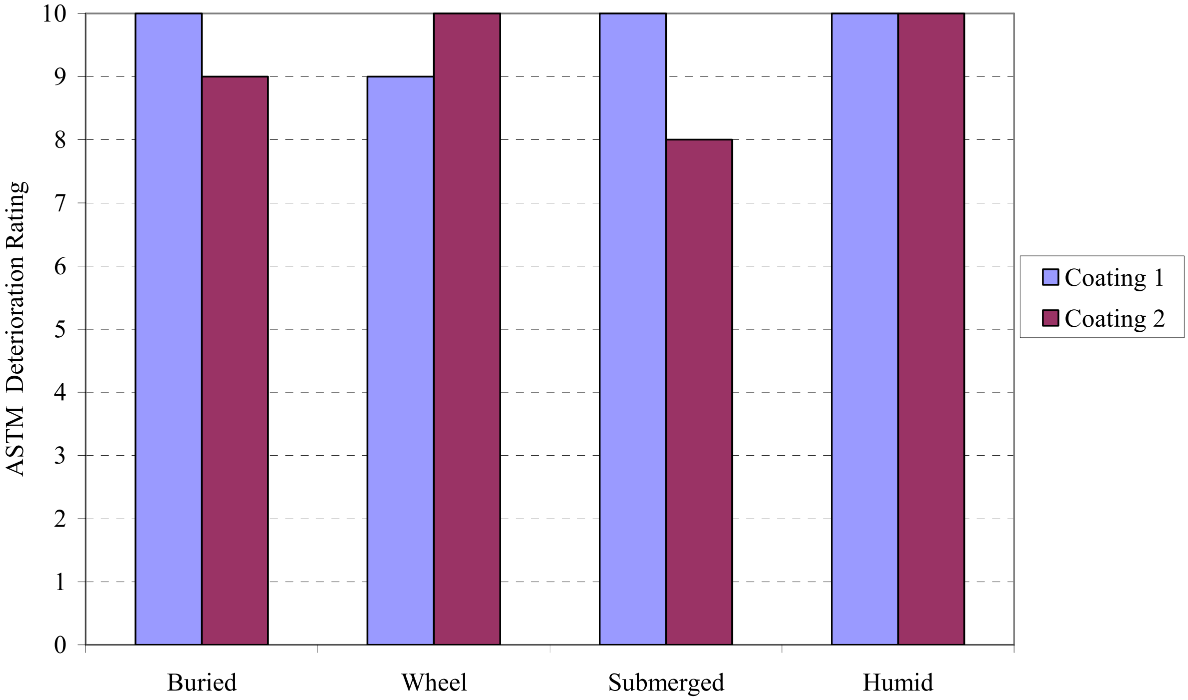

Figure 4.17(a): ASTM Score vs. Location in Tanks, 15 ppt Salt Water (Average across Control and SeaKleen™ Treated Tanks)

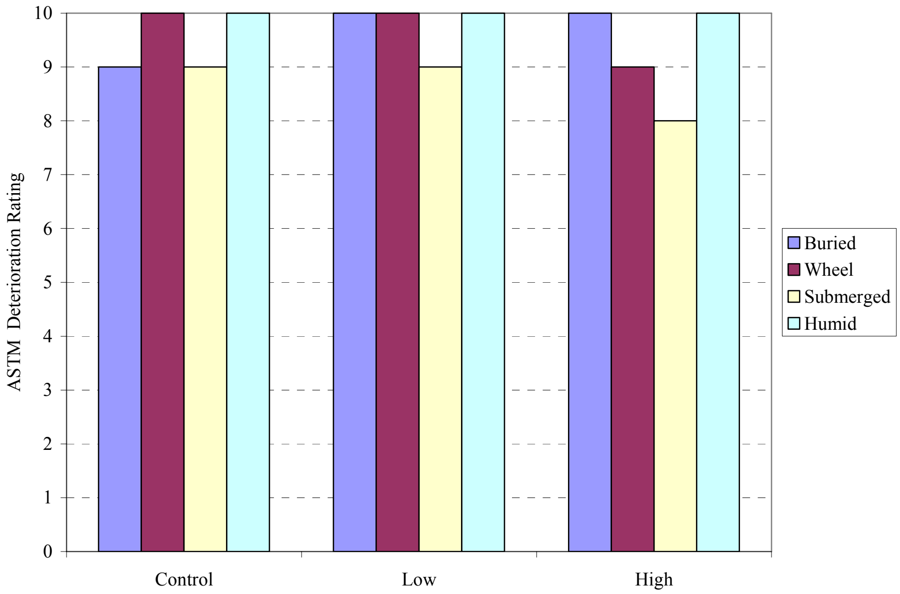

Figure 4.17(b): ASTM Score vs. Exposure (Average across all Coatings), 15 ppt Salt Water

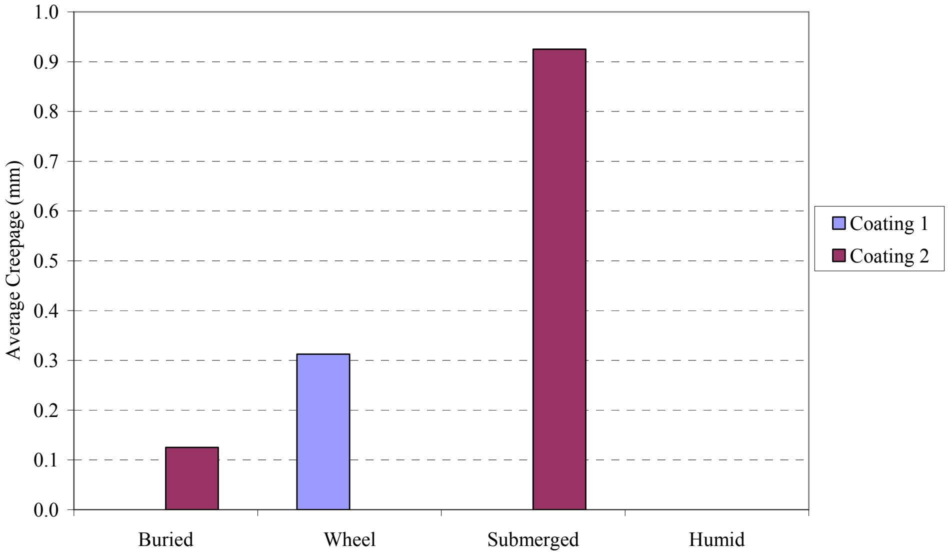

Figure 4.17(c): Average Creepage vs. Location in Tank, 15 ppt Salt Water

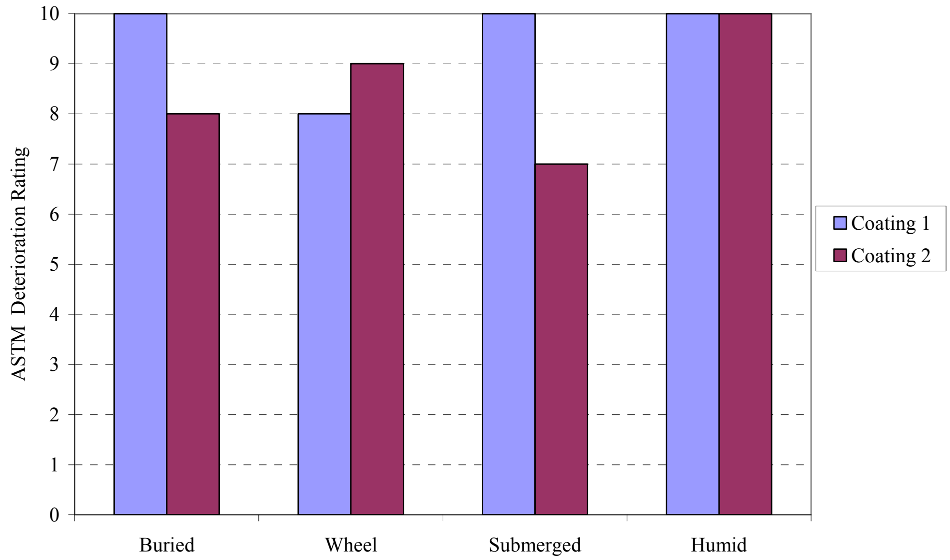

Figure 4.18(a): ASTM Score vs. Location in Tanks, 35 ppt Salt Water (Average across Control and SeaKleen™ Treated Tanks)

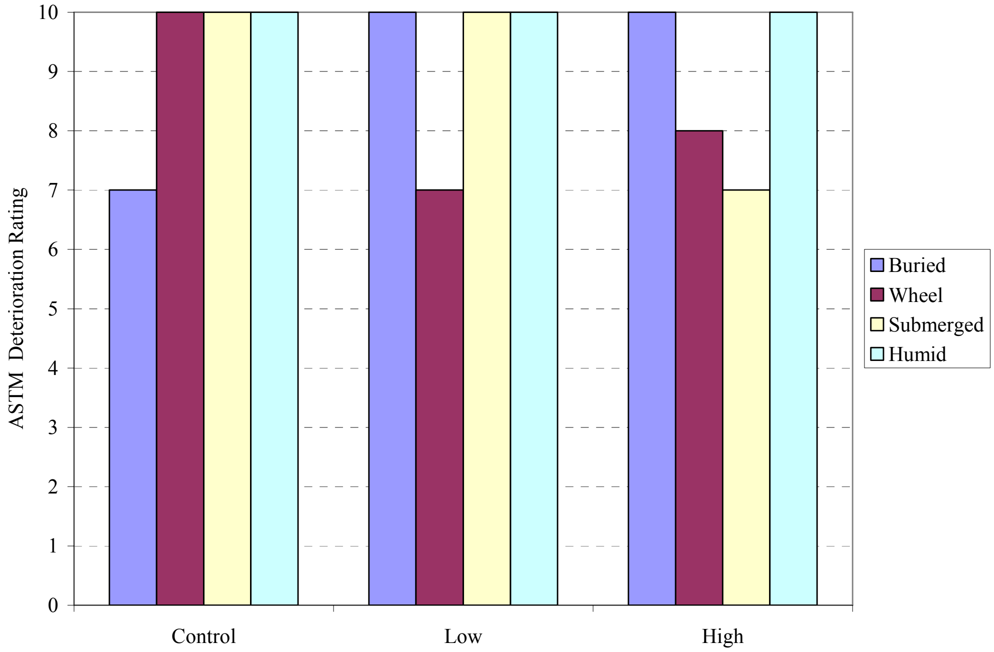

Figure 4.18(b): ASTM Score vs. Exposure (Average across all Coatings), 35 ppt Salt Water

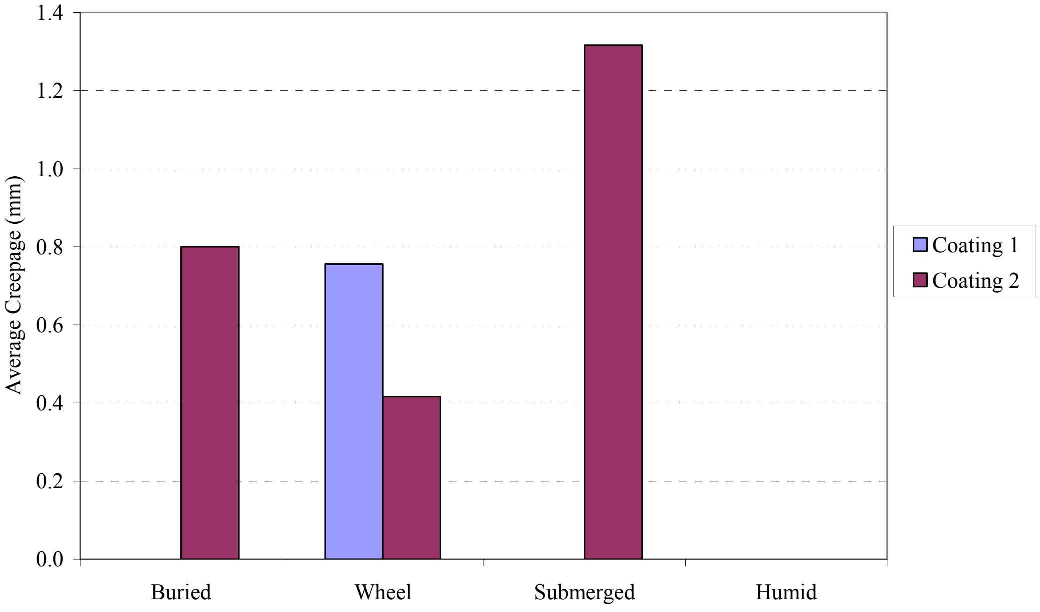

Figure 4.18(c): Average Creepage vs. Location in Tank, 35 ppt Salt Water

4.5 PERACLEAN® OCEAN

4.5.1 Bulk Solution pH Measurements

PERACLEAN® OCEAN was mixed in 1 litre of water in a beaker and the effect of concentration of PERACLEAN® OCEAN on bulk solution pH values of fresh water as well as simulated salt water (15 and 35 ppt salinity) was determined as shown in Figures 4.19(a), 4.19(b) and 4.19(c). pH readings of fresh water dropped from pH 8.5 to pH 3.7 with the addition of 1000 ppm of PERACLEAN® OCEAN. The maximum drop in the pH values from pH 8.5 to pH 4.8 occurred with the addition of the first 200 ppm. pH readings of salt water of salinity 15 ppt dropped from pH 8.4 to pH 4.0 with the addition of 1000 ppm of PERACLEAN® OCEAN, again the maximum drop in the pH values from pH 8.4 to pH 5.6 occurred with the addition of the first 200 ppm. Similarly, the pH readings of salt water of salinity 35 ppt dropped from pH 7.9 to pH 4.3 with the addition of 1000 ppm of PERACLEAN® OCEAN, again the maximum drop in the pH values from pH 7.9 to pH 6.1 occurred with the addition of the first 200 ppm. It appears that the maximum change in pH values due to the addition of PERACLEAN® OCEAN occurred in the fresh water followed by 15 ppt salt water and then 35 ppt salt water. If corrosion was controlled by pH alone then the relative corrosion rates in fresh water dosed with PERACLEAN® OCEAN should be more than those compared to the corrosion rates in salt water.

A further set of experiments were carried out to determine changes in bulk solution pH values of PERACLEAN® OCEAN treated fresh and simulated salt water over time. PERACLEAN® OCEAN concentration/dosage was kept at 200 ppm. The pH measurements were carried out over 55 hours and the results are shown in Figure 4.20(a) and 4.20(b)**.** The pH values of fresh water dosed with PERACLEAN® OCEAN remained unchanged over the 55 hours. In the case of PERACLEAN® OCEAN dosed salt water (35 ppt salinity) the pH values remained unchanged for the first seven hours and then increased marginally over the next 48 hours. This data only indicates that pH measurements cannot serve as the indicator of the half life of PERACLEAN® OCEAN in water since the manufacturer of this product had indicated that the half life in fresh water would be approximately 12 hours.

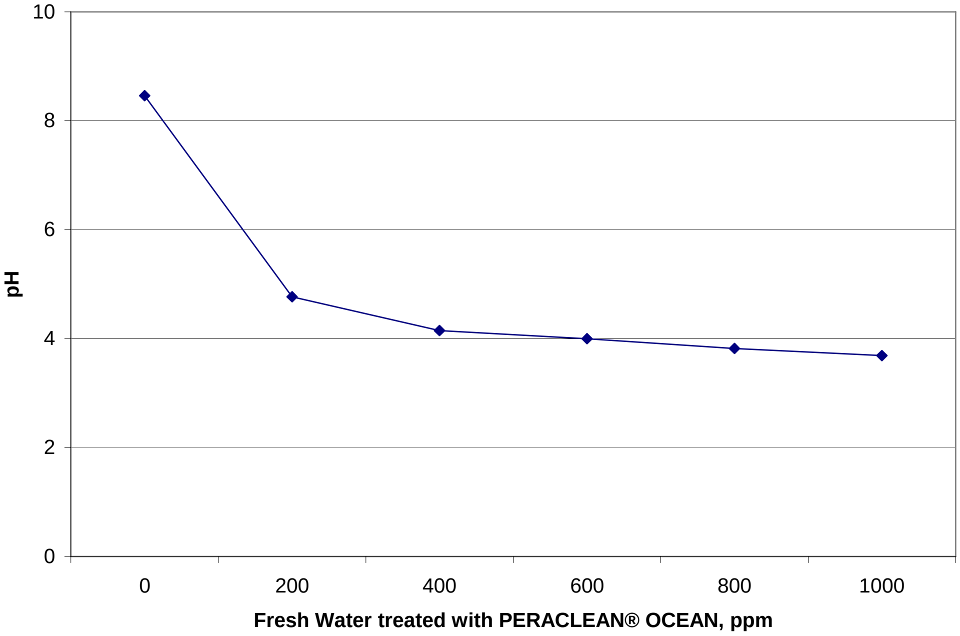

Figure 4.19(a): Effect of PERACLEAN® OCEAN Concentration on pH of Fresh Water

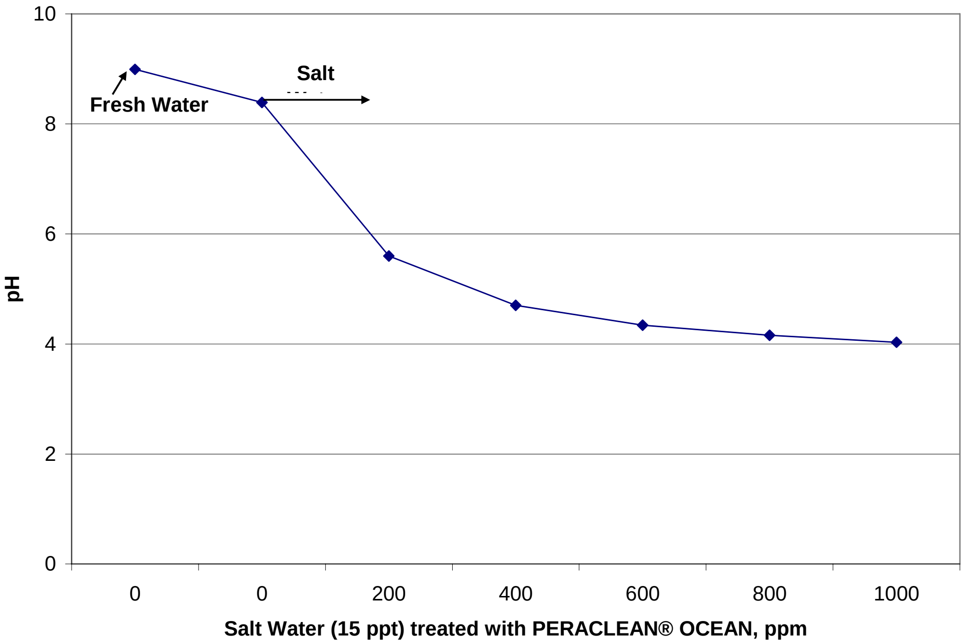

Figure 4.19(b): Effect of PERACLEAN® OCEAN Concentration on pH of Salt Water (15 ppt Salinity)

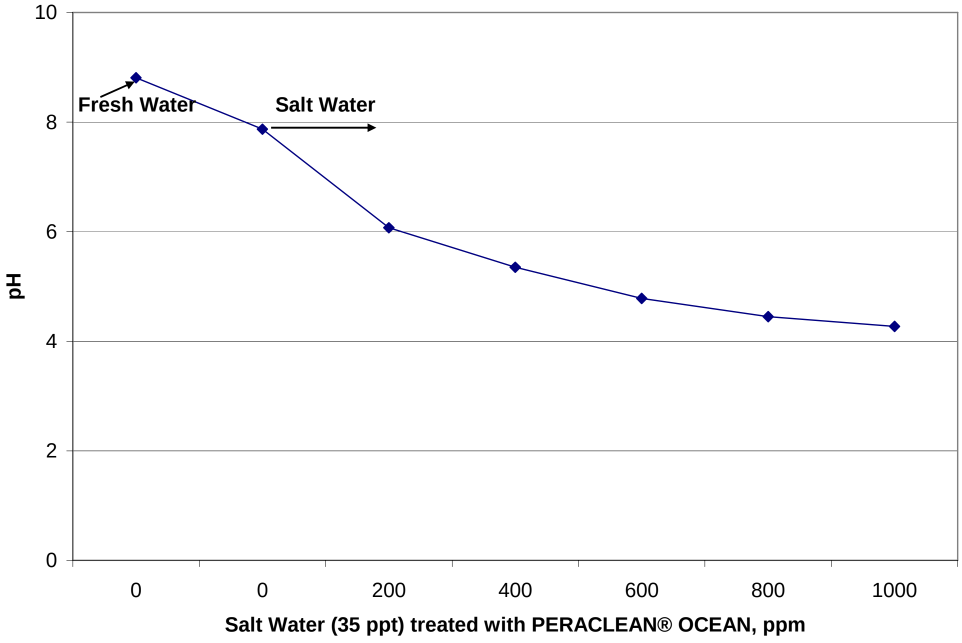

Figure 4.19(c): Effect of PERACLEAN® OCEAN Concentration on pH of Salt Water (35 ppt Salinity)

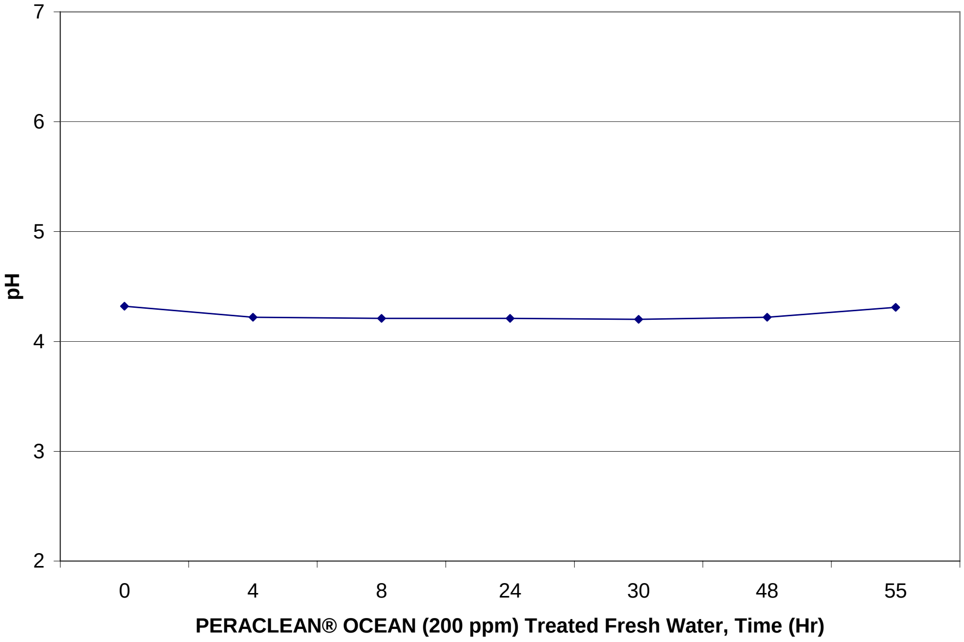

Figure 4.20(a): pH vs. Time for PERACLEAN® OCEAN (200 ppm) Treated Fresh Water

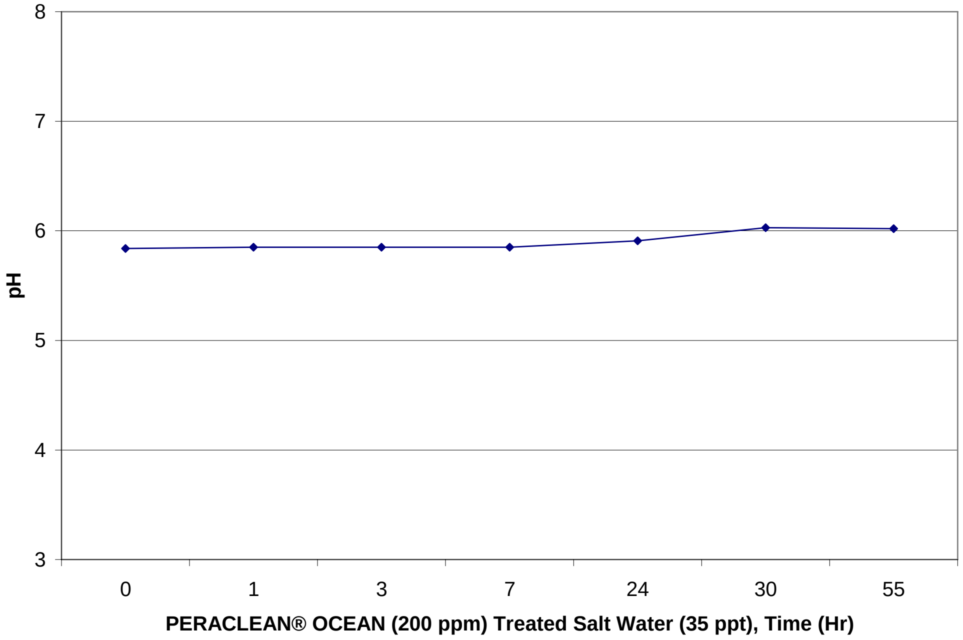

Figure 4.20(b): pH vs. Time for PERACLEAN® OCEAN (200 ppm) Treated Salt Water (35 ppt Salinity)

4.5.2 Corrosion of Bare Steel

PERACLEAN® OCEAN came in a liquid form. For 150 ppm dosage, 45 ml of PERACLEAN® OCEAN was required assuming a density of 1g/ml. However, the density of PERACLEAN® OCEAN is 1.15g/ml and therefore to achieve 150 ppm concentration only 39.1 ml is required. Therefore the PERACLEAN® OCEAN dosage in this test program was 15% higher than that recommended by the manufacturer.

According to the supplier, the half-life of PERACLEAN® OCEAN in tap water is 12 hours. Therefore, the 50% of the original dosage was added every 12 hours to maintain the required concentration. Every 48 hours, the water in the three tanks was drained and refilled with fresh tap water and the appropriate dosage (45ml in Tank 2 and 90 ml in Tank 3) of PERACLEAN® OCEAN was added. The ambient temperature was measured daily and was within ±3^{o}C, Figure 4.21**.** The bulk solution pH of three tanks was also monitored for one week and the data is shown in Figure 4.22. The pH values drop from an average of 7 in control tank to an average of 4 in low and high concentration tanks. However, there was no significant difference in pH values between the low concentration Tank 2 and high concentration Tank 3. The pH values though seem to be lower than the pH measurement tests carried out earlier in the laboratory as shown in Figure 4.19a. The spikes in pH values in control Tank 1 were observed when the measurements were carried out immediately after the water was drained and fresh water added every 48 hours.

Similar to SeaKleen™ tests, the testing with PERACLEAN® OCEAN was carried out simultaneously for 15 and 35 ppt salinity. Figure 4.23 shows the temperature during the 28 days of the testing with salt water. The sudden drop in temperature was due to a problem in the heating system unit controller that was later corrected and the temperature was maintained over the rest of the test program. The half life of PERACLEAN® OCEAN as indicated by the supplier was 6 hours in 15 ppt salt water and 4 hours in 35 ppt salt water. To ensure that at least half strength of PERACLEAN® OCEAN was maintained for the entire corrosion test, an automatic dosing system was built as shown in Figure 4.24. The automated dosing system ensured that the required amount of PERACLEAN® OCEAN was released after every 4 or 6 hours depending upon the salinity and the dosage. The dosing system consisted of a timer and a measuring tube that can only hold the required amount, i.e., 45 ml for a single dosage and 90 ml for a double dosage, of PERACLEAN® OCEAN. Every 10 days, fresh solutions were prepared and the testing continued.

Figures 4.25(a) and 4.25(b) show the pH measurements, carried out during the test program, for tanks 1, 2 and 3 and tanks 4, 5 and 6 respectively. The bulk solution pH measurements dropped from about 6.2 after the first dosage to approximately 4 after 24 hours. This was contrary to the measurements carried out earlier in the laboratory (See Figure 4.19(b) and 4.19 (c)) where pH dropped to 5.8-6.2 range with the addition of 150 ppm of PERACLEAN® OCEAN depending upon the salinity. This behaviour was similar to the fresh water tests where measurements carried out in the laboratory differed from the measurements carried out during corrosion test.

In order to verify the more than expected drop in pH measurements during the corrosion test, two separate tests were carried out. In the first test, a 35 ppt salt water solution was prepared and dosed with 150 ppm of PERACLEAN® OCEAN and its pH monitored over one week. The measurements are shown in Figure 4.26. The pH drops to 6.2 and remains relatively constant for two days and then increases to around 7.3 after five days. In the second test, a 35 ppt salt solution was repeated and dosed with 150 ppm PERACLEAN® OCEAN. Similar to the actual corrosion test, every four hours 75 ppm PERACLEAN® OCEAN was added to maintain the half strength of the chemical. The pH was measured for the entire duration and the measurements are shown in Figure 4.27. After the first dosage, the pH dropped to 6.2 as was seen earlier. The pH dropped to 5.5 after 24 hours and the pH value had dropped to 4 after 48 hours. The drop in pH values was attributed to the additional dosages that were added to maintain the half strength. This implies that the protocol of adding 50% of the required dosage after half life was responsible for the drop in the pH from 6.2 to 4. The manufacturers/suppliers of PERACLEAN® OCEAN indicated that this may be due to the degradation of PERACLEAN® OCEAN to acetic acid and the accumulation of acetic acid over time due to the continuing addition of the PERACLEAN® OCEAN to maintain the half strength. During the present corrosion testing, the plates were thus exposed to the reduced pH, i.e., 4, for an extensive period of time. In reality, however, the pH of PERACLEAN® OCEAN treated ballast tank water would be 6.2 since only a single dosage of the biocide is recommended. Therefore, the accelerated corrosion tests carried out in this program may not be reflecting the real life scenario as the test samples are exposed to highly acidic environment.

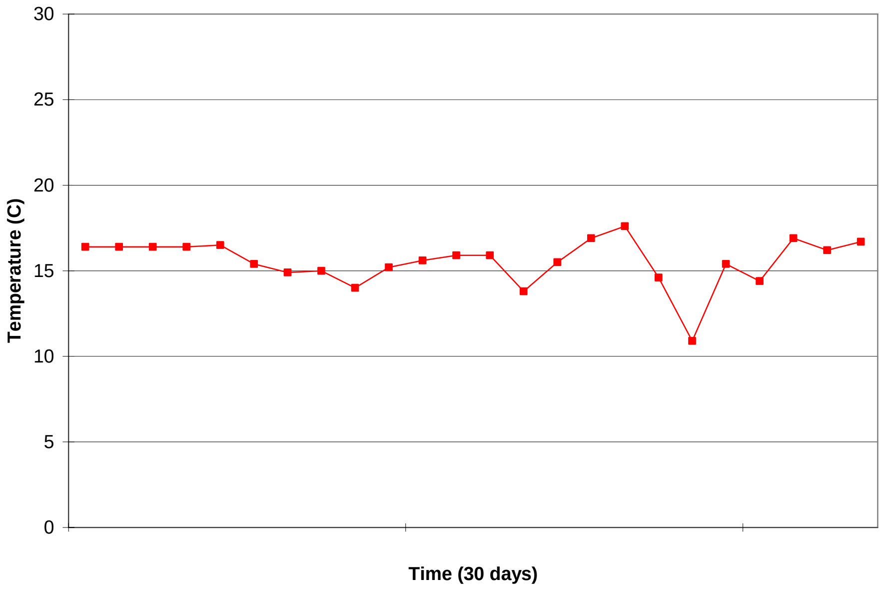

Figure 4.21: Test Temperature for the Duration of the Fresh Water Corrosion Test

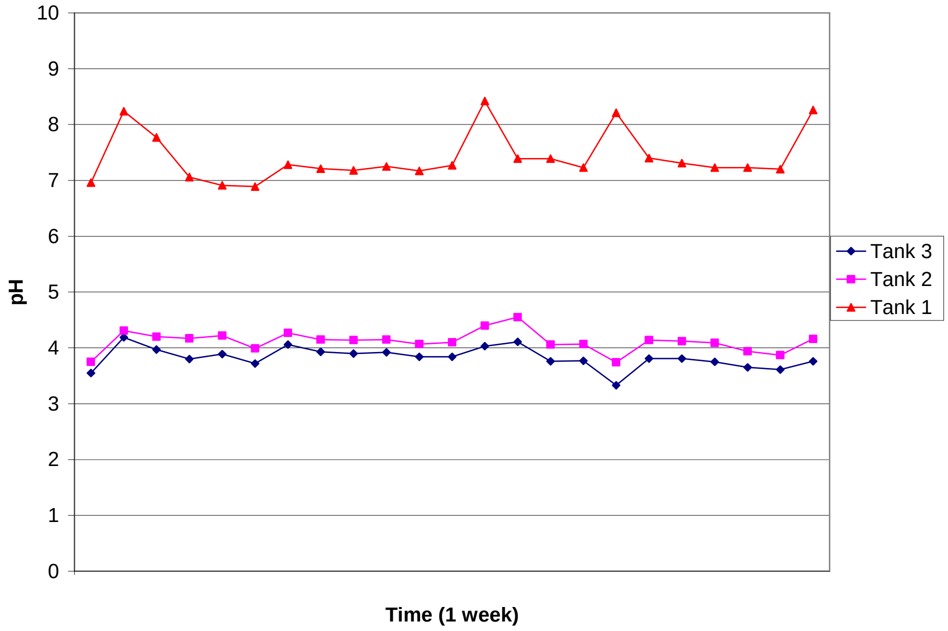

Figure 4.22: Bulk Solution pH Measurements Carried out in the Three Tanks for One Week During Fresh Water Tests

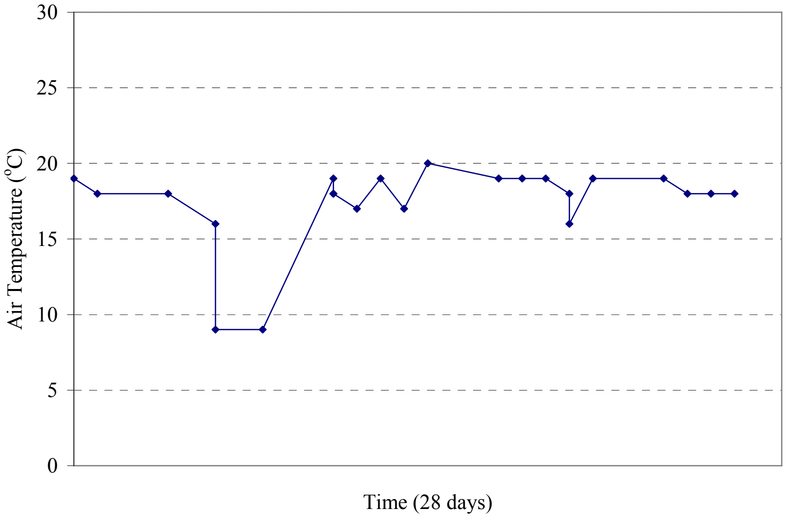

Figure 4.23: Test Temperature for the Duration of the Salt Water Corrosion Test

Figure 4.24: Experimental Set Up showing Automatic Dosing Arrangement for PERACLEAN® OCEAN during Salt Water Corrosion Tests

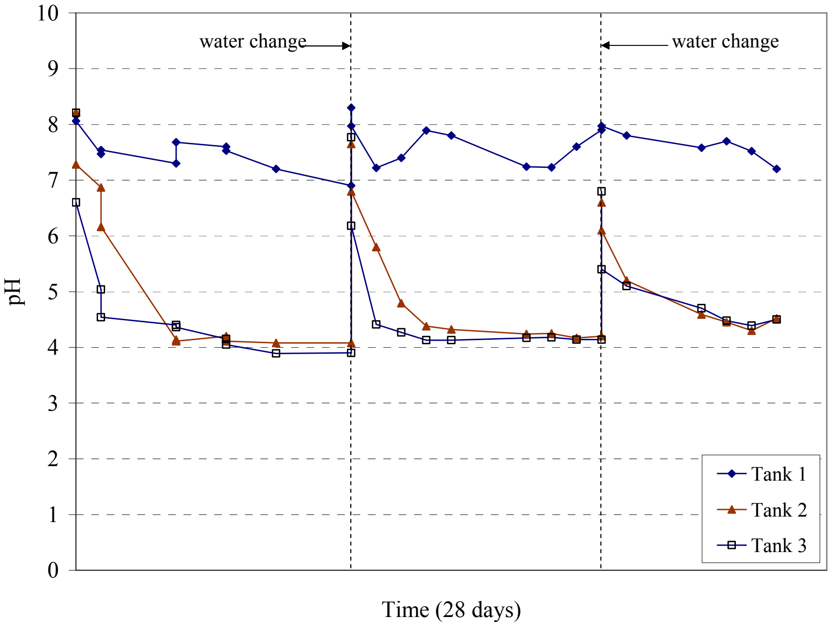

Figure 4.25(a): Bulk Solution pH Measurements Carried out During 15 ppt Salt Water Tests Treated with PERACLEAN® OCEAN

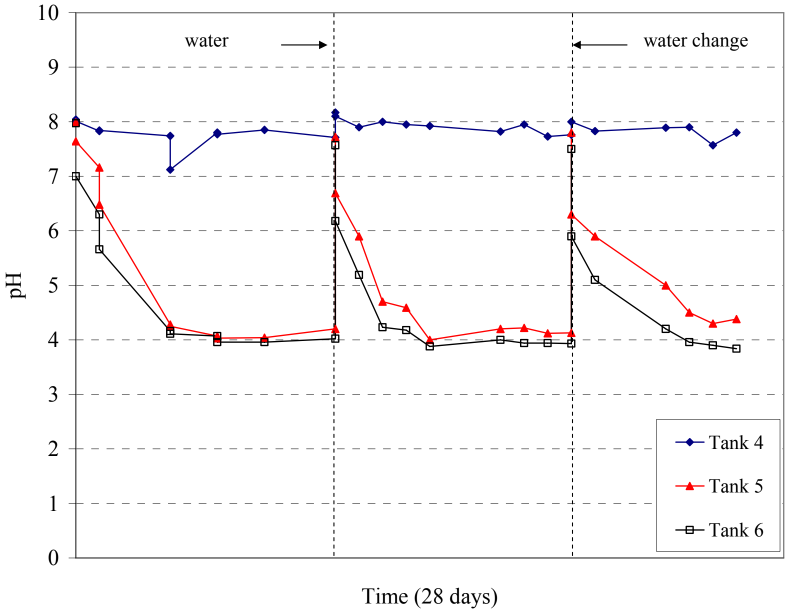

Figure 4.25(b): Bulk Solution pH Measurements Carried out during 35 ppt Salt Water Tests Treated with PERACLEAN® OCEAN

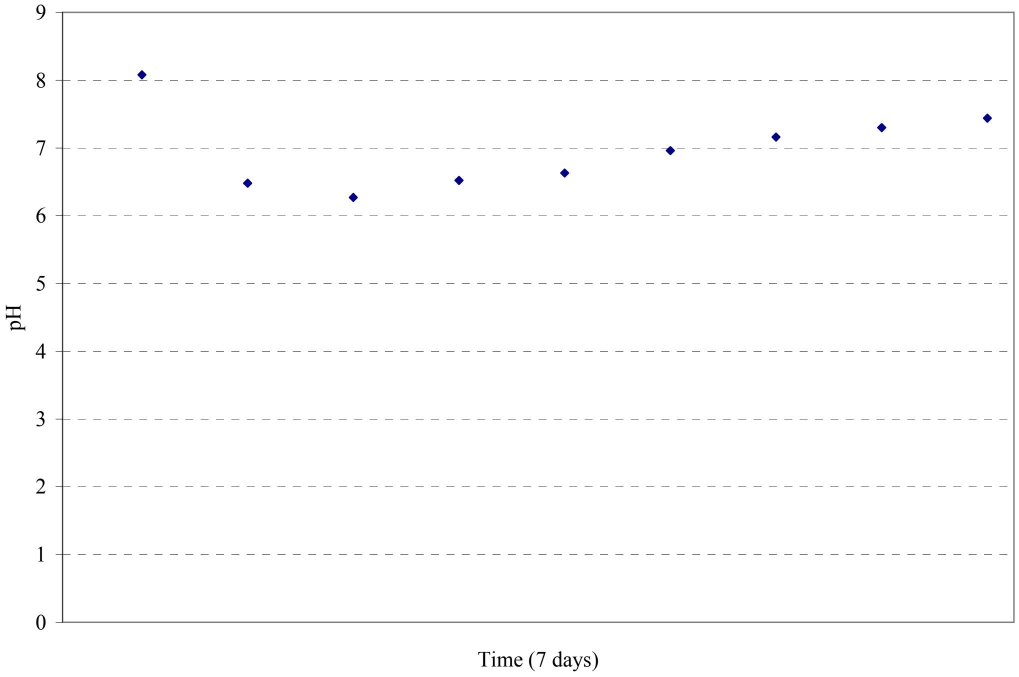

Figure 4.26: Bulk Solution pH vs. Time for Singe dose of PERACLEAN® OCEAN (150 ppm) Treated Salt Water (35 ppt Salinity)

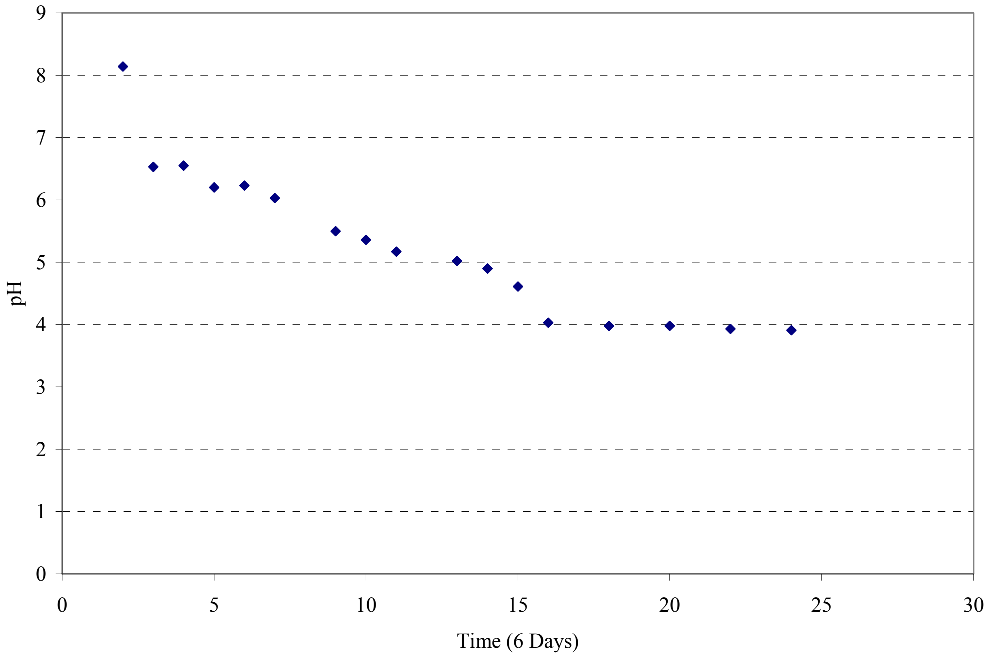

Figure 4.27: Effect of Addition of PERACLEAN® OCEAN on Bulk Solution pH in 35 ppt Salt Water Every 4 Hours to Maintain Half Strength

4.5.2.1 Fresh Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with fresh water are summarized in Table 4.5. The data was then converted to annualized thickness loss and the results are shown in Figure 4.28.

Table 4.5: Average Corrosion Weight Loss (gm) during Fresh Water Tests

Control			
Buried	Humid	Submerged	Wheel
0.50	0.24	4.20	3.21
Low Concentration			
Buried	Humid	Submerged	Wheel
0.34	0.23	5.48	5.99
High Concentration			
Buried	Humid	Submerged	Wheel
0.37	0.19	5.18	5.29

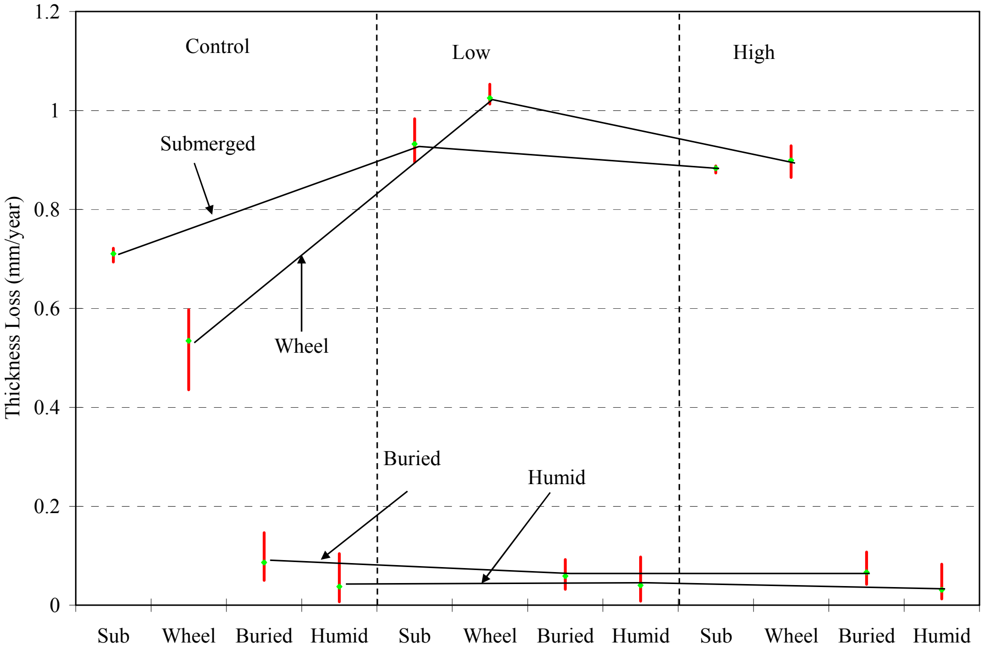

Figure 4.28: Loss of Thickness in Corrosion Tank, Fresh Water Tests

The plots presented in Figure 4.28 show that in general, the samples subjected to buried and humid environments experience much less corrosion than the samples in the submerged and wheel environment. However, the samples subjected to constant submergence experience more corrosion than those samples on the wheel in the control tank and experience almost similar corrosion rates in the high concentration Tank 3. The higher corrosion rate observed in the submerged samples compared to the wheel samples in control tank is odd and cannot be explained. The corrosion rate in the control tank varies from 0.05 mm per year to 0.7 mm per year and is less when compared to the corrosion rates observed in the control tank while carrying out SeaKleen™ testing. There is no statistical difference in the humid and buried environments between the control tank and PERACLEAN® OCEAN treated tanks. Similarly, there is no statistically significant difference in the corrosion rates between the low concentration and high concentration PERACLEAN® OCEAN treated tanks. However, there is an increase in corrosion rates between the control tank and PERACLEAN® OCEAN treated tanks in the case of the submerged and wheel environments and this is in agreement with the bulk solution pH measurements where the average value of pH was the same in low and high concentration tanks. The corrosion rates for submerged coupons and coupons exposed to splash zone environment tend to be slightly higher for low concentration as compared to the similar coupons exposed to high concentration of PERACLEAN® OCEAN.

4.5.2.2 15 ppt Salt Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with 15 ppt salt water are summarized in Table 4.6. The data was then converted to annualized thickness loss and the results are shown in Figure 4.29.

Table 4.6: Average Corrosion Weight Loss (gm) during 15ppt Salt Water

Control			
Buried	Humid	Submerged	Wheel
0.47	0.41	2.14	4.31
Low Concentration			
Buried	Humid	Submerged	Wheel
0.39	1.26	5.49	11.64
High Concentration			
Buried	Humid	Submerged	Wheel
0.33	1.07	5.07	6.62

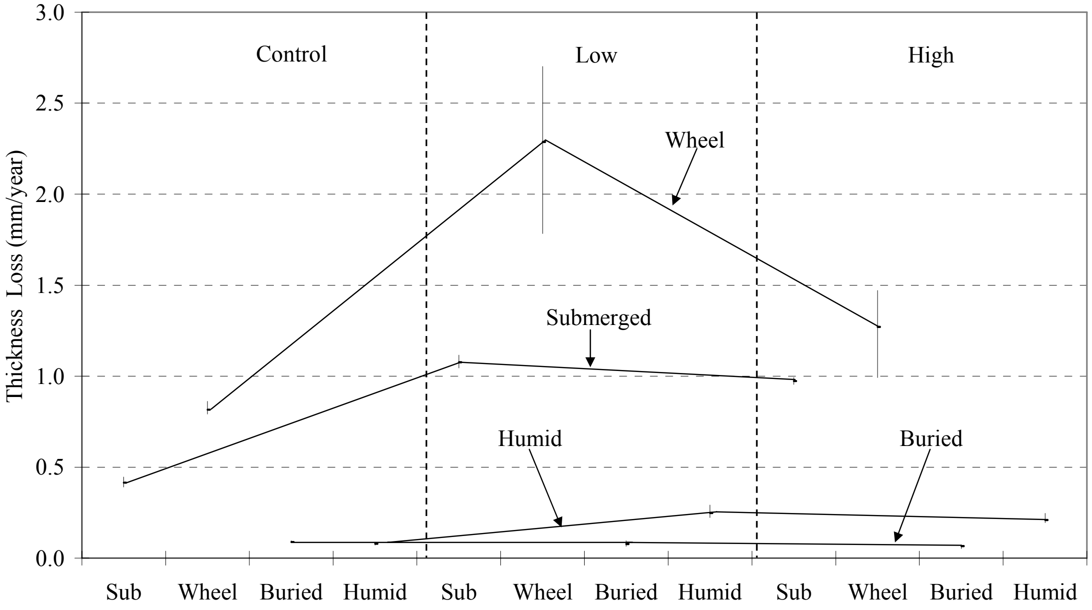

Figure 4.29: Loss of Thickness in Corrosion Tank, 15 ppt Salt Water Tests

Figure 4.29 shows the corrosion results for 15 ppt salt water tests. No difference in corrosion rates could be seen in coupons subjected to buried and humid environments in the control environment or PERACLEAN® OCEAN treated tanks. There is an increase in corrosion rates in continuously submerged coupons for PERACLEAN® OCEAN treated tanks as compared to control tanks. However, the corrosion rates are same or slightly lower for submerged coupons for high dosage PERACLEAN® OCEAN treated tank as compared to the low dosage PERACLEAN® OCEAN treated tanks. There is an increase in corrosion rates of coupons exposed to splash zone environment and PERACLEAN® OCEAN treated tanks compared to control tank coupons. Moreover, the corrosion rate has dropped significantly for the high dosage

PERACLEAN® OCEAN treated tank compared to the low concentration PERACLEAN® OCEAN treated tank. A similar trend, but to a lesser degree, was seen in fresh water corrosion tests. The reason for the drop in corrosion rates may be due to a stronger adherent corrosion layer forming quickly in the case of high concentration PERACLEAN® OCEAN treated tanks and thus resulting in a passive layer slowing down the further corrosion.

The corrosion rate of approximately 2.25mm/year observed for low concentration PERACLEAN® OCEAN treated tanks for coupons exposed to splash zone environment is very high and may be due to the reduced bulk solution pH value of 4. As described earlier the lower pH values were measured because of the continuous addition of 50% of the original dosage of PERACLEAN® OCEAN after every 6 hours. In reality however, this would not be the case as one batch of ballast water will be exposed to a single dose of PERACLEAN® OCEAN and the pH in that case would be around 6.2 rather than the pH 4.

The coupons exposed to submerged environments, however are not experiencing the significantly higher corrosion rates even though they are exposed to the same reduced bulk solution pH value of 4. The reason behind it may be the same as that responsible for reducing the corrosion rates of coupons subjected to splash zone environment and high concentration PERACLEAN® OCEAN where the corrosion layer acts as a passive film and helps reduce further corrosion. In the case of continuously submerged coupons, the corrosion layer is not mechanically disturbed and acts as a passive film even in the case of low concentration PERACLEAN® OCEAN and therefore the corrosion rates are similar for low and high concentrations of PERACLEAN® OCEAN. In the case of coupons subjected to splash zone environment, there would be a break down of corrosion layer due to mechanical disturbance. The corrosion layer formed may not be thick enough in low concentration treated tanks and will easily break down thus exposing fresh steel surface where as in higher concentration tanks the corrosion layer may be forming quickly and may be thick enough to avoid breaking down and act as a passive layer.

4.5.2.3 35 ppt Salt Water Corrosion

The corrosion/weight loss results for the bare metal specimens carried out with 35 ppt salt water are summarized in Table 4.7. The data was then converted to annualized thickness loss and the results are shown in Figure 4.30.

Table 4.7: Average Corrosion Weight Loss (gm) during 35 ppt Salt Water

Control			
Buried	Humid	Submerged	Wheel
2.32	0.36	2.08	4.68
Low Concentration			
Buried	Humid	Submerged	Wheel
0.45	3.66	5.83	24.43
High Concentration			
Buried	Humid	Submerged	Wheel
0.55	2.98	6.35	11.93

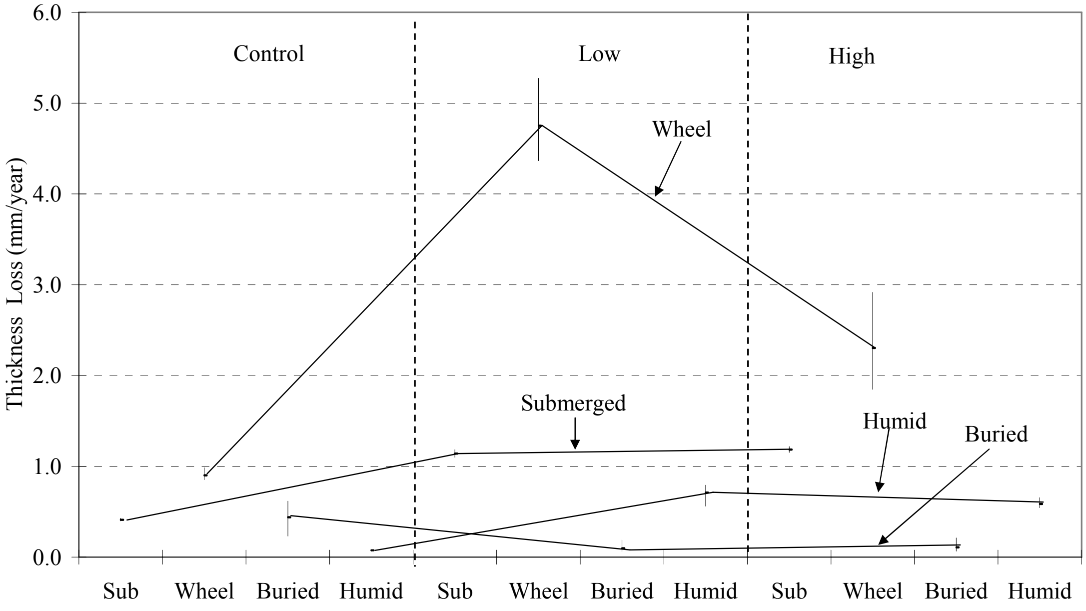

Figure 4.30: Loss of Thickness in Corrosion Tank, 35 ppt Salt Water Tests

Figure 4.30 shows the corrosion rates for 35 ppt salt water tests. Again, the corrosion rates are similar for coupons exposed to humid and buried environment irrespective of the tank condition i.e., control or low and high dosage PERACLEAN® OCEAN. The corrosion rates for submerged coupons exposed to PERACLEAN® OCEAN are higher compared to the control tank. Similar to the 15 ppt salt water tests, no difference in corrosion rates of submerged coupons exposed to either low or high concentration of PERACLEAN® OCEAN was observed. The results for coupons exposed to splash zone environment are again similar to 15 ppt salt water tests. There is an increase in corrosion rate due to the exposure to PERACLEAN® OCEAN as compared to the control tanks. Again, the corrosion rates for coupons exposed to splash zone environment experience much lower corrosion rates when exposed to high concentration

PERACLEAN® OCEAN as compared to low concentration. The corrosion rate of approximately 4.6 mm/year observed in splash zone coupons exposed to low concentration PERACLEAN® OCEAN is significantly higher compared to the same coupons in 15 ppt salt water tests.

4.5.2.4 Comparison of Fresh Water and Salt Water Corrosion Data

Figure 4.31(a) and Figure 4.31(b) show the comparison of the fresh water, 15 ppt salt water and 35 ppt salt water corrosion tests for the coupons subjected to constant submergence and splash zone environments for low dosages and high dosages of PERACLEAN® OCEAN respectively. In the case of continuously submerged coupons the corrosion rates are similar for low and high dosage of PERACLEAN® OCEAN. There is a slight increasing trend in corrosion rates as the test medium changes from fresh water to 15 ppt salt water to 35 ppt salt water. For the coupons exposed to splash zone environment, the corrosion rates increase as the test medium changes from fresh water to 15 ppt salt water to 35 ppt salt water. The corrosion rates are significantly higher for the low dosage compared to the high dosage PERACLEAN® OCEAN treated tanks for coupons exposed to splash zone environment. The reasons for the increased corrosion rates have already been explained in detail. The photographs of the steel plates from salt water tests and exposed to splash zone and submerged environment are provided in Appendix G.

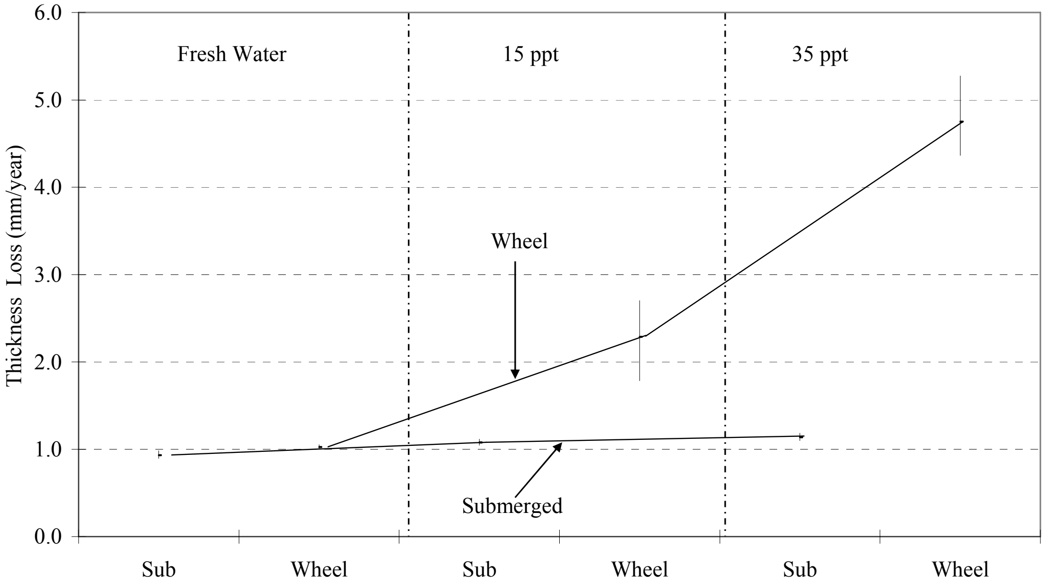

Figure 4.31(a): Comparison of Corrosion Rates in Fresh Water, 15 ppt Salt Water and 35 ppt Salt Water for Wheel and Submerged Coupons exposed to Low Dosage PERACLEAN® OCEAN Concentration.

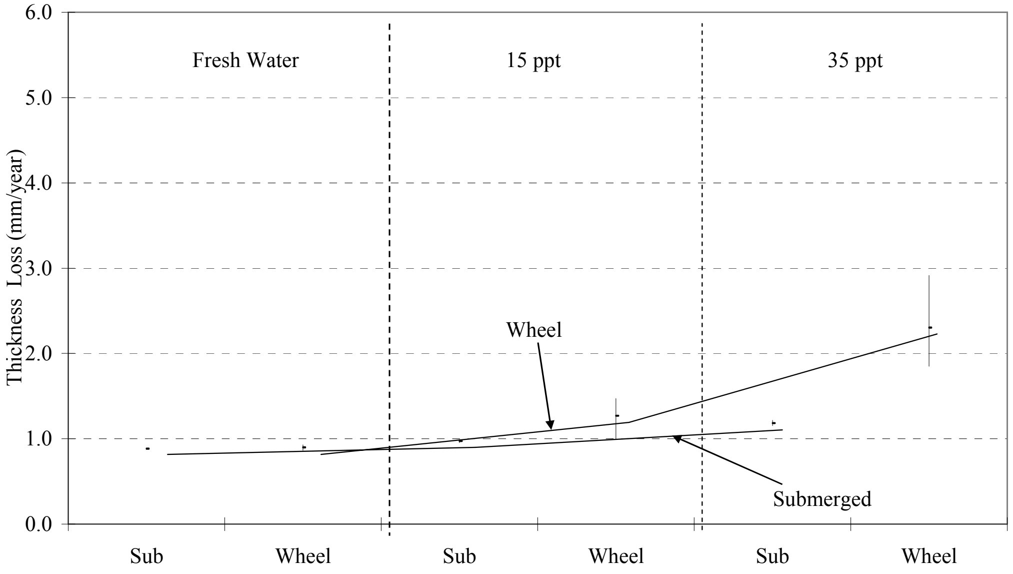

Figure 4.31(b): Comparison of Corrosion Rates in Fresh Water, 15 ppt Salt Water and 35 ppt Salt Water for Wheel and Submerged Coupons exposed to High Dosage PERACLEAN® OCEAN Concentration

4.5.3 Integrity of the Coating Systems

Coating deterioration measurements were carried out in a similar fashion as was explained in the section dealing with SeaKleen™. The results of the ASTM scribe test did not reveal any statistically valid differences in paint damage rates caused by the presence of PERACLEAN® OCEAN. Figure 4.32(a), 4.32(b) and 4.32(c) show the presentation of ASTM scores and creepage for different locations and exposures for fresh water tests. Similar data for 15 ppt salt water and 35 ppt salt water are shown in Figures 4.33(a), 4.33(b), 4.33(c) and Figures 4.34(a), 4.34(b), 4.34(c) respectively.

When comparing deterioration ratings to tank concentrations, few statistically significant correlations can be made. However, the variability in the data is less compared to the trends observed in the SeaKleen™ experimental program. Furthermore, it appears that the modified epoxy coating was much better than the coal tar epoxy coatings. When comparing coating type and environment (Wheel, Submerged, and Humid), the modified epoxy coating appeared to be the superior coating in the aggressive environment induced by the wheel. There was no creepage observed in both coatings in the humid environment. The individual results of the coatings vis-à-vis tanks are provided in Appendix H.

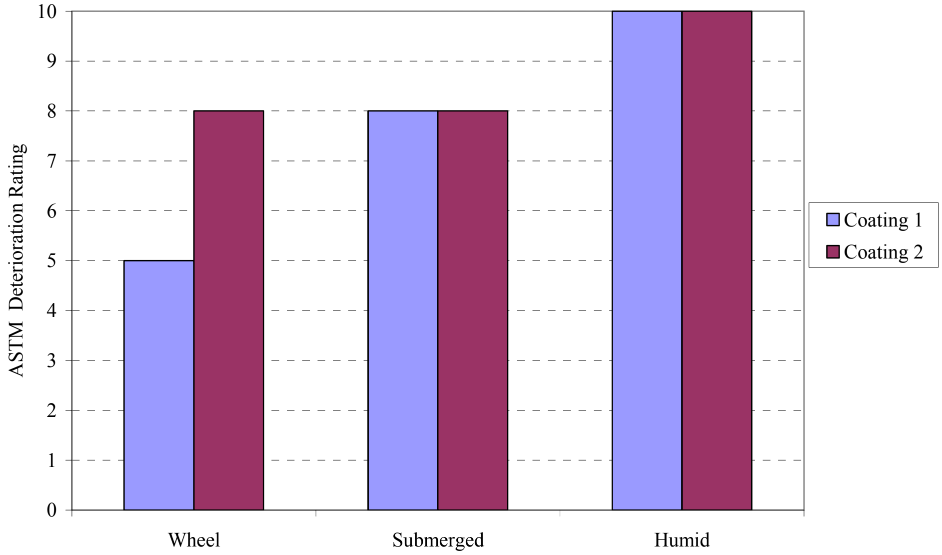

Figure 4.32(a): ASTM Score vs. Location in Tanks, Fresh Water (Average across Control and PERACLEAN® OCEAN Treated Tanks)

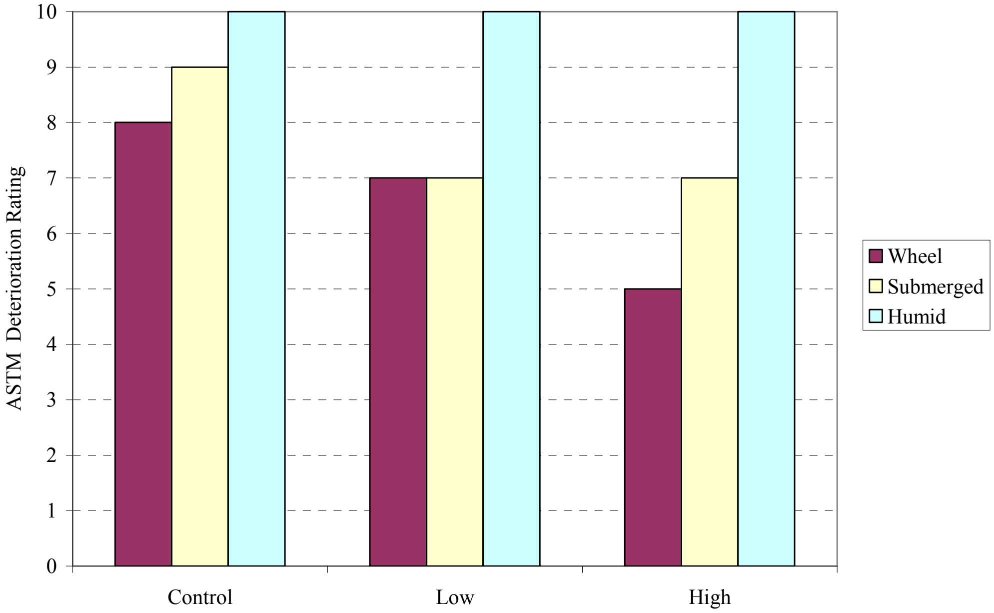

Figure 4.32(b): ASTM Score vs. Exposure (Average across all Coatings), Fresh Water

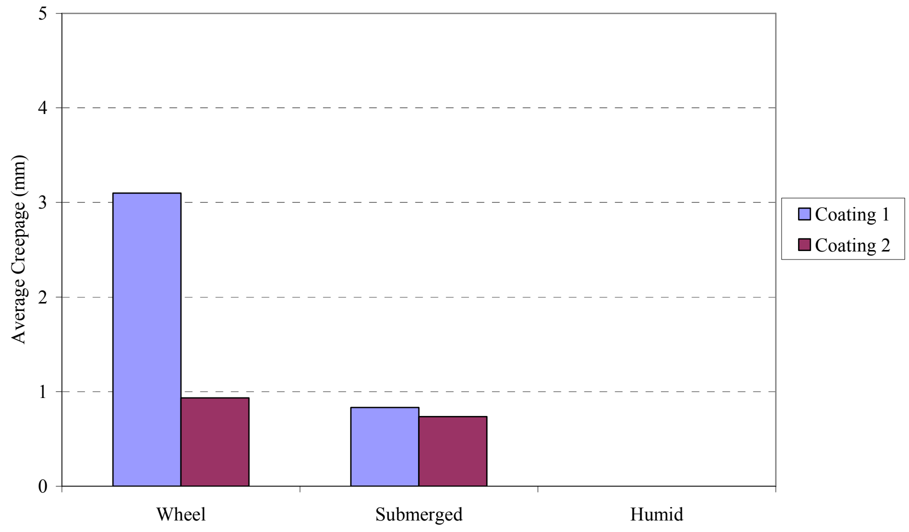

Figure 4.32(c): Average Creepage vs. Location in Tank, Fresh Water

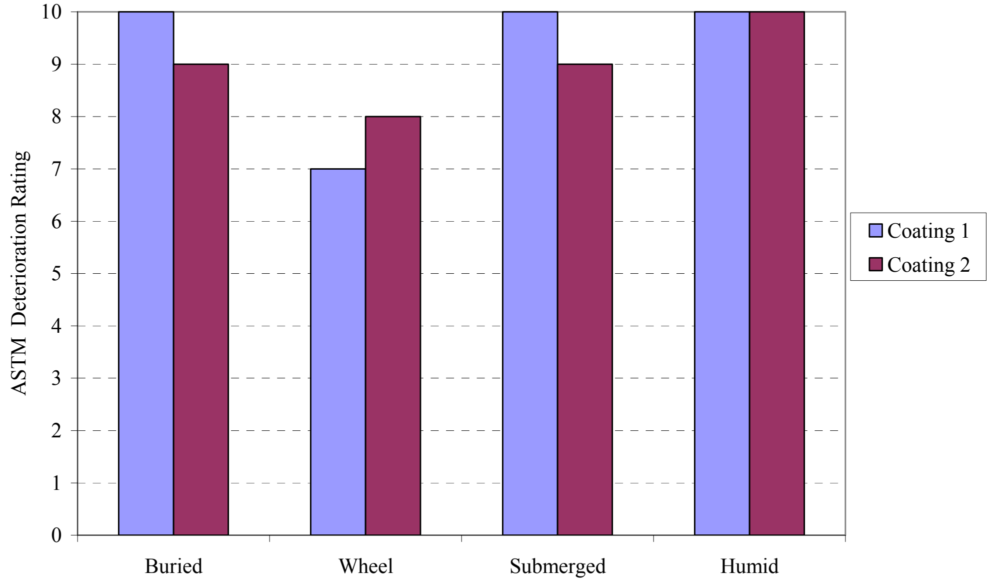

Figure 4.33(a): ASTM Score vs. Location in Tanks, 15 ppt Salt Water (Average across Control and PERACLEAN® OCEAN Treated Tanks)

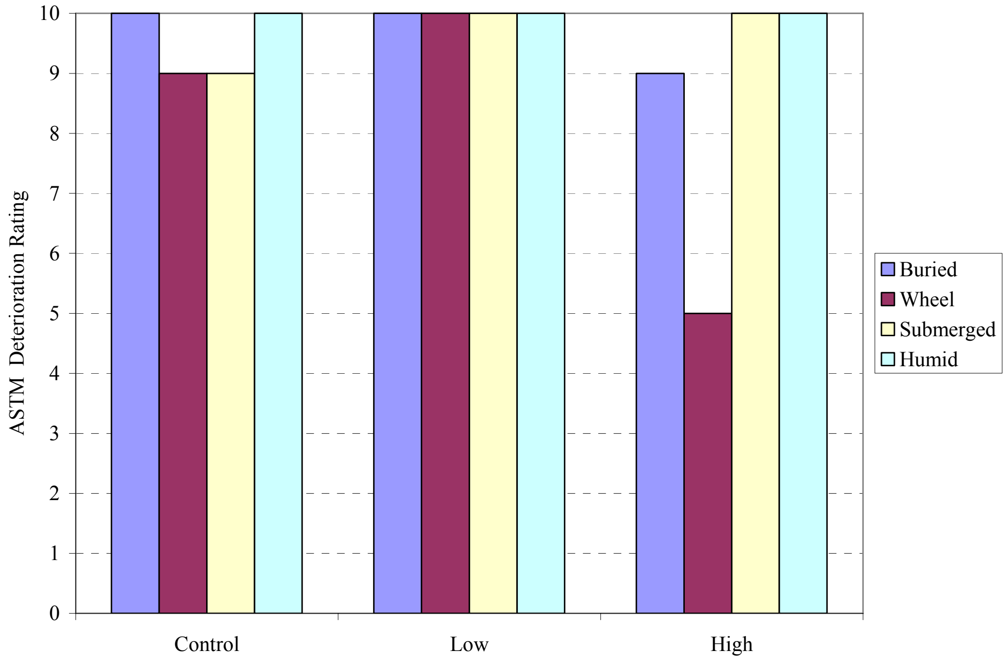

Figure 4.33(b): ASTM Score vs. Exposure (Average across all Coatings), 15 ppt Salt Water

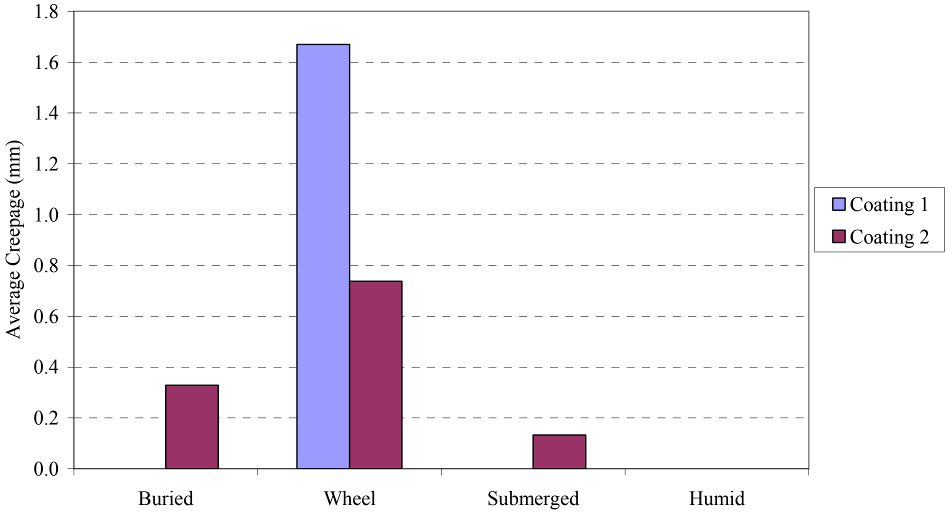

Figure 4.33(c): Average Creepage vs. Location in Tank, 15 ppt Salt Water

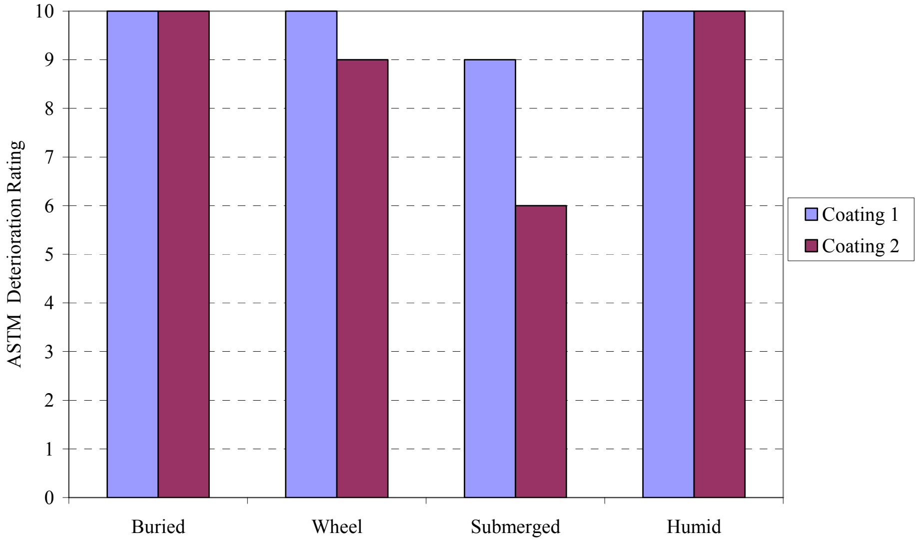

Figure 4.34(a): ASTM Score vs. Location in Tanks, 35 ppt Salt Water (Average across Control and PERACLEAN® OCEAN Treated Tanks)

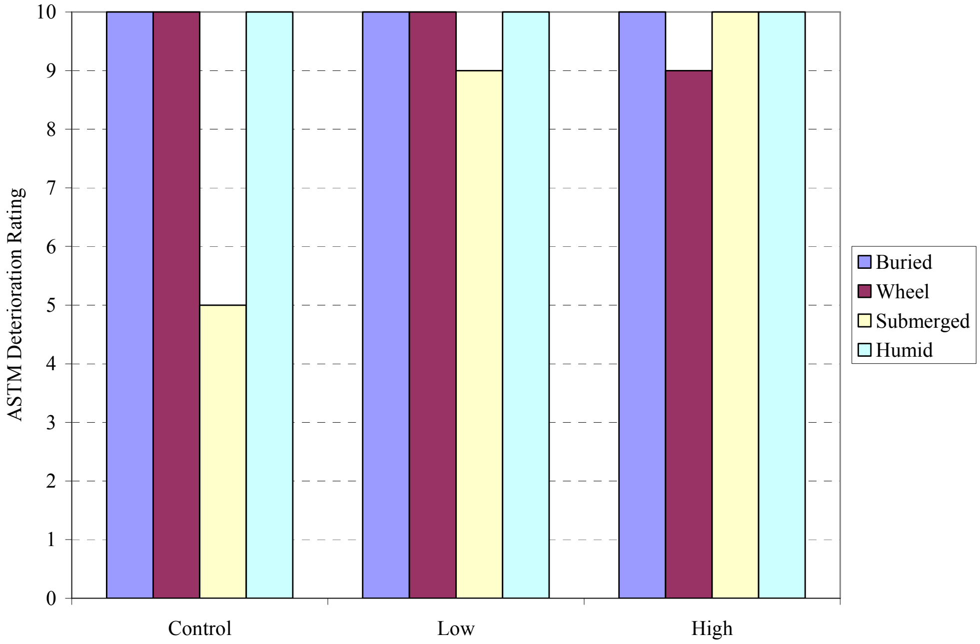

Figure 4.34(b): ASTM Score vs. Exposure (Average across all Coatings), 35 ppt Salt Water

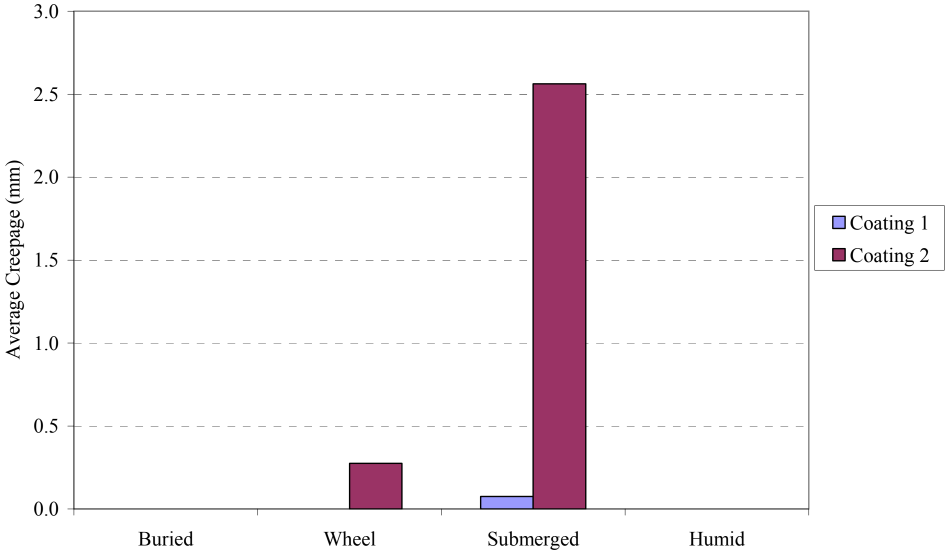

Figure 4.34(c): Average Creepage vs. Location in Tank, 35 ppt Salt Water

5. CONCLUSIONS

5.1 SeaKleen™

5.1.1 Corrosion

Corrosion rates are dependent on the availability of oxygen. A ballast tank is constantly going through low frequency cycles of wet and dry. Our study attempted to reproduce these ballast tank conditions in an accelerated manner and determine whether SeaKleen™ does accelerate and promote corrosion.

For fresh water tests, the results demonstrated that SeaKleen™ does not increase corrosion unless the exposed steel is located in an aggressive area of the tank. All the other areas appeared to sustain little damage from the differing concentrations of SeaKleen™. The corrosion rate did increase in our simulated aggressive location; the wheel. Onboard a ship, this area would be the waterline in a ballast tank and areas in the splash zone. This experiment shows that under these conditions the presence of SeaKleen™ can increase corrosion rates.

For 15 ppt salt water corrosion tests the results indicate that SeaKleen™ did not increase the corrosion rates in any of the simulated locations in the short duration tests.

For 35 ppt salt water tests the results again indicate that SeaKleen™ did not significantly increase the corrosion rates compared to the control conditions in the short duration tests. However, similar to fresh water, there was an increasing trend in corrosion with SeaKleen™ for the simulated aggressive location; i.e., coupons mounted on a wheel. However, longer test duration of 90-120 days will be required to ascertain whether there is any statistically significant increase in corrosion rates.

Corrosion rates were generally higher in SeaKleen™ treated fresh water compared to the salt water for submerged coupons and coupons exposed to splash zone environment.

The annualized corrosion rates determined in the present study are based on the assumption that the coupons are exposed to at least half strength SeaKleen™ 24 hours a day and 365 days a year. However, onboard a ship SeaKleen™ will be supplied in a single dosage for one ballast operation and therefore depending upon the operation of a ship, the annual corrosion rates determined here may be conservative.

5.1.2 Coating Systems

Corrosion of steel can only take place when the coating system is damaged. The presence of SeaKleen™ does not accelerate the damage of coatings.

Typically, the steel structure of a ballast tank is coated with a zinc rich primer under an epoxy top coating. This coating system did not experience any increase in failure attributable to the presence of SeaKleen™ when using the ASTM “Testing Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments ASTM D1654-92”.

5.2 PERACLEAN® OCEAN

5.2.1 Corrosion

For fresh water tests, the results demonstrated that PERACLEAN® OCEAN does not increase corrosion in the buried and humid environments. The results also suggested that the relative concentration of PERACLEAN® OCEAN (i.e., comparison between low concentration and high concentration) had no effect on the total corrosion. However, there was an increase in corrosion in the samples subjected to wheel and submerged environments compared to the control samples in the similar environment.

The results for 15 ppt salt water and 35 ppt salt water were similar to the fresh water results, i.e., PERACLEAN® OCEAN did increase the corrosion rates for coupons subjected to submerged and splash zone environment compared to the control samples in the similar environment.

There was an increase in the corrosion rates in PERACLEAN® OCEAN treated tanks for coupons simulating splash zone environment as the test medium changed from fresh water to 15 ppt salt water to 35 ppt salt water. A similar trend of increasing corrosion could be seen for submerged coupons, however, longer test duration would be required to ascertain whether there is any statistically significant increase in the corrosion rates.

The experimental protocol dealing with the addition of PERACLEAN® OCEAN to maintain half strength resulted in a significant drop in pH after the first 24-36 hours and therefore, may not represent the actual scenario onboard a ship. The drop in pH may be responsible for the increased corrosion rates. Onboard a ship, only a single dose of PERACLEAN® OCEAN would be required for one ballast operation. The experimental protocol requires modification and longer duration corrosion tests (at least 90-120 days duration) need to be carried out.

The annualized corrosion rates calculated here are based on the premise that the coupons are exposed to at least half strength PERACLEAN® OCEAN 24 hours a day and 365 days a year. However, onboard a ship PERACLEAN® OCEAN would be applied in a single dosage for one ballast operation and therefore depending upon the operation of a ship, the annual corrosion rates determined here may be conservative.

5.2.2 Coating Systems

Corrosion of steel can only take place when the coating system is damaged. The presence of PERACLEAN® OCEAN does not seem to significantly accelerate the damage of coatings.

Typically, the steel structure of a ballast tank is coated with a zinc rich primer under an epoxy top coating. This coating system did not experience any significant increase in failure attributable to the presence of PERACLEAN® OCEAN when using the ASTM “Testing Method for Evaluation of Painted or Coated Specimens Subjected to Corrosive Environments ASTM D1654-92”.

6. RECOMMENDATIONS

- Corrosion testing should be carried out for longer test durations, i.e. for atleast 90-120 days (or for longer duration) with SeaKleen™ and PERACLEAN® OCEAN to evaluate the longer term impacts on corrosion rates.

- Corrosion rates should be measured at different exposure times, e.g. subjecting samples to 30, 60 and 90 days both with the SeaKleen™ and the PERACLEAN® OCEAN. The corrosion rate testing will, in the first instance, provide the much needed data as well as help to explain some of the variability observed in the corrosion rates with both the SeaKleen™ and PERACLEAN® OCEAN treated tanks.

- The experimental protocol for corrosion testing with PERACLEAN® OCEAN should be modified so that the tests are carried out at bulk solution pH values representing in-service scenarios.

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APPENDIX A

COMMENTS ON LITERATURE REVIEW

Ballast Tanks Corrosion - The vast majority of the world's fleet of ships, including military and commercial vessels, are constructed of carbon steel. Steel corrodes quickly when exposed to oxygen and water. Ocean-going vessels are particularly susceptible to corrosion, due to the accelerated corrosion rate in exposure to salt water. Corroded steel structures on a vessel decrease seaworthiness so extensive measures are taken to prevent corrosion and, inevitably, in repair. The cost to prevent, maintain, and repair corrosion on individual vessels can run into the millions of dollars (e.g., $5.5 million to replace 1400 tonnes of ballast tank steel on Wind Conquest, Marine Engineering Review, 1991).

One area in a ship where corrosion is of particular concern is in the ballast tanks. Prolonged exposure of the ballast tank structure to water (often salt water) creates a condition conducive to rapid corrosion. The cost to paint ballast tanks is typically $5.00 to $10.00 per square meter with the cost to repair corroded areas at approximately $500 per square meter (Fairplay, 1993). With large cargo vessels and oil tankers having hundreds of thousands of square feet of ballast tank surface area, preventing and treating corrosion is extremely costly.

Therefore, any measure for controlling aquatic invasive species in ballast tanks cannot be evaluated without consideration of the impact on corrosion. For example, both chlorination (McCraken, 2001) and ozonation (Andersen, 2001) of seawater are known to exacerbate corrosion of steel. Clearly, removal or reduction of oxygen will eliminate or reduce direct oxidation reactions related to corrosion. However, de-oxygenation could increase corrosion resulting from the activities of naturally occurring microaerophilic, facultative or obligate anaerobic bacteria. Acid-producing bacteria (APB) and sulfate-reducing bacteria (SRB) grow under anoxic conditions and produce corrosive metabolic by-products (organic acids and sulfides, respectively).

The corrosion rate of carbon steel is not influenced by pH over the range of 4.5 to 9.5 in distilled and tap waters (Boyer and Gall, 1985). Over this range, corrosion products maintain a pH of 9.5 at the metal surface. Below pH 4.0, hydrogen evolution begins and corrosion increases dramatically. Although it is extremely unlikely that APB will change the bulk pH of carbonate buffered seawater, APB can reduce pH locally under colonies and produce corrosion in carbon steel (Pope, 1995).

All seawater contains 2 gm l-1 sulfate that can be reduced to sulfide by SRB in the absence of oxygen. Reviews by Miller and Tiller (1970), Iverson (1974) and Postgate (1979) provide examples and details of microbiologically influenced corrosion of iron and mild steel under anaerobic conditions caused by SRB. Microbiologically influenced corrosion failures have been reported for mild steel piping and equipment exposed in the marine environment (Sanders and Hamilton, 1986; Eidsa and Risberg, 1986; Eashwar et al., 1990) soil (King et al., 1983; Kasahara and Kajiyama, 1986; Alanis et al., 1986; Pope et al., 1988; Dias and Bromel, 1990), oil refining industry (Winters and Badelek, 1987) , fossil fuel and nuclear power plants (Soraco et al, 1988; Licina, 1988, Pope 1986 &1987; Bibb, 1986) and process industries (Pacheco, 1987;Honneysett, 1985; Tatnall et al., 1981).

De-oxygenation can also result in putrefaction, anaerobic breakdown of sulfur-rich proteins, and levels of sulfides will not be limited to the sulfate concentration in the seawater. Sulfide reacts with iron oxide, formed in the atmosphere or in oxygenated seawater, to produce a non-tenacious iron sulfide layer that can be removed with stress or converted back to an oxide by the introduction of oxygen. In either case, the sulfide layer is not uniformly removed or oxidized, creating adjacent anodic and cathodic regions and aggressive corrosion.

The most corrosive operating condition is one in which carbon steel is exposed to alternating oxygenated/deoxygenated conditions (Hardy and Bown, 1984: Lee et al., 1993a; Lee et al., 1993b). Under constant oxygenation an oxide will form that provides corrosion resistance. Under anaerobic conditions, a sulfide layer will form and the corrosion rate will decrease until oxygen is introduced. The result of alternating operating conditions is severe pitting. Additionally, concentrations of sulfides can produce sulfide assisted stress corrosion cracking in carbon steel. 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, 1986). Anaerobic conditions and sulfides form within marine biofilms at biofilm/metal interfaces, independent of bulk oxygen concentrations. Exposure of iron sulfide corrosion products to oxygen creates differential aeration cells and localized corrosion. However, because aerobic microorganisms form biofilms, continuous deoxygenation to prevent biofilm production has been suggested as a way to reduce microbial induced corrosion (Lutey, 2001; Pope and Pope, 2001).

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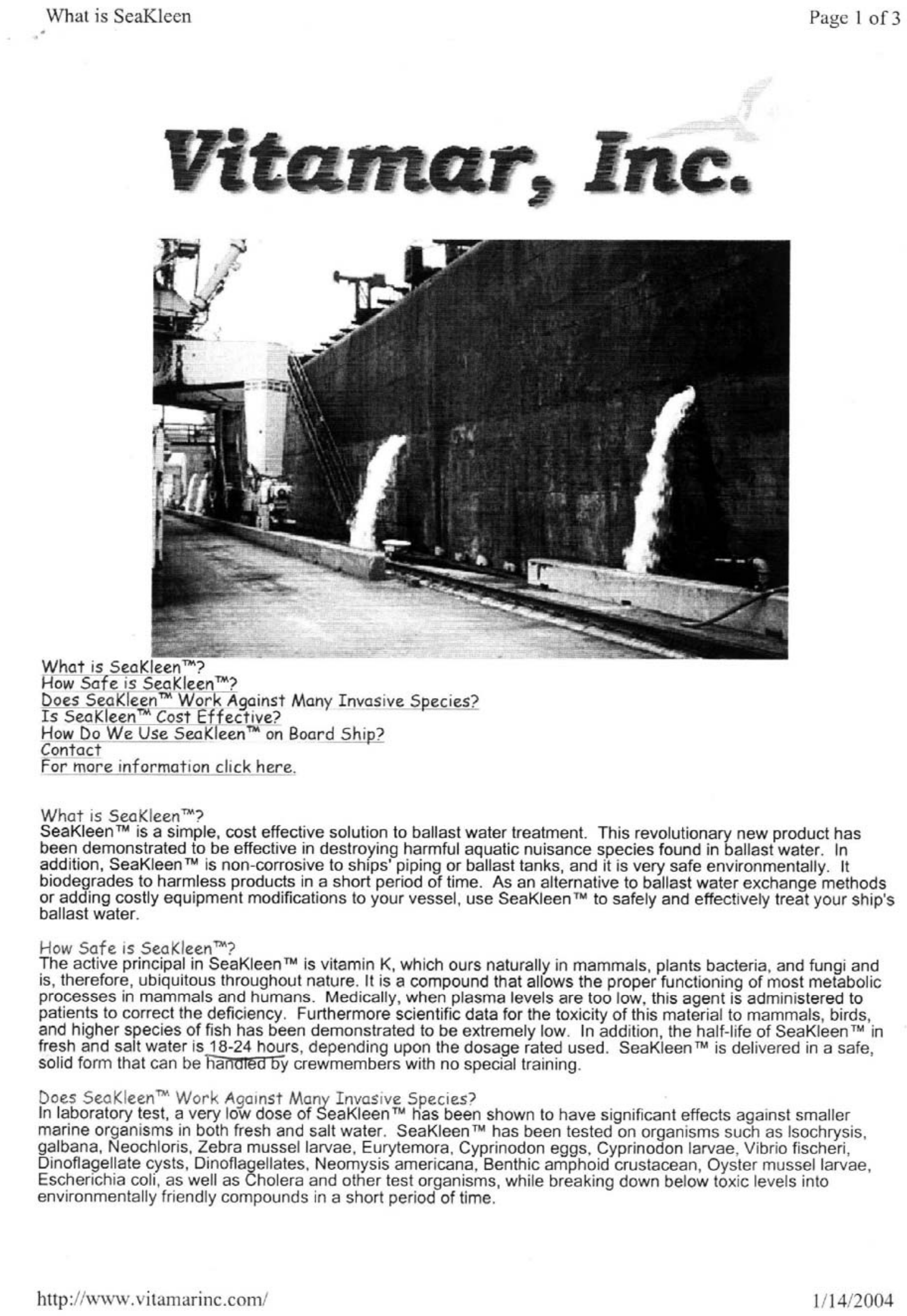
APPENDIX B

SeaKleen™

(from www.vitamarinc.com)



Vitamar, Inc.

What is SeaKleen™?
How Safe is SeaKleen™?
Does SeaKleen™ Work Against Many Invasive Species?
Is SeaKleen™ Cost Effective?
How Do We Use SeaKleen™ on Board Ship?
Contact
For more information click here.

What is SeaKleen™?

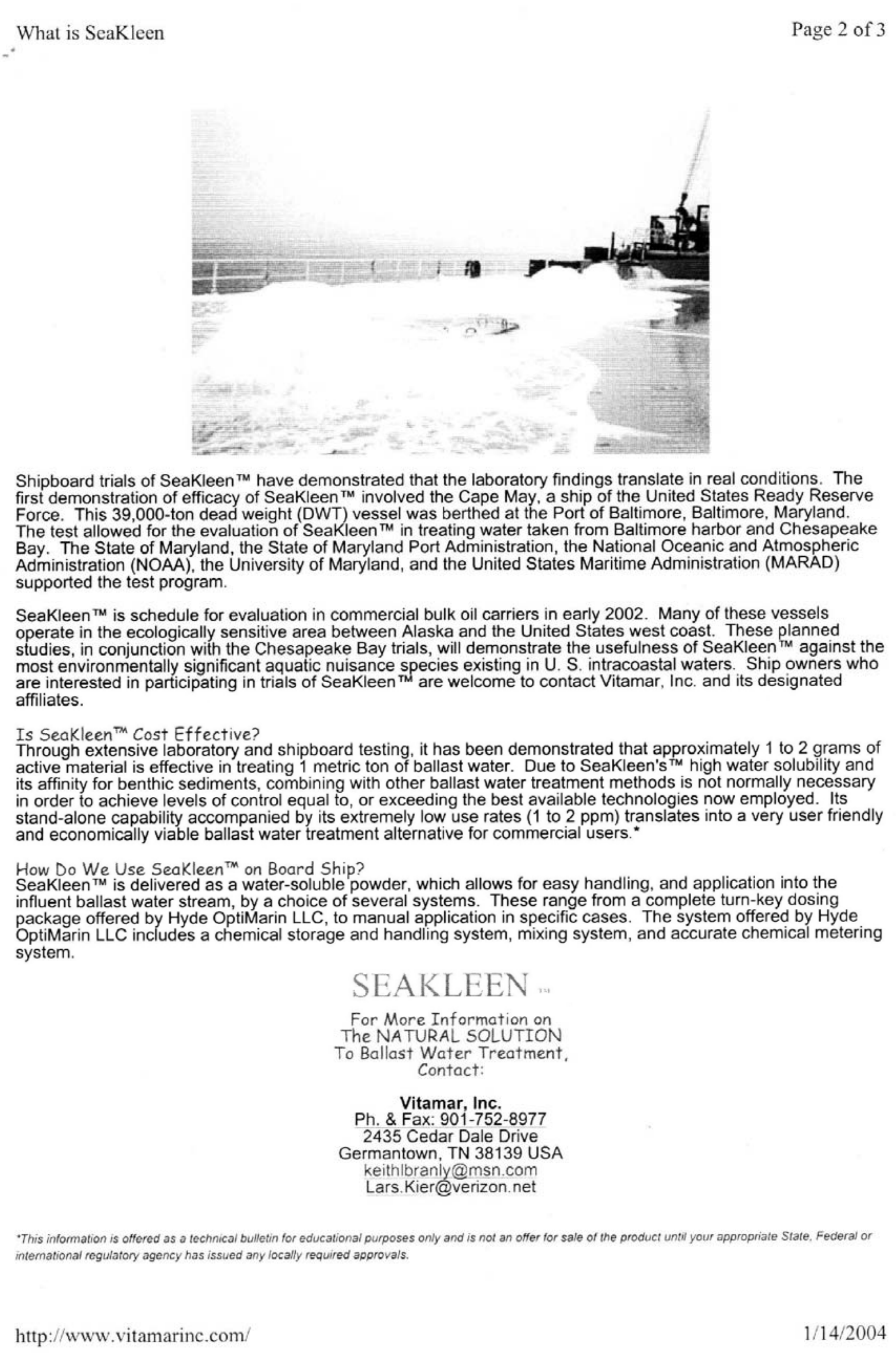
SeaKleen™ is a simple, cost effective solution to ballast water treatment. This revolutionary new product has been demonstrated to be effective in destroying harmful aquatic nuisance species found in ballast water. In addition, SeaKleen™ is non-corrosive to ships' piping or ballast tanks, and it is very safe environmentally. It biodegrades to harmless products in a short period of time. As an alternative to ballast water exchange methods or adding costly equipment modifications to your vessel, use SeaKleen™ to safely and effectively treat your ship's ballast water.

How Safe is SeaKleen™?

The active principal in SeaKleen™ is vitamin K, which ours naturally in mammals, plants bacteria, and fungi and is, therefore, ubiquitous throughout nature. It is a compound that allows the proper functioning of most metabolic processes in mammals and humans. Medically, when plasma levels are too low, this agent is administered to patients to correct the deficiency. Furthermore scientific data for the toxicity of this material to mammals, birds, and higher species of fish has been demonstrated to be extremely low. In addition, the half-life of SeaKleen™ in fresh and salt water is 18-24 hours, depending upon the dosage rated used. SeaKleen™ is delivered in a safe, solid form that can be handled by crewmembers with no special training.

Does SeaKleen™ Work Against Many Invasive Species?

In laboratory test, a very low dose of SeaKleen™ has been shown to have significant effects against smaller marine organisms in both fresh and salt water. SeaKleen™ has been tested on organisms such as Isochrysis, galbana, Neochloris, Zebra mussel larvae, Eurytemora, Cyprinodon eggs, Cyprinodon larvae, Vibrio fischeri, Dinoflagellate cysts, Dinoflagellates, Neomysis americana, Benthic amphoid crustacean, Oyster mussel larvae, Escherichia coli, as well as Cholera and other test organisms, while breaking down below toxic levels into environmentally friendly compounds in a short period of time.



What is SeaKleen Page 2 of 3

Shipboard trials of SeaKleen™ have demonstrated that the laboratory findings translate in real conditions. The first demonstration of efficacy of SeaKleen™ involved the Cape May, a ship of the United States Ready Reserve Force. This 39,000-ton dead weight (DWT) vessel was berthed at the Port of Baltimore, Baltimore, Maryland. The test allowed for the evaluation of SeaKleen™ in treating water taken from Baltimore harbor and Chesapeake Bay. The State of Maryland, the State of Maryland Port Administration, the National Oceanic and Atmospheric Administration (NOAA), the University of Maryland, and the United States Maritime Administration (MARAD) supported the test program.

SeaKleen™ is schedule for evaluation in commercial bulk oil carriers in early 2002. Many of these vessels operate in the ecologically sensitive area between Alaska and the United States west coast. These planned studies, in conjunction with the Chesapeake Bay trials, will demonstrate the usefulness of SeaKleen™ against the most environmentally significant aquatic nuisance species existing in U. S. intracoastal waters. Ship owners who are interested in participating in trials of SeaKleen™ are welcome to contact Vitamar, Inc. and its designated affiliates.

Is SeaKleen™ Cost Effective?

Through extensive laboratory and shipboard testing, it has been demonstrated that approximately 1 to 2 grams of active material is effective in treating 1 metric ton of ballast water. Due to SeaKleen's™ high water solubility and its affinity for benthic sediments, combining with other ballast water treatment methods is not normally necessary in order to achieve levels of control equal to, or exceeding the best available technologies now employed. Its stand-alone capability accompanied by its extremely low use rates (1 to 2 ppm) translates into a very user friendly and economically viable ballast water treatment alternative for commercial users.*

How Do We Use SeaKleen™ on Board Ship?

SeaKleen™ is delivered as a water-soluble powder, which allows for easy handling, and application into the influent ballast water stream, by a choice of several systems. These range from a complete turn-key dosing package offered by Hyde OptiMarin LLC, to manual application in specific cases. The system offered by Hyde OptiMarin LLC includes a chemical storage and handling system, mixing system, and accurate chemical metering system.

SEAKLEEN™

For More Information on
The NATURAL SOLUTION
To Ballast Water Treatment,
Contact:

Vitamar, Inc.
Ph. & Fax: 901-752-8977
2435 Cedar Dale Drive
Germantown, TN 38139 USA
keithlbranly@msn.com
Lars.Kier@verizon.net

**This information is offered as a technical bulletin for educational purposes only and is not an offer for sale of the product until your appropriate State, Federal or international regulatory agency has issued any locally required approvals.*

http://www.vitamarinc.com/ 1/14/2004

APPENDIX C

PERACLEAN® OCEAN (from Degussa)

degussa.

PERACLEAN® Ocean

Environmentally Sound Chemical Ballast Water Treatment

Introduction

A major global problem: transmission of **harmful aquatic organisms** by annually **5-10 Billion tonnes** of ballast water.

PERACLEAN® Ocean, developed by **Degussa AG**, Frankfurt, Germany, is a **new chemical treatment option**.
It has been successfully tested in field trials. Results show that in real ballast water of the cost at Baltimore, USA, or Hamburg, Germany, it kills all detectable phytoplancton and zooplankton with concentrations of less than 200 ppm.
PERACLEAN® Ocean is able to meet the D-2 standard of the IMO Ballast Water Convention. It offers a highly viable method for **safe, environmentally sound and effective ballast water treatments**.

Treatment of organisms

In **laboratory trials**, PERACLEAN® Ocean showed a significant effectiveness against a variety of organisms: Artemia salina: eggs, nauplii, adults; Eggs of Atlantic Herring; Chlorella sp.; In situ Plankton Baltic Sea: Copepods, Nauplii, Cladocera; Fresh Water Plankton: Cyclops sp., Bosmina sp., Daphnia sp.
In **field trials** with harbour water and ballast water, 50-200 ppm is effective against all detectable phytoplankton and zooplankton.

Dosage container for PERACLEAN® Ocean
(Degussa AG)
The complete unit was lifted by crane onboard the CAPE MAY.
This Degussa field trial dosage unit can be adapted to different ballast water treatment systems

CAPE MAY:
This vessel with 10,000 t ballast water was used as a test platform together for separation of solids + PERACLEAN® Ocean. Separation of solids and experimental setup: by **Maritime Solutions Inc.**, USA

PERACLEAN® Ocean

- **liquid**, chlorine free formulation, developed by DEGUSSA
- based on **hydrogen peroxide** / peroxygen chemistry
- excellent **biocidal**, **virucidal** and **fungicidal** properties at very low concentrations (5-100 ppm)
- good effectiveness on **phytoplankton**, **zooplankton** in the ballast water of ships (50 - 200 ppm)
- effective at any **salinity**, at various **temperatures**, and even at **high sediment loads**
- is not persistent
- does not accumulate
- even the decomposition products are **readily biodegradable**
- decomposes in ballast water to water, acetic acid and oxygen, **not causing environmental harm** after ballast water discharge
- **half-life** in ballast water ranges from 30 minutes to about 24 hours depending on pH, salinity and temperature
- is **safe to ship and crew**
- is **commercially available** in 220-l drums, 1-m³ IBC (intermediate bulk containers) or in bulk containers
- under appropriate **storage** conditions it exhibits an excellent shelf life and looses less than 10% of its original activity per year
- **analytical methods** for the determination of PERACLEAN® Ocean in ballast water have been developed.

How to apply PERACLEAN® OCEAN

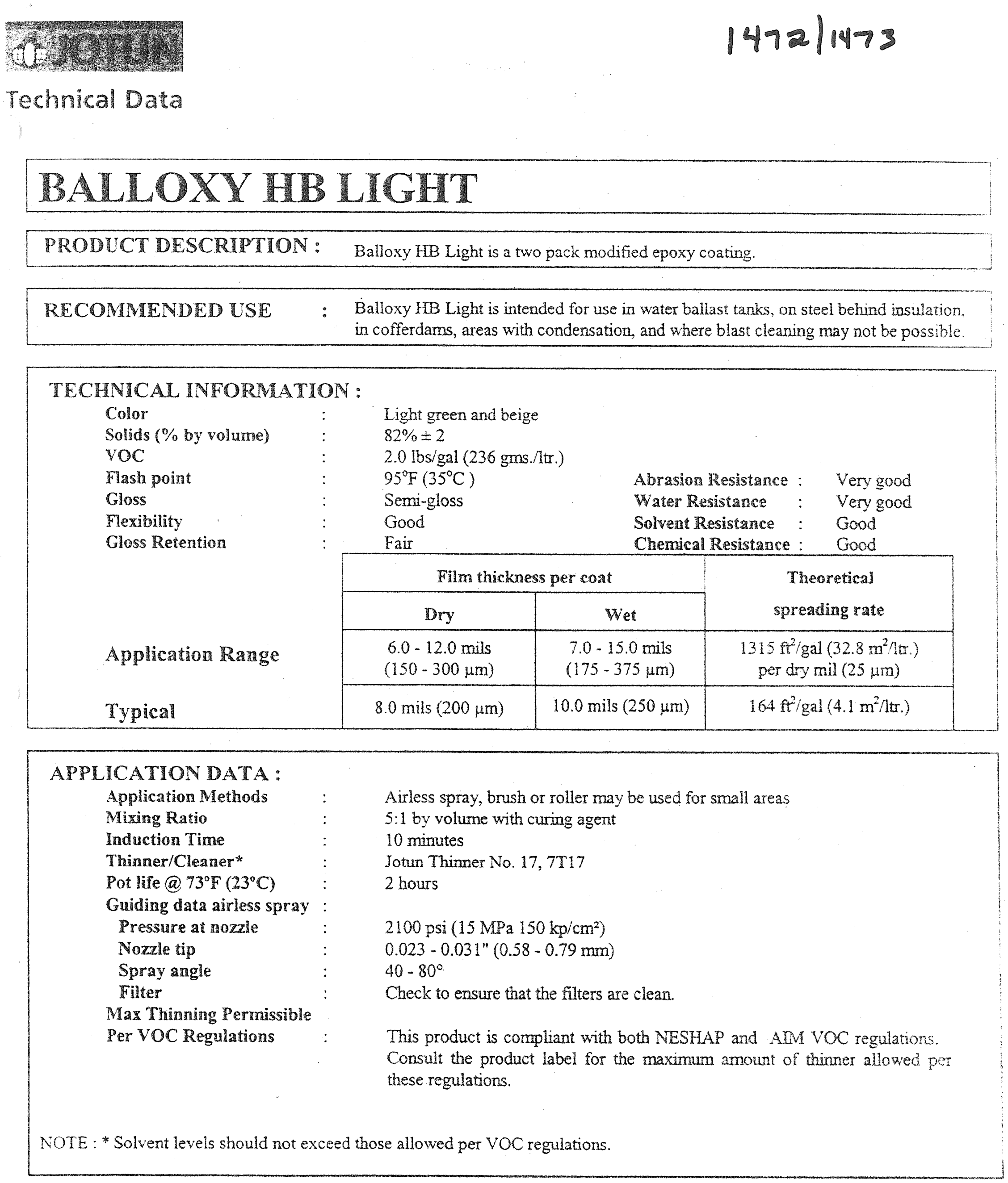
- Liquid formulation can be dosed automatically into ballast water flow during uptake of ballast water
- 50-200 litres of PERACLEAN® Ocean can treat 1,000 t of ballast water

Use **on ships** or at **harbour facilities** as
- single option PERACLEAN® Ocean
- separation + PERACLEAN® Ocean
- emergency treatment with PERACLEAN® Ocean

Contact Adress:

Degussa AG, Germany
Dr. Rainer-G. Fuchs
Tel.: [0049]-6181-59-3892
Fax: [0049]-6181-59-3311
e-mail: rainer-g.fuchs@degussa.com

APPENDIX D
PAINT COATINGS



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JOTUN

Technical Data

BALLOXY HB LIGHT

PRODUCT DESCRIPTION : Balloxy HB Light is a two pack modified epoxy coating.

RECOMMENDED USE : Balloxy HB Light is intended for use in water ballast tanks, on steel behind insulation, in cofferdams, areas with condensation, and where blast cleaning may not be possible.

TECHNICAL INFORMATION :

Color : Light green and beige
Solids (% by volume) : 82% ± 2
VOC : 2.0 lbs/gal (236 gms./ltr.)
Flash point : 95°F (35°C)
Gloss : Semi-gloss
Flexibility : Good
Gloss Retention : Fair

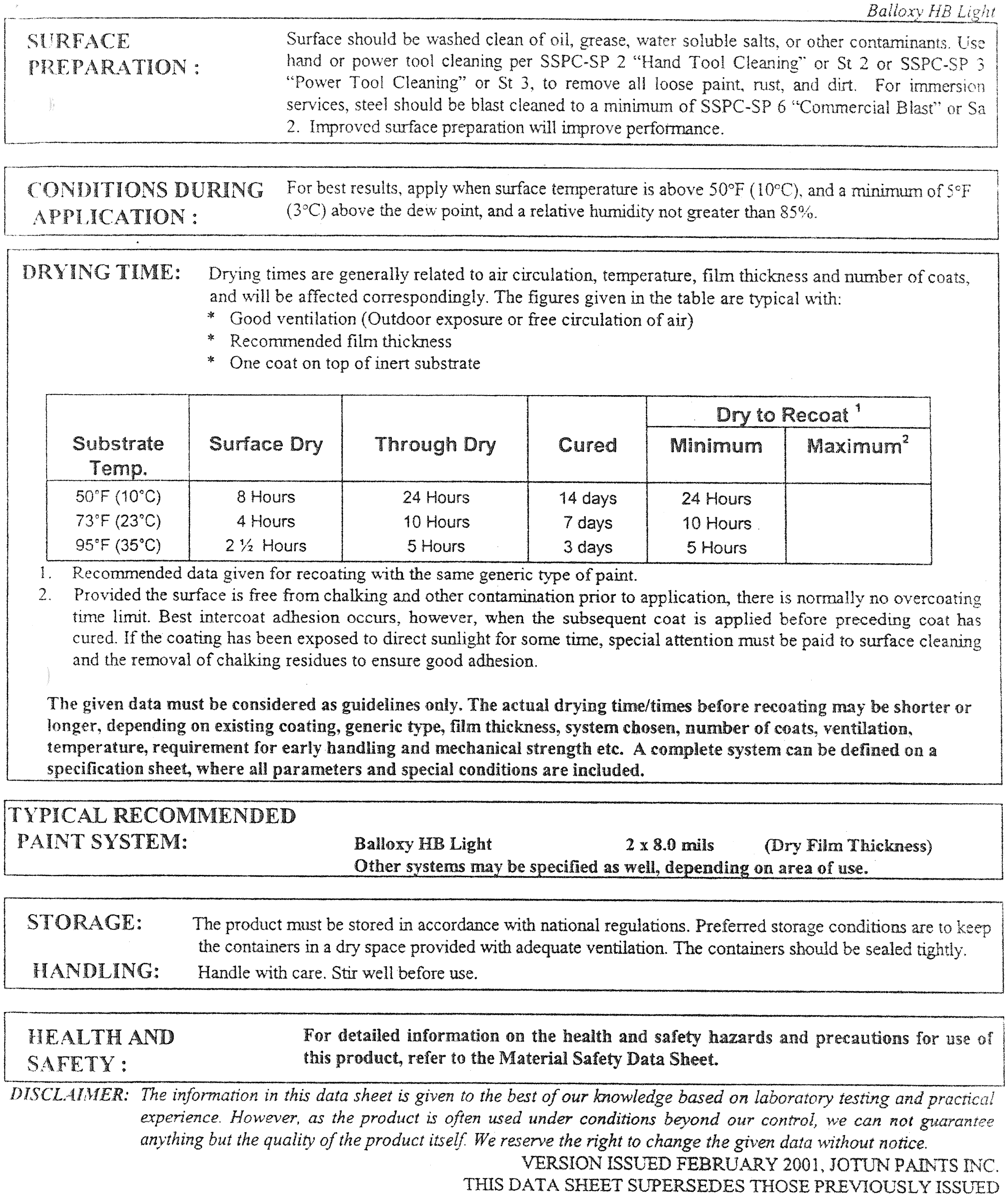
Abrasion Resistance : Very good
Water Resistance : Very good
Solvent Resistance : Good
Chemical Resistance : Good

	Film thickness per coat		Theoretical spreading rate
	Dry	Wet	
Application Range	6.0 - 12.0 mils (150 - 300 μm)	7.0 - 15.0 mils (175 - 375 μm)	1315 ft^2/gal (32.8 m^2/ltr.) per dry mil (25 μm)
Typical	8.0 mils (200 μm)	10.0 mils (250 μm)	164 ft^2/gal (4.1 m^2/ltr.)

APPLICATION DATA :

Application Methods : Airless spray, brush or roller may be used for small areas
Mixing Ratio : 5:1 by volume with curing agent
Induction Time : 10 minutes
Thinner/Cleaner* : Jotun Thinner No. 17, 7T17
Pot life @ 73°F (23°C) : 2 hours
Guiding data airless spray :
Pressure at nozzle : 2100 psi (15 MPa 150 kp/cm^2)
Nozzle tip : 0.023 - 0.031" (0.58 - 0.79 mm)
Spray angle : 40 - 80°
Filter : Check to ensure that the filters are clean.
Max Thinning Permissible Per VOC Regulations : This product is compliant with both NESHAP and AIM VOC regulations. Consult the product label for the maximum amount of thinner allowed per these regulations.

NOTE : * Solvent levels should not exceed those allowed per VOC regulations.



Balloxy HB Light

SURFACE PREPARATION : Surface should be washed clean of oil, grease, water soluble salts, or other contaminants. Use hand or power tool cleaning per SSPC-SP 2 "Hand Tool Cleaning" or St 2 or SSPC-SP 3 "Power Tool Cleaning" or St 3, to remove all loose paint, rust, and dirt. For immersion services, steel should be blast cleaned to a minimum of SSPC-SP 6 "Commercial Blast" or Sa 2. Improved surface preparation will improve performance.

CONDITIONS DURING APPLICATION : For best results, apply when surface temperature is above 50°F (10°C), and a minimum of 5°F (3°C) above the dew point, and a relative humidity not greater than 85%.

DRYING TIME: Drying times are generally related to air circulation, temperature, film thickness and number of coats, and will be affected correspondingly. The figures given in the table are typical with:

* Good ventilation (Outdoor exposure or free circulation of air)
* Recommended film thickness
* One coat on top of inert substrate

Substrate Temp.	Surface Dry	Through Dry	Cured	Dry to Recoat [1]	
				Minimum	Maximum[2]
50°F (10°C) 73°F (23°C) 95°F (35°C)	8 Hours 4 Hours 2 ½ Hours	24 Hours 10 Hours 5 Hours	14 days 7 days 3 days	24 Hours 10 Hours 5 Hours	

1. Recommended data given for recoating with the same generic type of paint.
2. Provided the surface is free from chalking and other contamination prior to application, there is normally no overcoating time limit. Best intercoat adhesion occurs, however, when the subsequent coat is applied before preceding coat has cured. If the coating has been exposed to direct sunlight for some time, special attention must be paid to surface cleaning and the removal of chalking residues to ensure good adhesion.

The given data must be considered as guidelines only. The actual drying time/times before recoating may be shorter or longer, depending on existing coating, generic type, film thickness, system chosen, number of coats, ventilation, temperature, requirement for early handling and mechanical strength etc. A complete system can be defined on a specification sheet, where all parameters and special conditions are included.

TYPICAL RECOMMENDED PAINT SYSTEM: **Balloxy HB Light 2 x 8.0 mils (Dry Film Thickness)**
Other systems may be specified as well, depending on area of use.

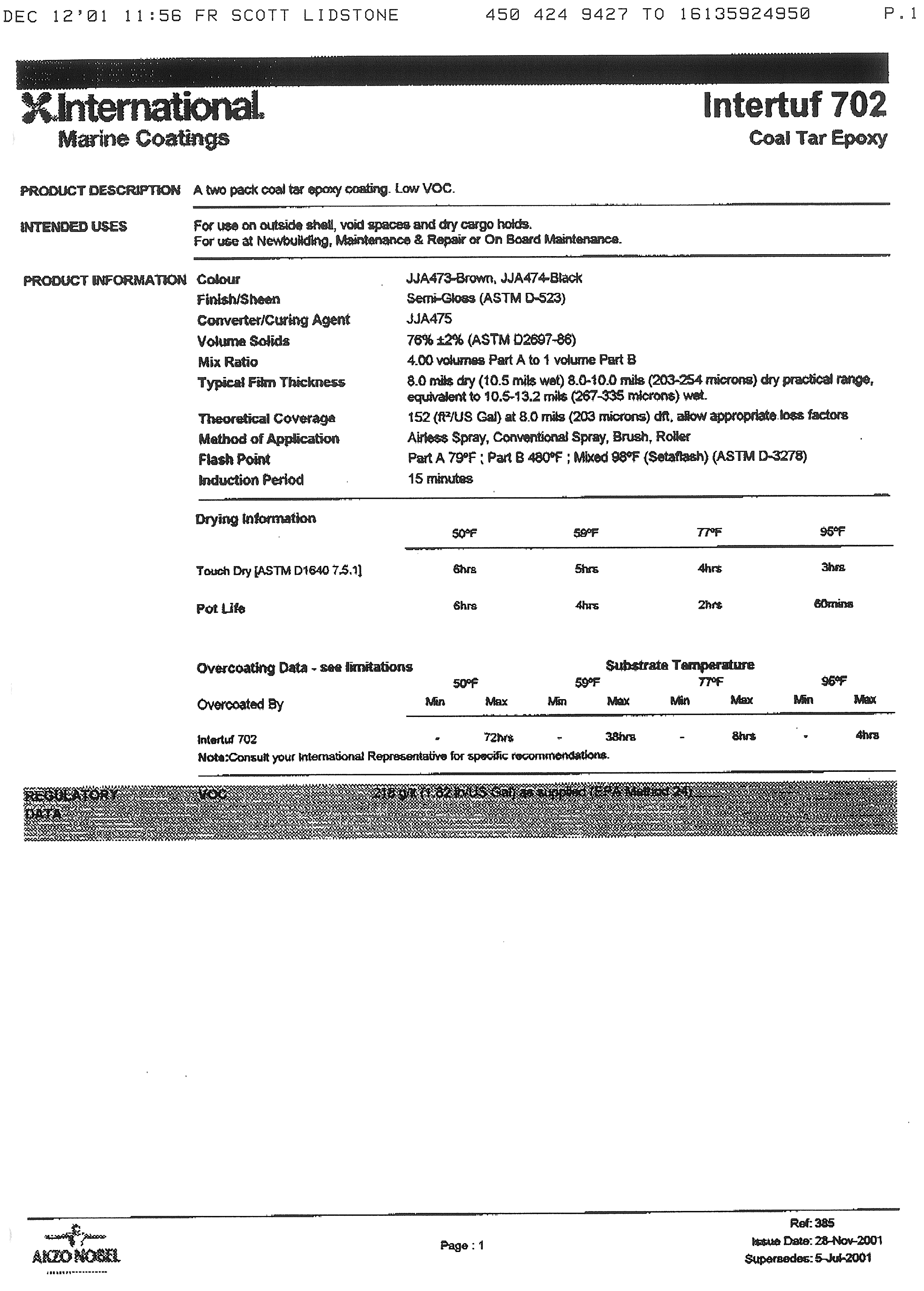
STORAGE: The product must be stored in accordance with national regulations. Preferred storage conditions are to keep the containers in a dry space provided with adequate ventilation. The containers should be sealed tightly.

HANDLING: Handle with care. Stir well before use.

HEALTH AND SAFETY : **For detailed information on the health and safety hazards and precautions for use of this product, refer to the Material Safety Data Sheet.**

DISCLAIMER: The information in this data sheet is given to the best of our knowledge based on laboratory testing and practical experience. However, as the product is often used under conditions beyond our control, we can not guarantee anything but the quality of the product itself. We reserve the right to change the given data without notice.

VERSION ISSUED FEBRUARY 2001, JOTUN PAINTS INC.
THIS DATA SHEET SUPERSEDES THOSE PREVIOUSLY ISSUED



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International
Marine Coatings

Intertuf 702

Coal Tar Epoxy

PRODUCT DESCRIPTION A two pack coal tar epoxy coating. Low VOC.

INTENDED USES For use on outside shell, void spaces and dry cargo holds.
For use at Newbuilding, Maintenance & Repair or On Board Maintenance.

PRODUCT INFORMATION

Colour	JJA473-Brown, JJA474-Black
Finish/Sheen	Semi-Gloss (ASTM D-523)
Converter/Curing Agent	JJA475
Volume Solids	76% ±2% (ASTM D2697-86)
Mix Ratio	4.00 volumes Part A to 1 volume Part B
Typical Film Thickness	8.0 mils dry (10.5 mils wet) 8.0-10.0 mils (203-254 microns) dry practical range, equivalent to 10.5-13.2 mils (267-335 microns) wet.
Theoretical Coverage	152 (ft²/US Gal) at 8.0 mils (203 microns) dft, allow appropriate loss factors
Method of Application	Airless Spray, Conventional Spray, Brush, Roller
Flash Point	Part A 79°F ; Part B 480°F ; Mixed 98°F (Setaflash) (ASTM D-3278)
Induction Period	15 minutes

Drying Information

	50°F	59°F	77°F	95°F
Touch Dry [ASTM D1640 7.5.1]	6hrs	5hrs	4hrs	3hrs
Pot Life	6hrs	4hrs	2hrs	60mins

Overcoating Data - see limitations

	Substrate Temperature							
	50°F		59°F		77°F		95°F	
Overcoated By	Min	Max	Min	Max	Min	Max	Min	Max
Intertuf 702	-	72hrs	-	38hrs	-	8hrs	-	4hrs

Note: Consult your International Representative for specific recommendations.

REGULATORY DATA VOC 215 g/lt (1.82 lb/US Gal) as supplied (EPA Method 24)

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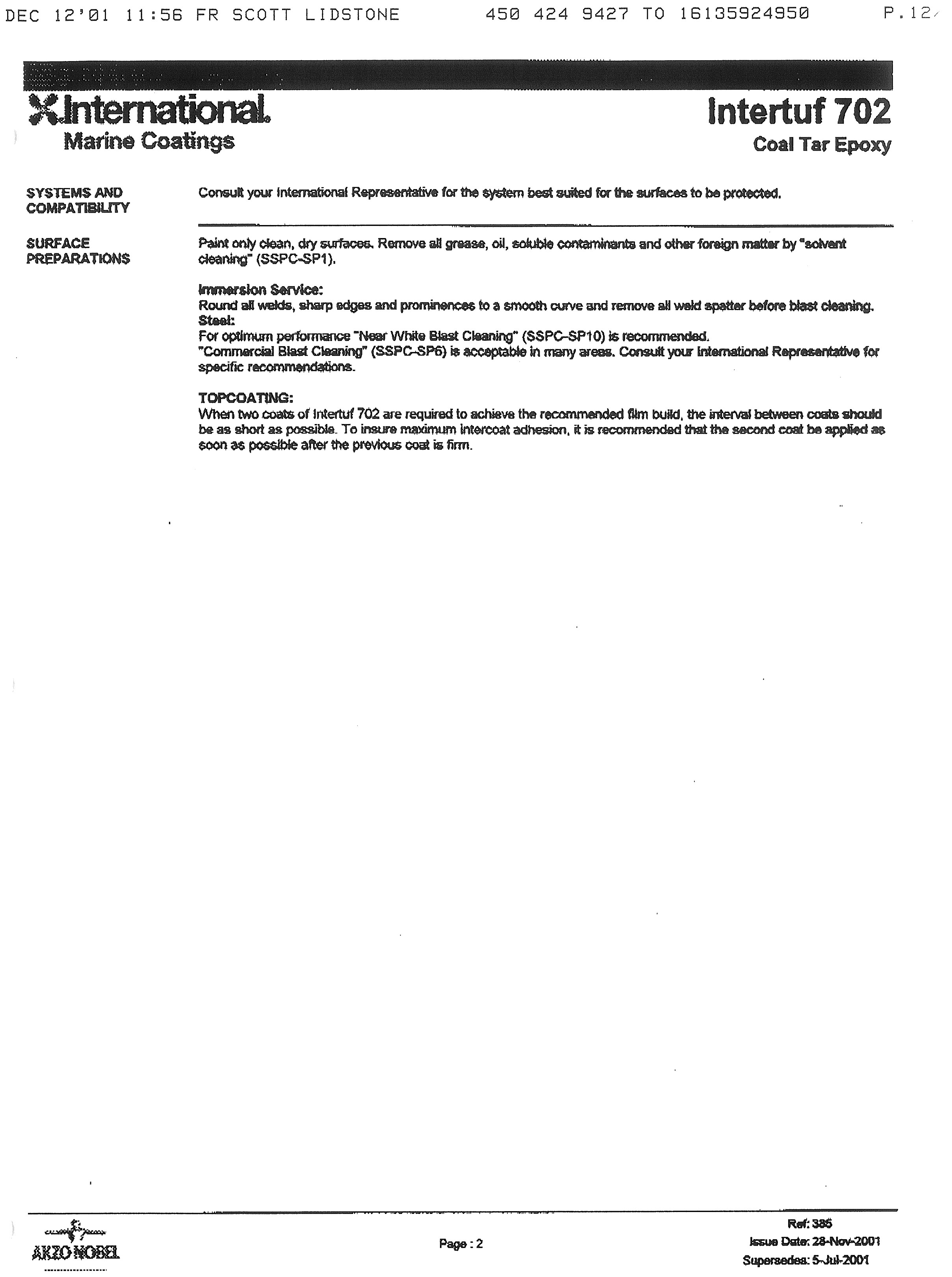

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International
Marine Coatings

Intertuf 702
Coal Tar Epoxy

SYSTEMS AND COMPATIBILITY

Consult your International Representative for the system best suited for the surfaces to be protected.

SURFACE PREPARATIONS

Paint only clean, dry surfaces. Remove all grease, oil, soluble contaminants and other foreign matter by "solvent cleaning" (SSPC-SP1).

Immersion Service:
Round all welds, sharp edges and prominences to a smooth curve and remove all weld spatter before blast cleaning.
Steel:
For optimum performance "Near White Blast Cleaning" (SSPC-SP10) is recommended.
"Commercial Blast Cleaning" (SSPC-SP6) is acceptable in many areas. Consult your International Representative for specific recommendations.

TOPCOATING:
When two coats of Intertuf 702 are required to achieve the recommended film build, the interval between coats should be as short as possible. To insure maximum intercoat adhesion, it is recommended that the second coat be applied as soon as possible after the previous coat is firm.

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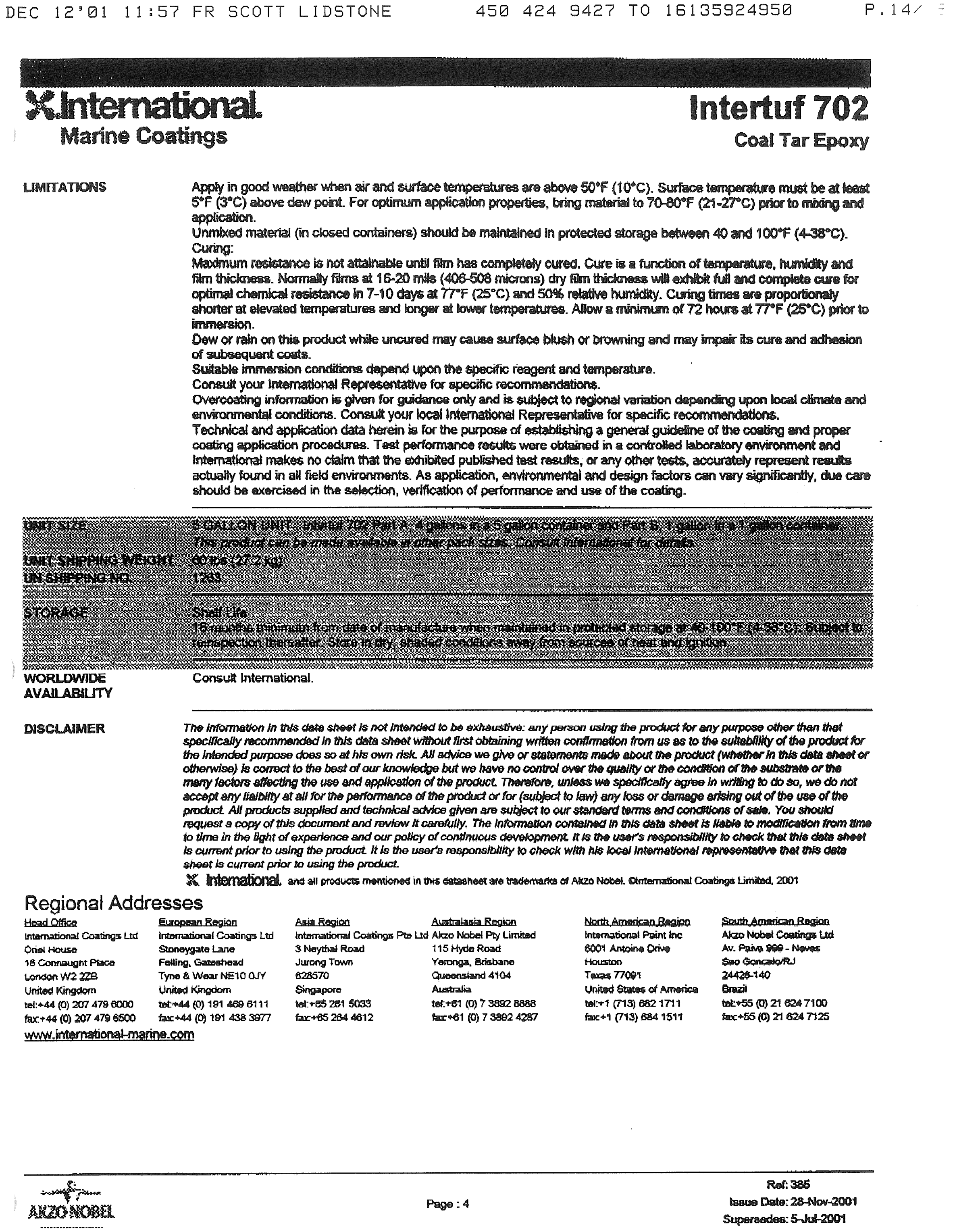
Marine Coatings

Intertuf 702
Coal Tar Epoxy

APPLICATION	Apply by conventional or airless spray. Application by other methods, brush or roller may require more than one coat and is suggested for small areas only. Apply at 10.5 mils wet (267 microns) which will yield 8.0 mils (203 microns) dry film thickness. Recoat schedule must be adhered to. Surfaces must be abraded prior to applying additional coats if maximum recoat time has been exceeded. Consult the following equipment recommendations or utilize suitable equal.
Mixing	Material is supplied in 2 containers as a unit. Always mix a complete unit in the proportions supplied. (1) Agitate A with a power agitator. (2) Combine entire contents of Part A and B and mix thoroughly with a power agitator. (3) Allow the coating a 15 minute sweat-in period.
Thinner	DO NOT THIN BEYOND YOUR STATE'S COMPLIANCY. Material is supplied at spray viscosity and normally does not need thinning. If thinning is necessary, thin up to a maximum of 4 ounces/gal. (118 ml) with International GTA007 Thinner.
Airless Spray	Graco 206-718 gun; 0.019"- 0.027" (483-686 microns) orifice tip with a 60 mesh element mounted behind the gun; 3/8" (9.5 mm) ID high pressure material hose; 30:1 ratio pump or greater.
Conventional Spray	DeVilbiss MBC-510 gun; D tip (.086-2.2 mmm) and 64 air cap; 1/2" (12.7 mm) ID material hose; double regulated pressure tank or 8:1 ratio barrel type paint pump with fluid relaxing valve preferred for maximum production; oil and moisture separators on all air supplies are esential.
Brush	Use appropriate size China bristle brush.
Roller	Use All Purpose Roller cover with 3/8" (9.5mm) smooth medium nap. Prewash roller cover to remove loose fibers prior to use.
Work Stoppages and Cleanup	Clean all equipment immediately after use with International GTA007. Spray equipment requires flushing with this solvent. It is good working practice to periodically flush out spray equipment during the course of the working day. Frequency will depend upon factors such as amount sprayed, temperature and elapsed time including work stoppages. Monitor material condition. Do not exceed pot life limitations. All surplus materials and empty containers should be disposed of in accordance with appropriate regional regulations/legislation.
Inspection	(when required) After the last coat has dried, the coating system dry film thickness should be measured using a suitable non-destructive magnetic gauge (such as Mikrotest). The average dry film thickness should be between 16 and 20.0 mils (406-508 microns). The coating system should be free of all pinholes or other holidays as determined with a suitable non-destructive (100 volts or less) holiday detector (such as Tinker & Rasor Model M-1). The dried film should be essentially free of runs, sags, drips, inclusions or other defects. All deficiencies and defects should be corrected and the touch-up areas allowed to cure as specified before placing the finished coating system into service.
Welding	In the event welding or flame cutting is performed on metal coated with this product, dust and fumes will be emitted which will require the use of appropriate personal protective equipment and adequate local exhaust ventilation. In North America do so in accordance with instruction in ANSI/ASC Z49.1 "Safety in Welding and Cutting."
SAFETY	**All work involving the application and use of this product should be performed in compliance with all relevant national Health, Safety & Environmental standards and regulations.** **Prior to use, obtain, consult and follow the Material Safety Data Sheet for this product concerning health and safety information. Read and follow all precautionary notices on the Material Safety Data Sheet and container labels. If you do not fully understand these warnings and instructions or if you can not strictly comply with them, do not use this product. Proper ventilation and protective measures must be provided during application and drying to keep solvent vapour concentrations within safe limits and to protect against toxic or oxygen deficient hazards. Take precautions to avoid skin and eye contact (ie. gloves, goggles, face masks, barrier creams etc.) Actual safety measures are dependant on application methods and work environment.** **EMERGENCY CONTACT NUMBERS:** **USA/Canada - Medical Advisory Number 1-800-854-6813** **Europe - Contact (44) 191 4696111. For advice to Doctors & Hospitals only contact (44) 207 6359191** **R.O.W. - Contact Regional Office (see page 4 of Data Sheet)**



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International
Marine Coatings

Intertuf 702
Coal Tar Epoxy

LIMITATIONS

Apply in good weather when air and surface temperatures are above 50°F (10°C). Surface temperature must be at least 5°F (3°C) above dew point. For optimum application properties, bring material to 70-80°F (21-27°C) prior to mixing and application.
Unmixed material (in closed containers) should be maintained in protected storage between 40 and 100°F (4-38°C).
Curing:
Maximum resistance is not attainable until film has completely cured. Cure is a function of temperature, humidity and film thickness. Normally films at 16-20 mils (406-508 microns) dry film thickness will exhibit full and complete cure for optimal chemical resistance in 7-10 days at 77°F (25°C) and 50% relative humidity. Curing times are proportionaly shorter at elevated temperatures and longer at lower temperatures. Allow a minimum of 72 hours at 77°F (25°C) prior to immersion.
Dew or rain on this product while uncured may cause surface blush or browning and may impair its cure and adhesion of subsequent coats.
Suitable immersion conditions depend upon the specific reagent and temperature.
Consult your International Representative for specific recommendations.
Overcoating information is given for guidance only and is subject to regional variation depending upon local climate and environmental conditions. Consult your local International Representative for specific recommendations.
Technical and application data herein is for the purpose of establishing a general guideline of the coating and proper coating application procedures. Test performance results were obtained in a controlled laboratory environment and International makes no claim that the exhibited published test results, or any other tests, accurately represent results actually found in all field environments. As application, environmental and design factors can vary significantly, due care should be exercised in the selection, verification of performance and use of the coating.

UNIT SIZE	5 GALLON UNIT. Intertuf 702 Part A: 4 gallons in a 5 gallon container and Part B: 1 gallon in a 1 gallon container. *This product can be made available in other pack sizes. Consult International for details.*
UNIT SHIPPING WEIGHT	60 lbs (27.2 kg)
UN SHIPPING NO.	1263
STORAGE	Shelf Life 18 months minimum from date of manufacture when maintained in protected storage at 40-100°F (4-38°C). Subject to reinspection thereafter. Store in dry, shaded conditions away from sources of heat and ignition.
WORLDWIDE AVAILABILITY	Consult International.

DISCLAIMER

The information in this data sheet is not intended to be exhaustive: any person using the product for any purpose other than that specifically recommended in this data sheet without first obtaining written confirmation from us as to the suitability of the product for the intended purpose does so at his own risk. All advice we give or statements made about the product (whether in this data sheet or otherwise) is correct to the best of our knowledge but we have no control over the quality or the condition of the substrate or the many factors affecting the use and application of the product. Therefore, unless we specifically agree in writing to do so, we do not accept any liability at all for the performance of the product or for (subject to law) any loss or damage arising out of the use of the product. All products supplied and technical advice given are subject to our standard terms and conditions of sale. You should request a copy of this document and review it carefully. The information contained in this data sheet is liable to modification from time to time in the light of experience and our policy of continuous development. It is the user's responsibility to check that this data sheet is current prior to using the product. It is the user's responsibility to check with his local International representative that this data sheet is current prior to using the product.

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APPENDIX E

PHOTOGRAPHS OF BARE STEEL COUPONS (SEAKLEEN™)

Figure E1: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 1, (Control Tank)

Figure E2: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 2, (Low Dosage,SeaKleen™)

Figure E3: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 3, (High Dosage, SeaKleen™)

Figure E4: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 4, (Control Tank)

Figure E5: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 5, (Low Dosage, SeaKleen™)

Figure E6: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 6, (High Dosage, SeaKleen™)

Figure E7: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 1, (Control Tank)

Figure E8: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 2, (Low Dosage, SeaKleen™)

Figure E9: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 3, (High Dosage, SeaKleen™)

Figure E10: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 4, (Control Tank)

Figure E11: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 5, (Low Dosage, SeaKleen™)

Figure E12: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 6, (High Dosage, SeaKleen™)

APPENDIX F

COATINGS PERFORMANCE (SeaKleen™)

Figure F1: Tank 1 (Fresh Water) - Deterioration Rating vs. Location (SeaKleen™)

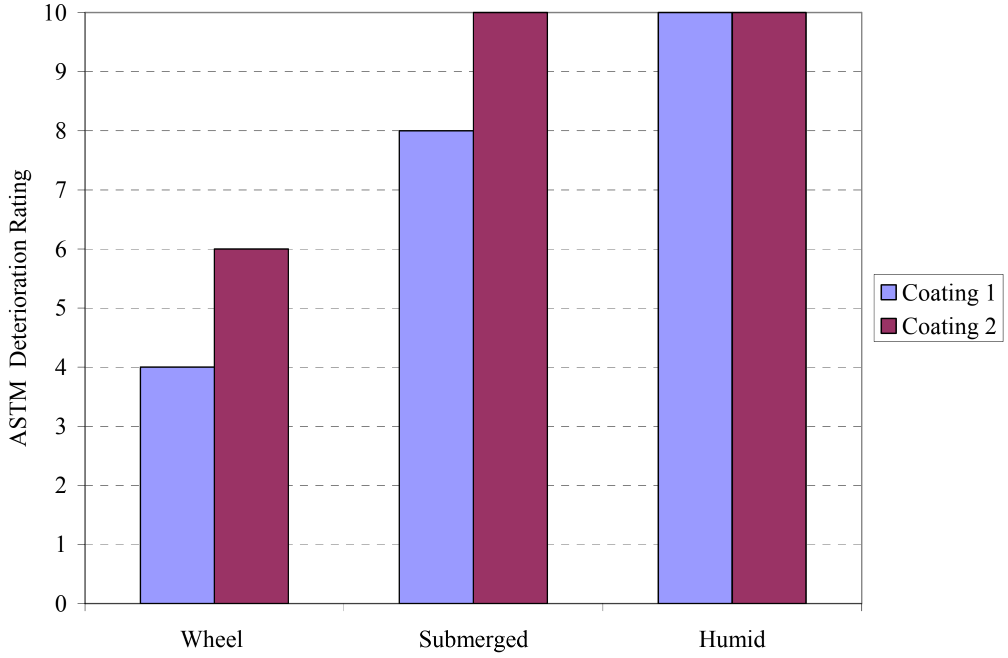

Figure F2: Tank 2 (Fresh Water) - Deterioration Rating vs. Location (SeaKleen™)

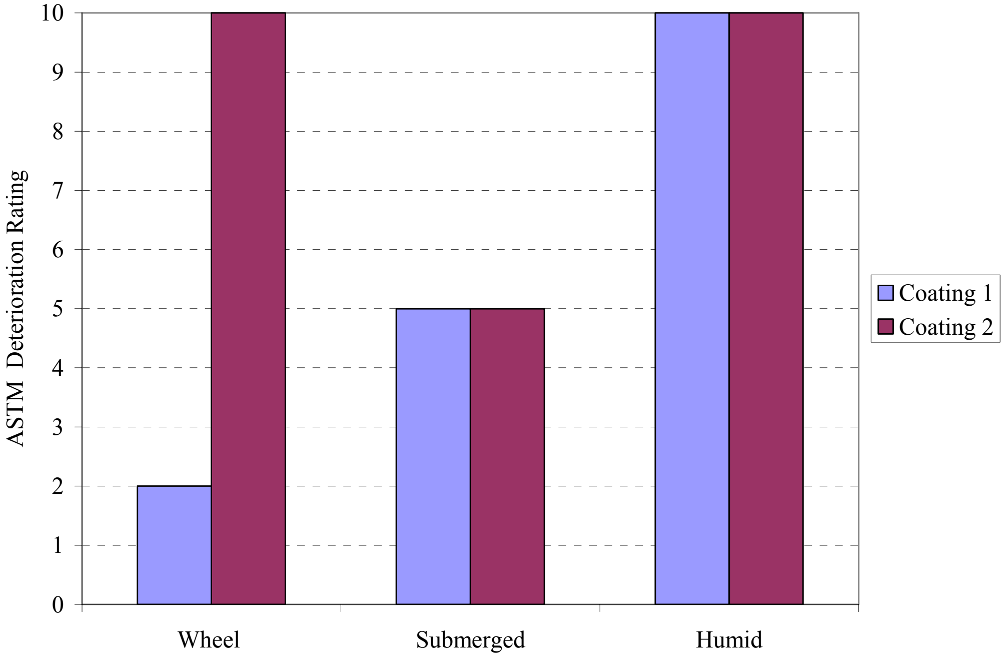

Figure F3: Tank 3 (Fresh Water) - Deterioration Rating vs. Location (SeaKleen™)

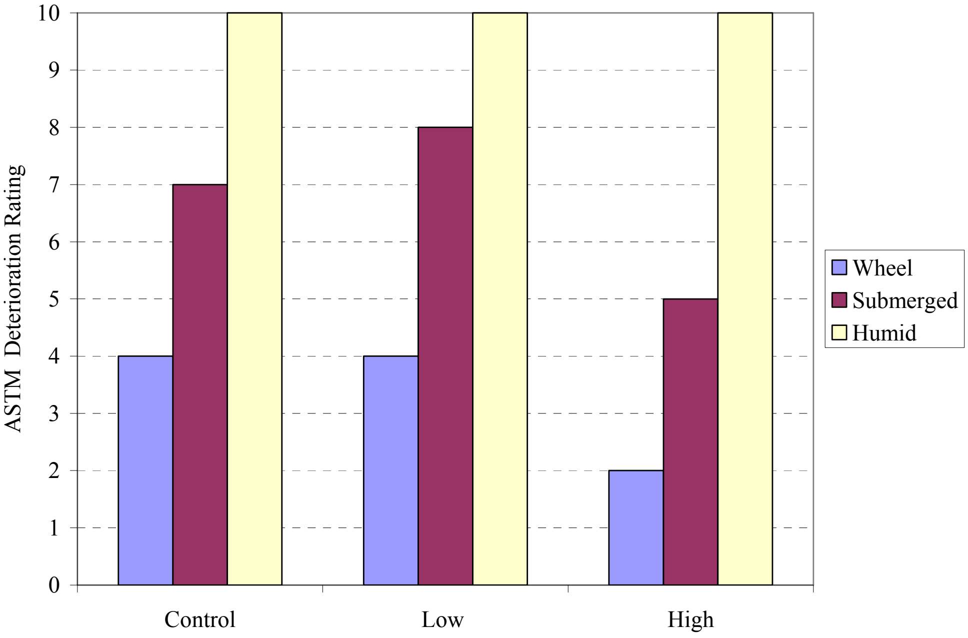

Figure F4: Coating 1 (Fresh Water) - Deterioration Rating vs. Concentration (SeaKleen™)

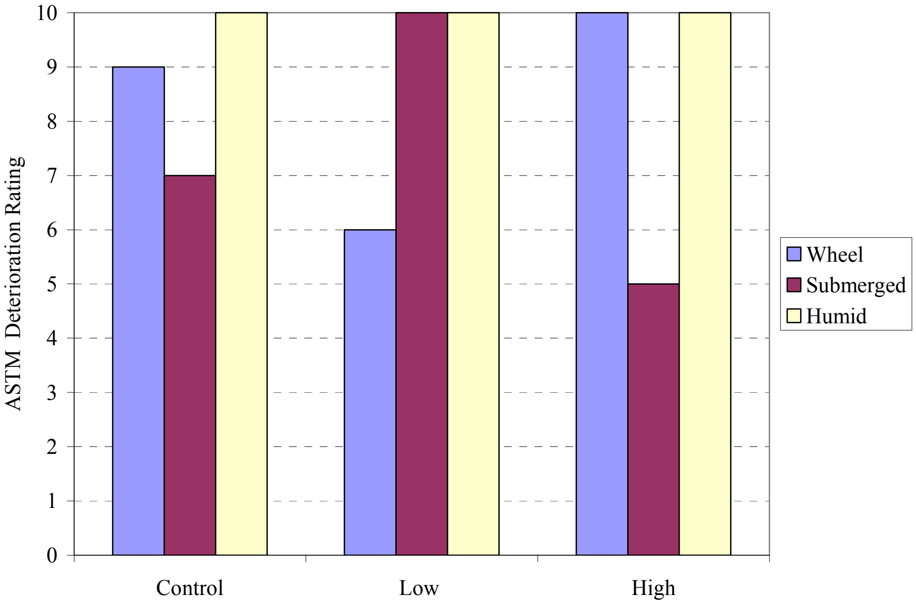

Figure F5: Coating 2 (Fresh Water) - Deterioration Rating vs. Concentration (SeaKleen™)

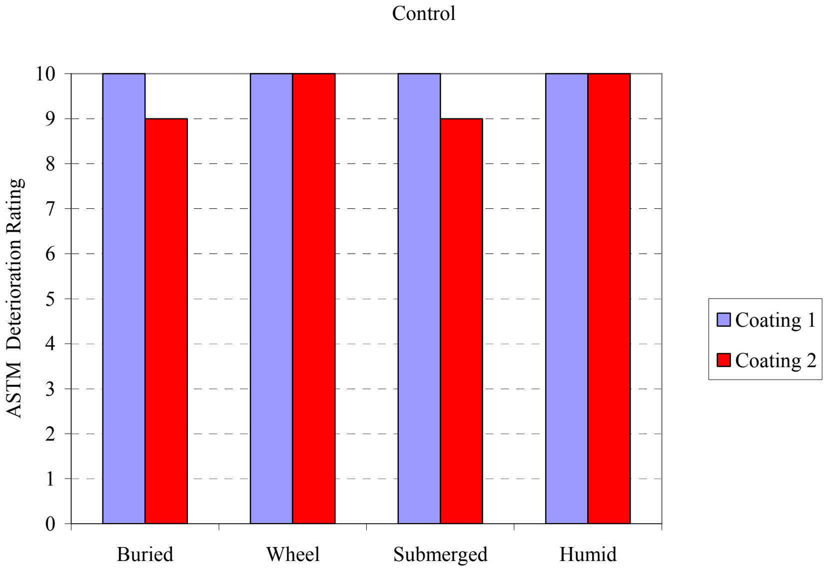

Figure F6: Tank 1 (15 ppt) - Deterioration Rating vs. Location (SeaKleen™)

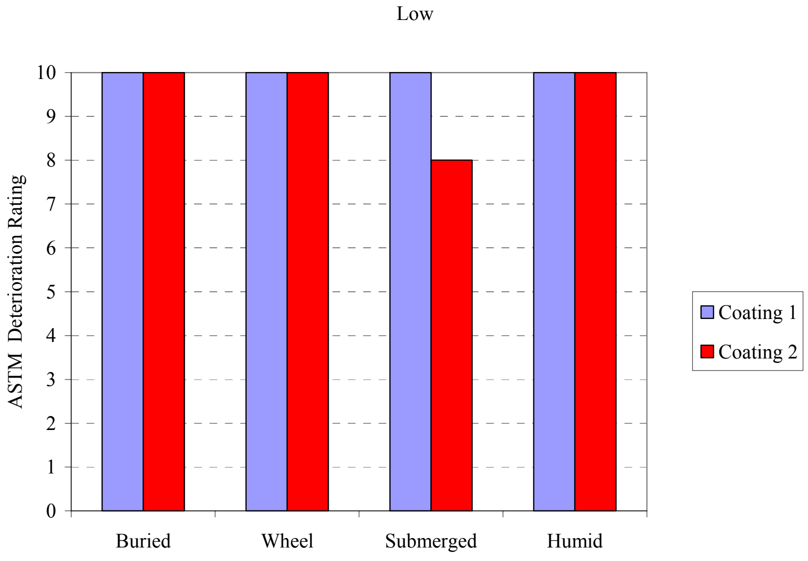

Figure F7: Tank 2 (15 ppt) - Deterioration Rating vs. Location (SeaKleen™)

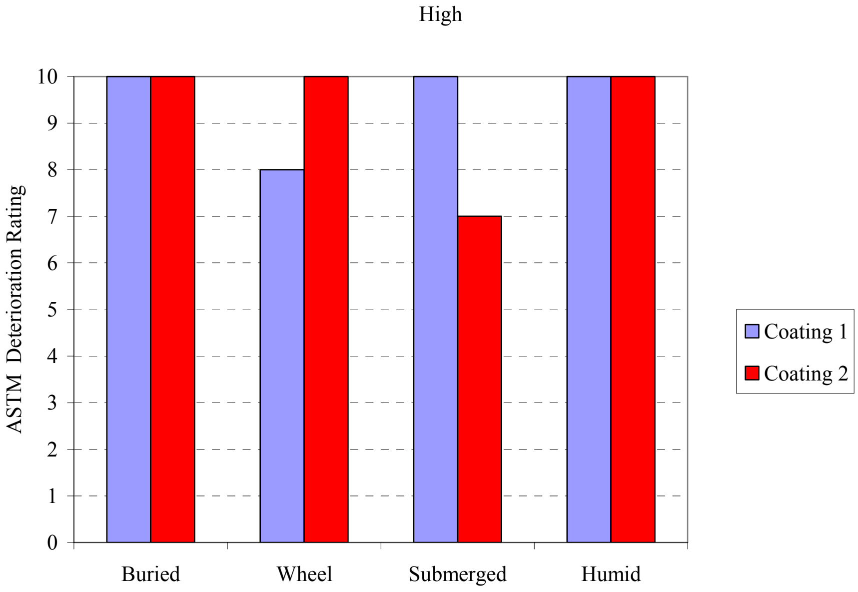

Figure F8: Tank 3 (15 ppt) - Deterioration Rating vs. Location (SeaKleen™)

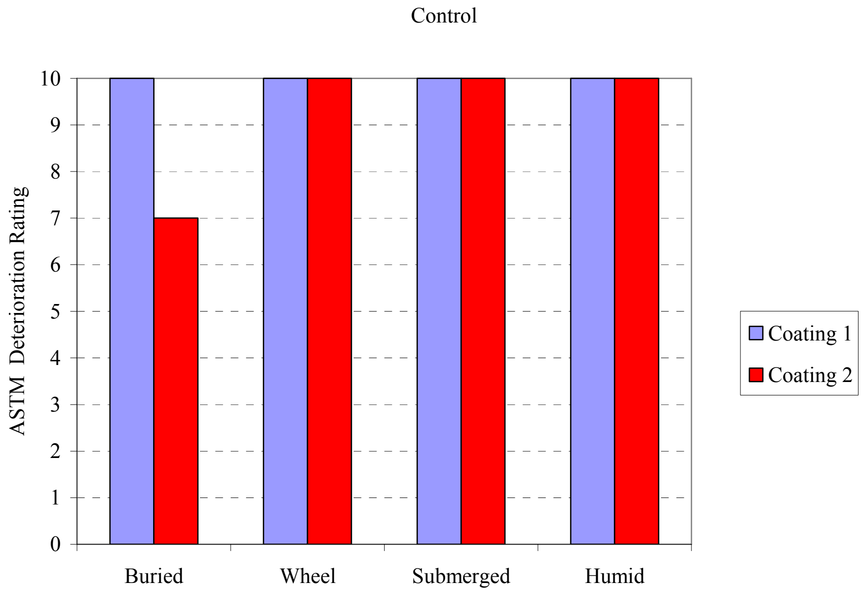

Figure F9: Tank 4 (35 ppt) - Deterioration Rating vs. Location (SeaKleen™)

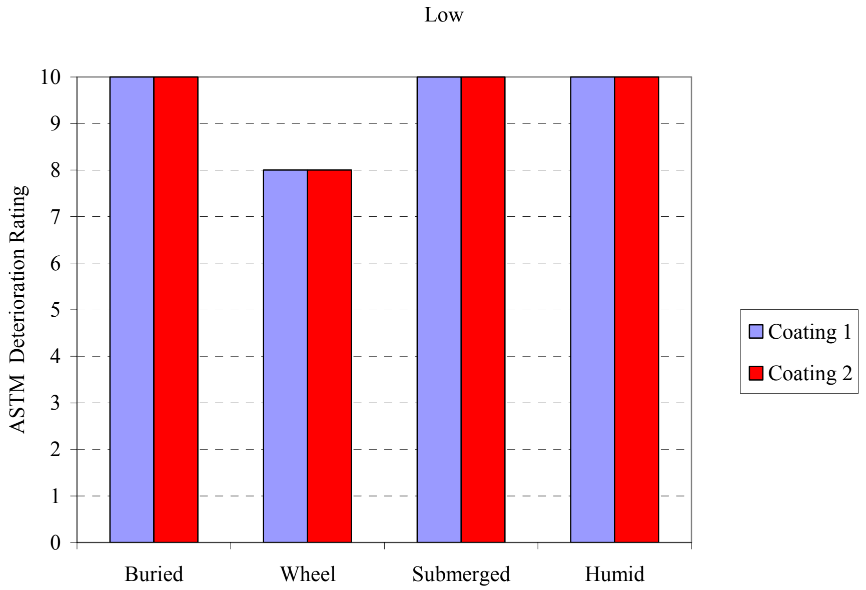

Figure F10: Tank 5 (35 ppt) - Deterioration Rating vs. Location (SeaKleen™)

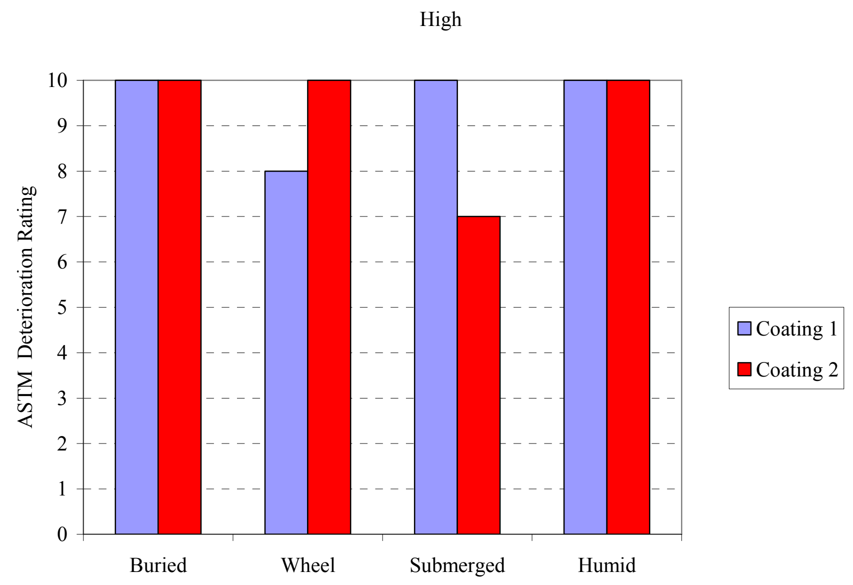

Figure F11: Tank 6 (35 ppt) - Deterioration Rating vs. Location (SeaKleen™)

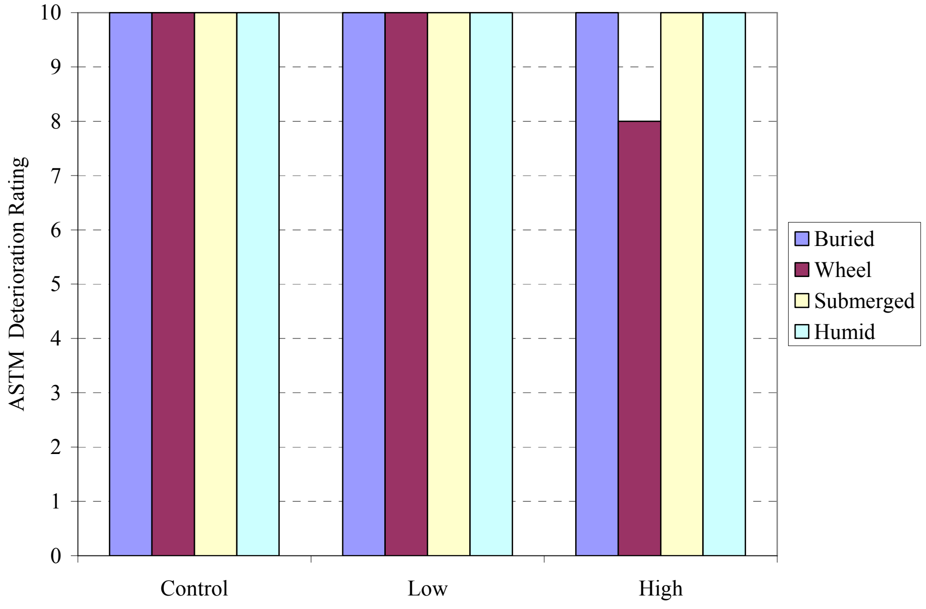

Figure F12: Coating 1 (15 ppt) - Deterioration Rating vs. Concentration (SeaKleen™)

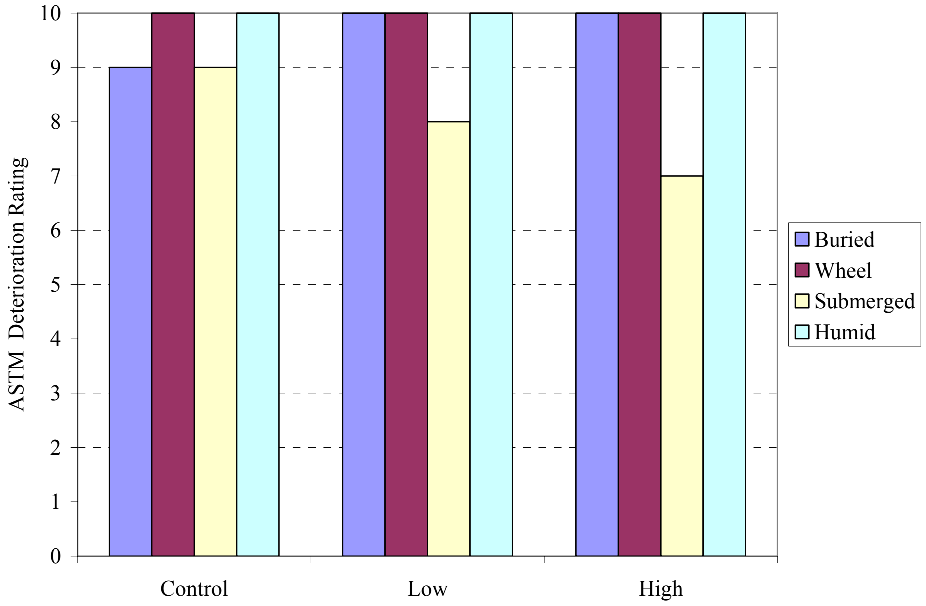

Figure F13: Coating 2 (15 ppt) - Deterioration Rating vs. Concentration (SeaKleen™)

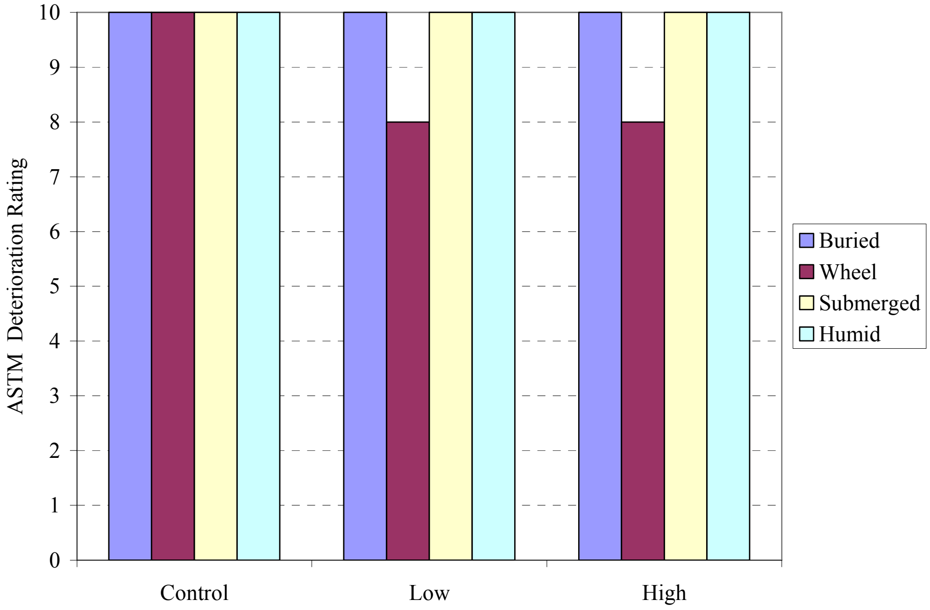

Figure F14: Coating 1 (35 ppt) - Deterioration Rating vs. Concentration (SeaKleen™)

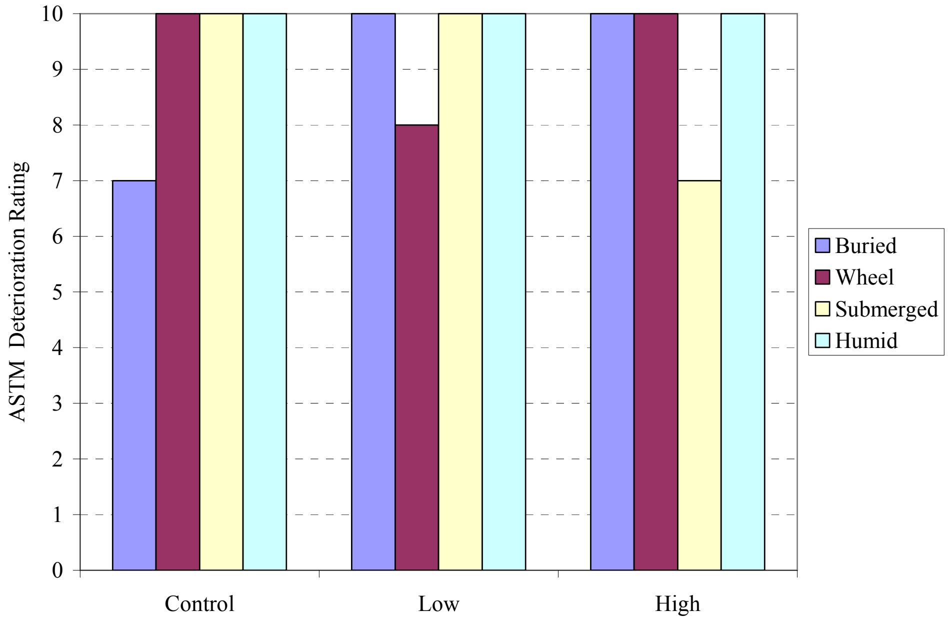

Figure F15: Coating 2 (35 ppt) - Deterioration Rating vs. Concentration (SeaKleen™)

APPENDIX G

PHOTOGRAPHS OF BARE STEEL COUPONS (PERACLEAN® OCEAN)

Figure G1: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 1, (Control Tank)

Figure G2: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 2, (Low Dosage, PERACLEAN® OCEAN)

Figure G3: Corroded Plates Exposed to Splash Zone Environment in 15 ppt Salt Water, Tank 3, (High Dosage, PERACLEAN® OCEAN)

Figure G4: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 4, (Control Tank)

Figure G5: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 5, (Low Dosage, PERACLEAN® OCEAN)

Figure G6: Corroded Plates Exposed to Splash Zone Environment in 35 ppt Salt Water, Tank 6, (High Dosage, PERACLEAN® OCEAN)

Figure G7: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 1, (Control Tank)

Figure G8: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 2, (Low Dosage, PERACLEAN® OCEAN)

Figure G9: Corroded Plates Exposed to Submerged Environment in 15 ppt Salt Water, Tank 3, (High Dosage, PERACLEAN® OCEAN)

Figure G10: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 4, (Control Tank)

Figure G11: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 5, (Low Dosage, PERACLEAN® OCEAN)

Figure G12: Corroded Plates Exposed to Submerged Environment in 35 ppt Salt Water, Tank 6, (High Dosage, PERACLEAN® OCEAN)

APPENDIX H

COATINGS PERFORMANCE (PERACLEAN® OCEAN)

Figure H1: Tank 1 (Fresh Water) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

Figure H2: Tank 2 (Fresh Water) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

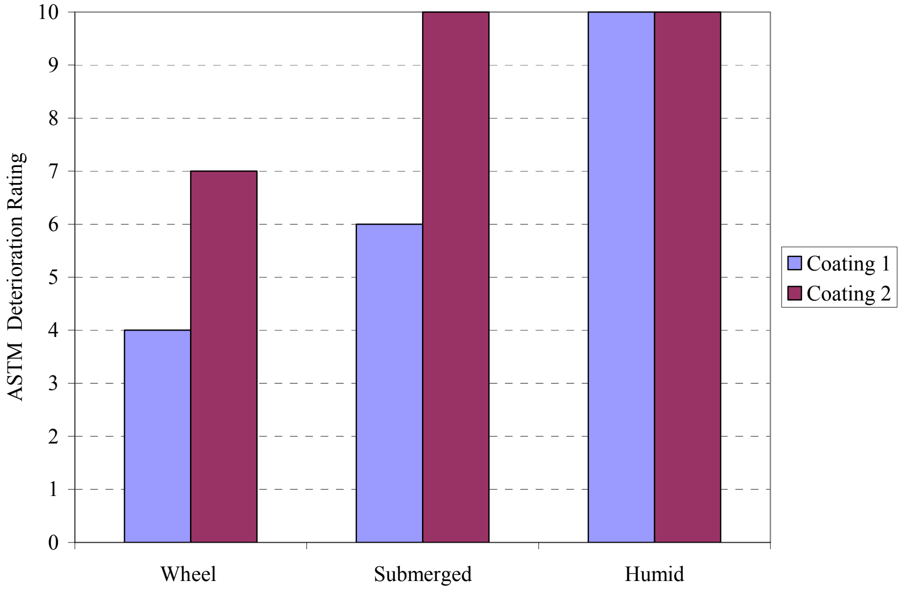

Figure H3: Tank 3 (Fresh Water) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

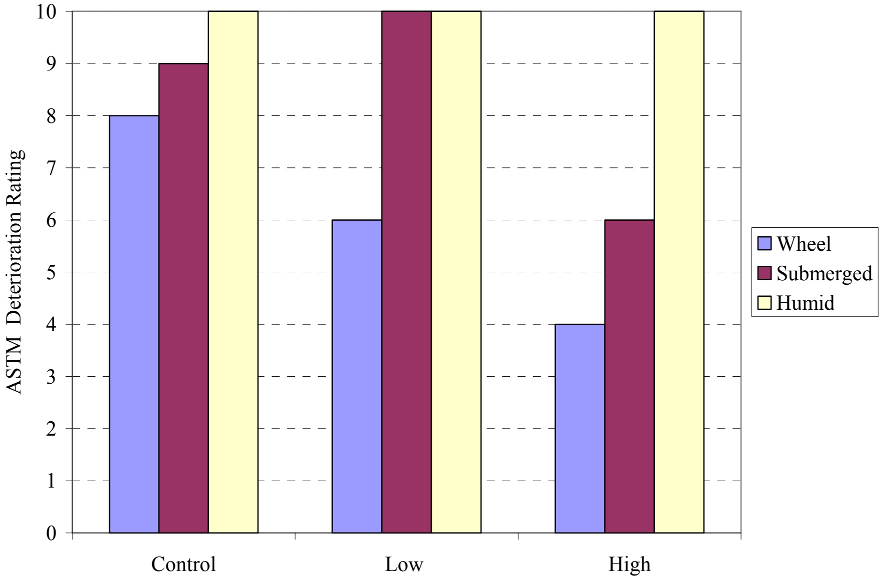

Figure H4: Coating 1(Fresh Water) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)

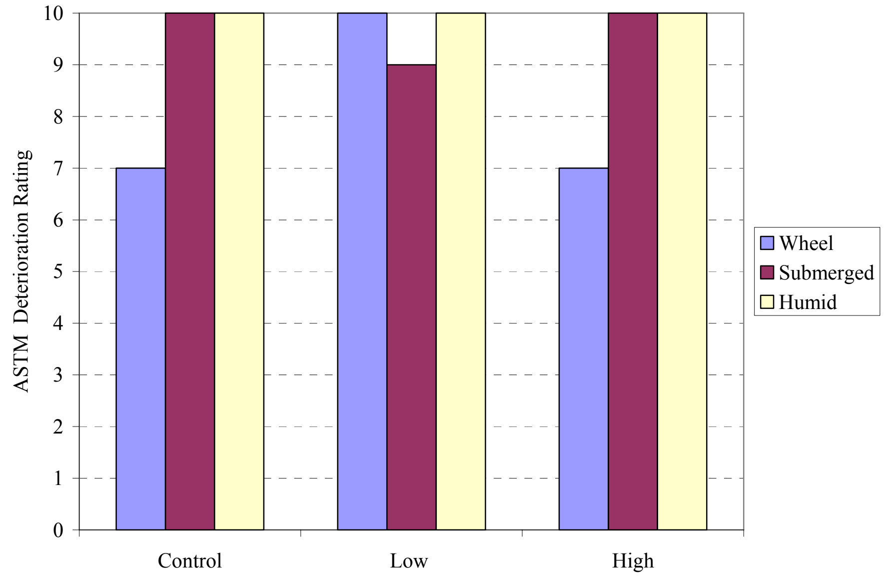

Figure H5: Coating 2 (Fresh Water) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)

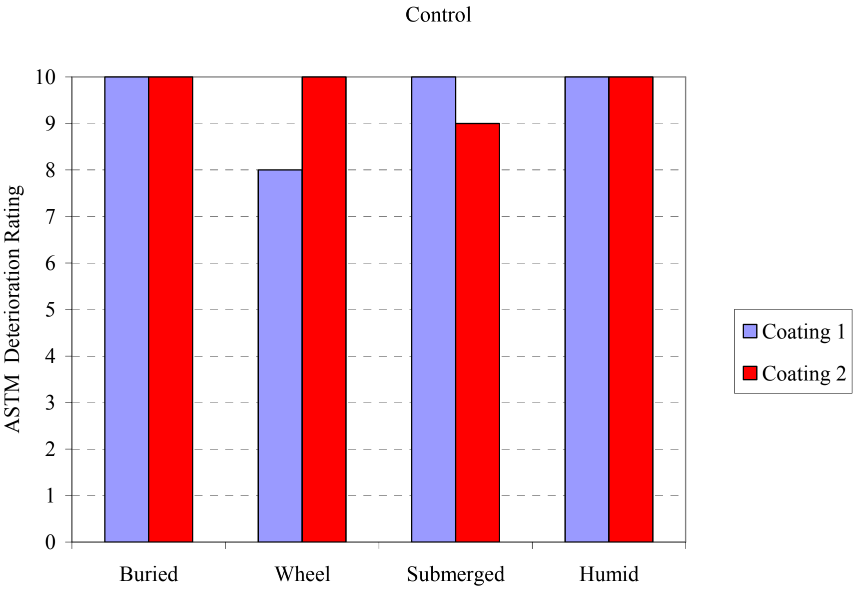

Figure H6: Tank 1 (15 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

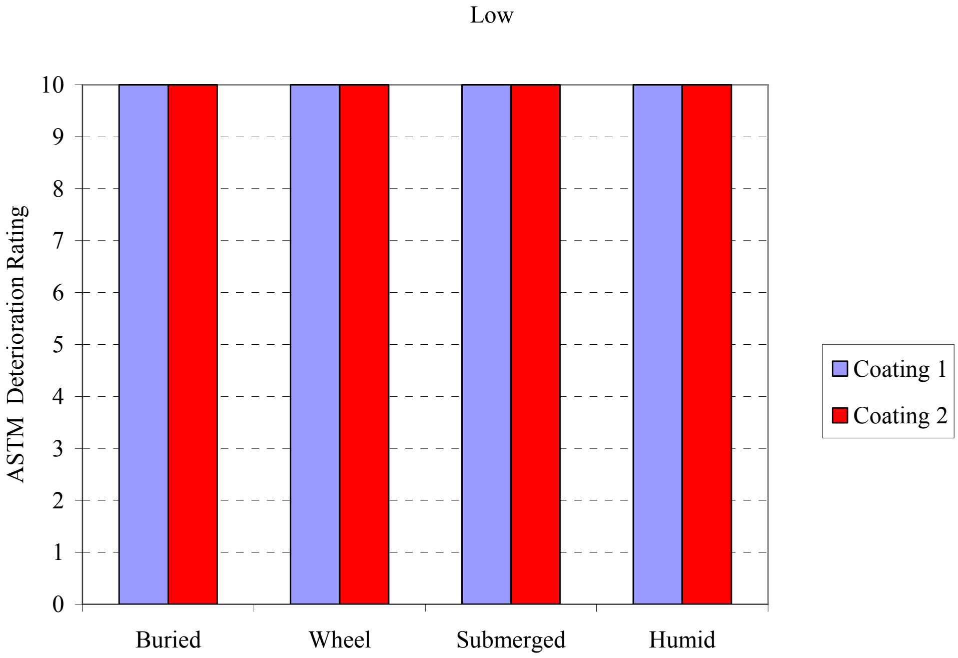

Figure H7: Tank 2 (15 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

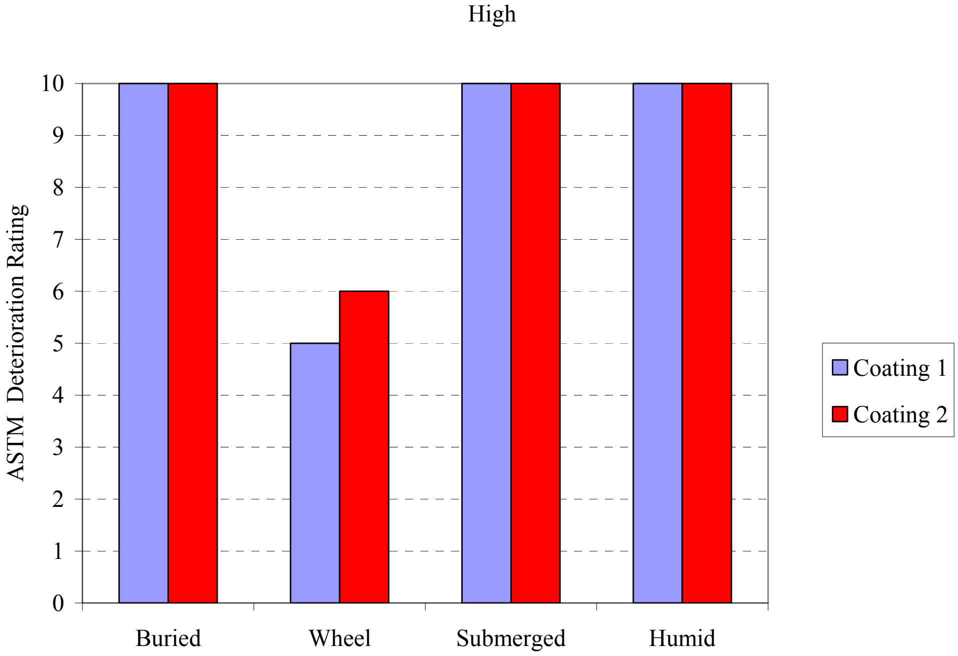

Figure H8: Tank 3 (15 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

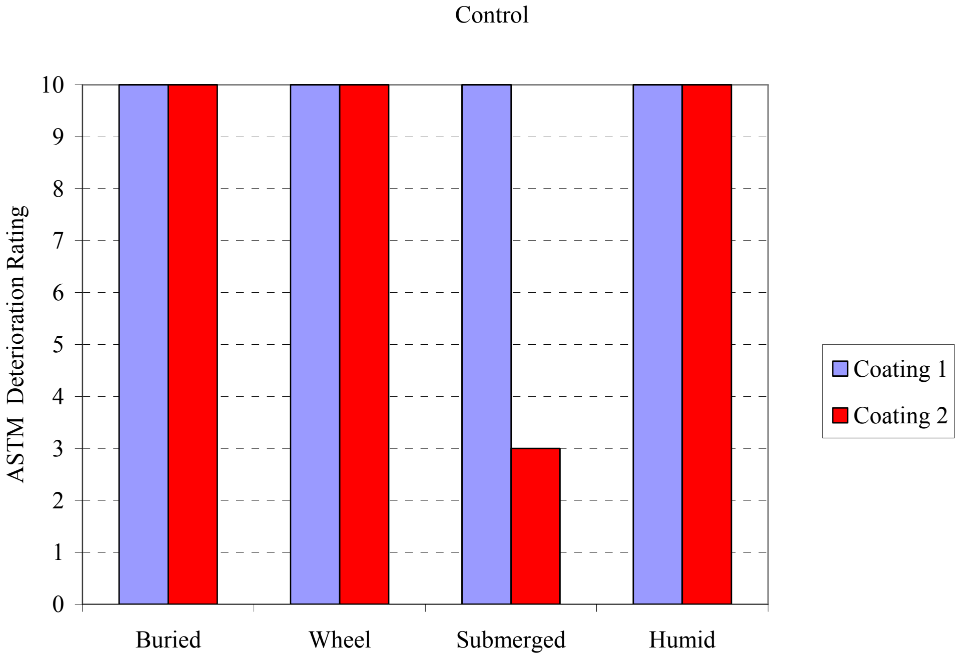

Figure H9: Tank 4 (35 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

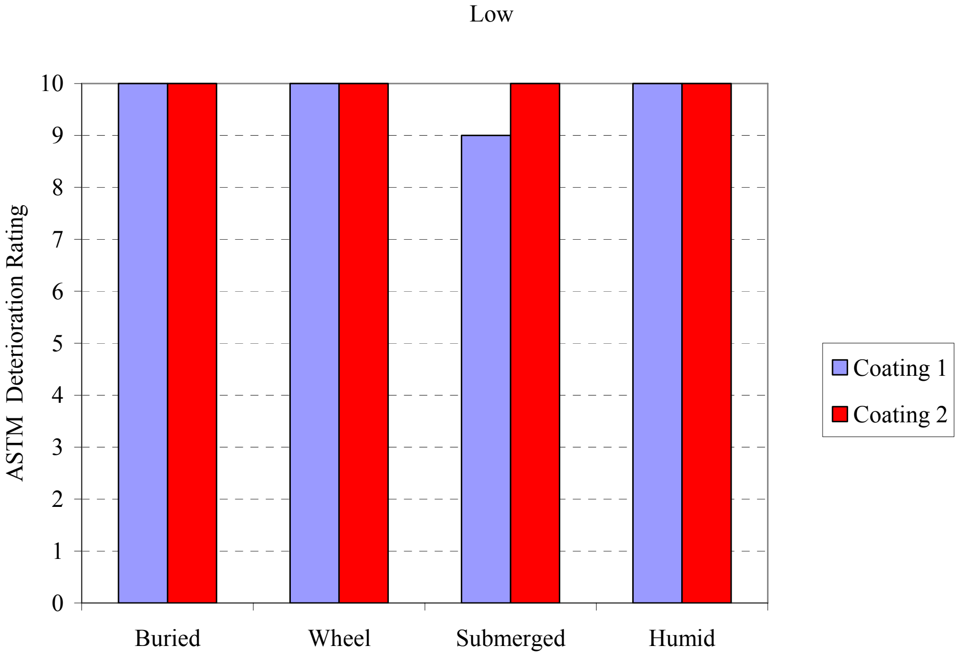

Figure H10: Tank 5 (35 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

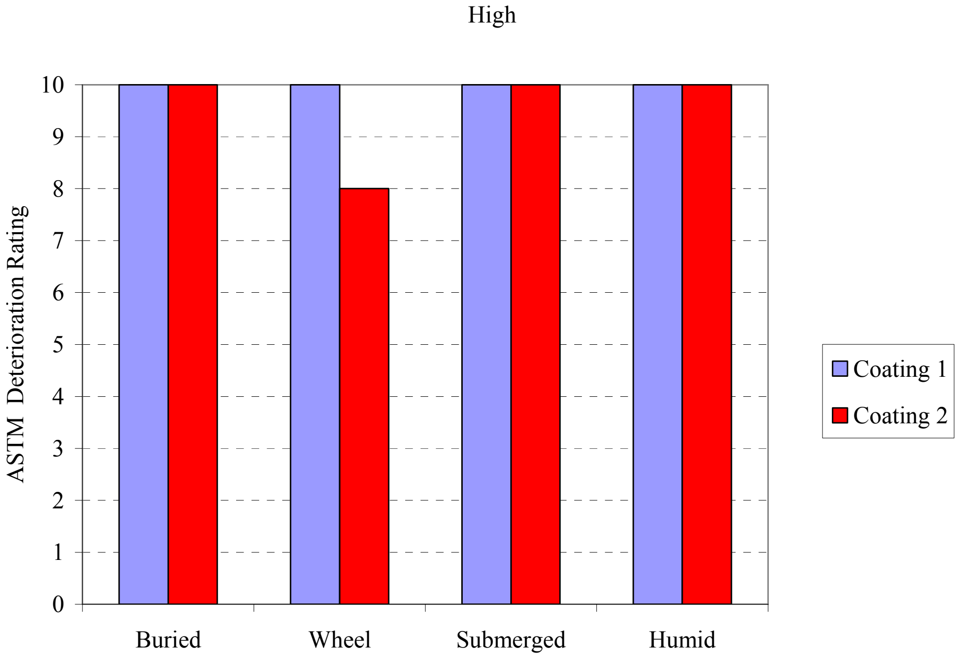

Figure H11: Tank 6 (35 ppt) - Deterioration Rating vs. Location (PERACLEAN® OCEAN)

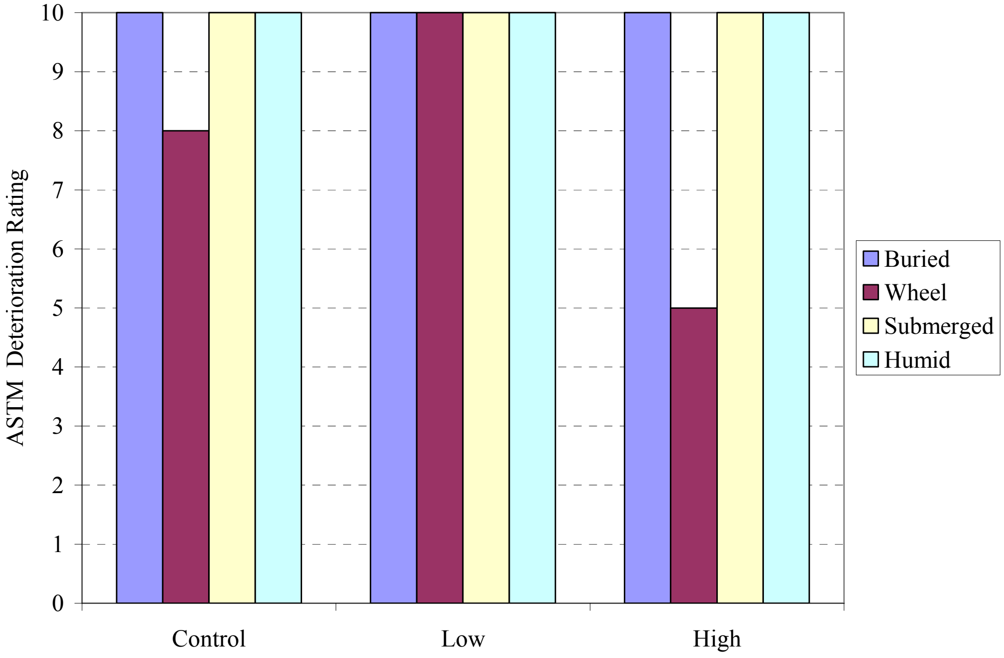

Figure H12: Coating 1 (15 ppt) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)

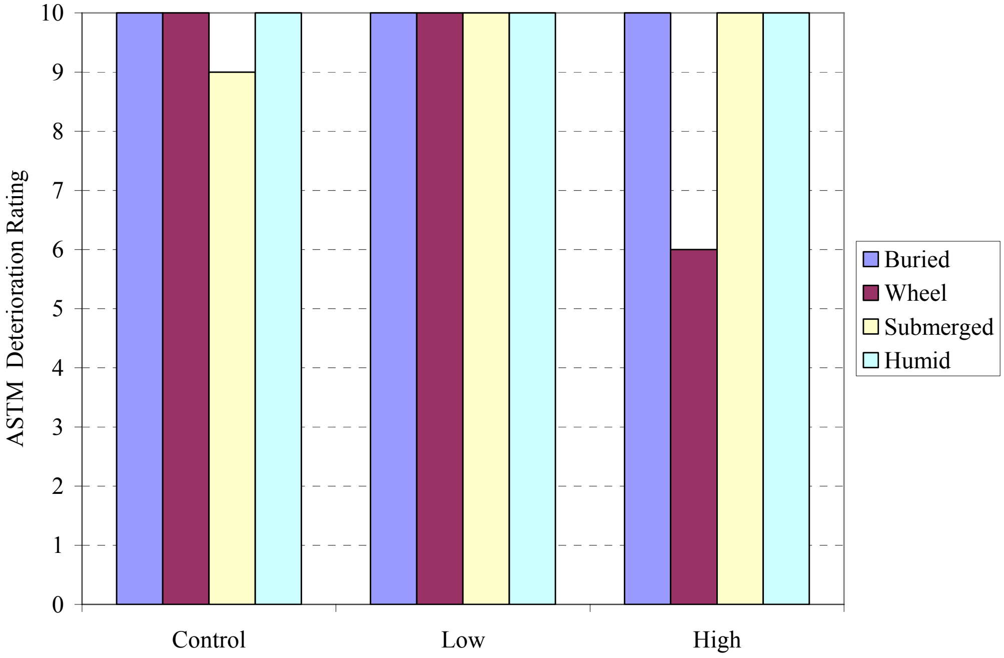

Figure H13: Coating 2 (15 ppt) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)

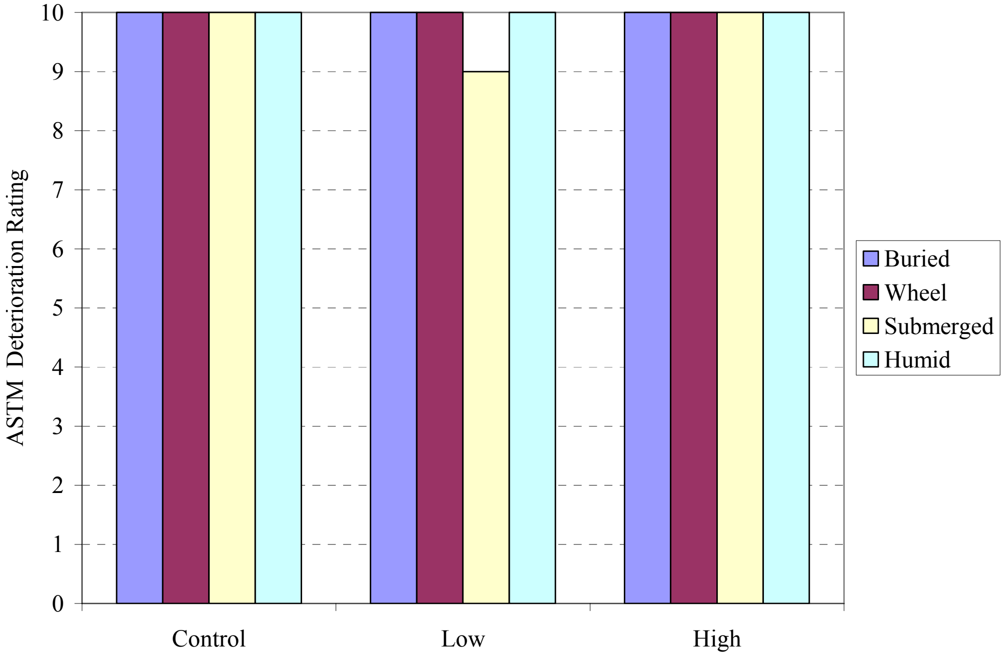

Figure H14: Coating 1 (35 ppt) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)

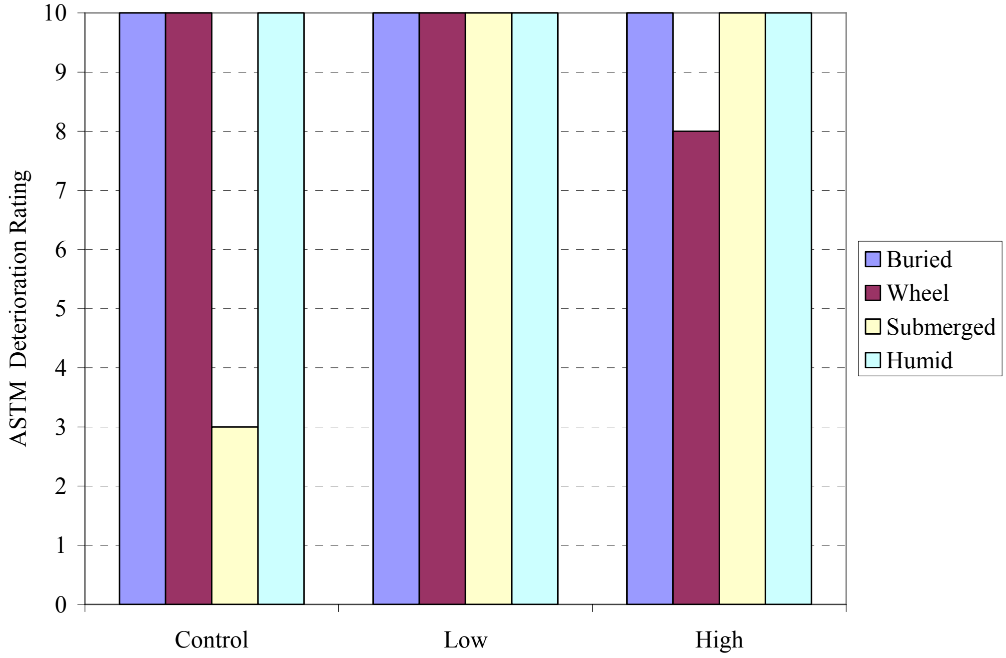

Figure H15: Coating 2 (35 ppt) - Deterioration Rating vs. Concentration (PERACLEAN® OCEAN)