

# Environmental impact on the corrosion behavior of marine grade steel in the Arabian Sea conditions - a comparative analysis of field and laboratory based corrosion tests

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## Abstract

Corrosion-induced degradation of marine steel structures is highly dependent on the surrounding environmental conditions and so varies significantly around global seawaters. This research has investigated the dependence of corrosion of carbon steel alloy for marine service on seawater composition and climatic conditions typical of the Arabian Sea. Natural and polluted seawater sites in the Arabian Sea were selected for field exposures. In addition, environmental conditions spanning those anticipated for the shipping structures operating in the Arabian Sea have been simulated in laboratory-based experiments by using heated and aerated artificial seawater. Following their exposures, the performance of samples have been investigated using the weight-loss and dimensional metrology methods. High overall corrosion losses were observed in the polluted seawaters than in the natural seawater conditions of Arabian Sea.

## 1. Introduction

In the marine environment corrosion induced structural degradation accounts for the highest failure incidents in marine/shipping structures despite the application of protective measures such as corrosion resistant paint schemes and cathodic protection measures [1,2]. The rates of corrosion processes in marine grade low carbon steel are highly dependent on the severity of operating and sea environmental conditions; seawater composition and temperature in particular. Variations in these parameters are quite significant across global seawater reservoirs [3]. In addition to the temperature, dissolved oxygen (DO) concentration, salinity level, pH level, water velocity, chlorides, sulphates, microbiological agents, and nutrients in the form of dissolved inorganic nitrogenous (DIN) compounds in the seawater are considered as the influential factors towards corrosion processes in marine assets. Although, the standard ASTM method G1-03 provides a good approximation for the uniform corrosion loss, however, the use of such data in design maintenance planning may lead to serious consequences by underestimating the real rate of deterioration and failure probabilities.

In this paper, a new corrosion measuring approach based on the 'Dimensional Metrology' (DM) has been used for the first time to investigate the corrosion behaviour of ship grade steel under seawater immersion conditions. Two sites in the Arabian Sea near the southern coast of Karachi have been selected for field corrosion experiments (i.e. a clean open natural seawater site and a pollutant-rich seawater site). In addition, environmental conditions spanning those anticipated for the Arabian Sea have been simulated in the laboratory-based experiments by using artificial seawater followed by a comparative analysis for corrosion loss between the dimensional metrology and standard weight-loss methods. The accumulated corrosion products have been characterized using the scanned electron microscopy/ energy dispersive X-ray spectroscopy (SEM/EDS) and X-ray diffraction (XRD) methods.

## 2. Experimental Procedure and Methodology

### 2.1 Material selection and experimental plan

During the corrosion experiments, coupons were immersed in the two sites in the Arabian Sea; clean natural seawater, and pollutant-rich seawater, respectively. In the laboratory-based experiments, influential seawater parameters of Arabian Sea were simulated using artificial seawater. Contrary to the average seawater surface temperatures of the Arabian Sea (27-30 °C), the seawater in the laboratory-based experiments was maintained at ~40 °C, so as to simulate the temperature of slightly heated seawaters flowing in the ship structures operating in these regions. The laboratory based experiments were also repeated at a mean seawater temperature of ~18 °C with water specifications as for the experiments conducted at ~40 °C. Table 1 (a & b) shows the compositions of the steel coupons.

**Table 1** Elemental compositions (wt.%) of (a) laboratory coupons (b) field coupons.

C	Mn	Si	P	S	Al	Mo	Fe
0.1	0.34	0.13	1.2	0.006	0.3	0.2	balance

(a)

C	Mn	Si	P	Cu	Ni	Cr	Fe
0.06	0.9	0.4	0.01	0.4	0.7	0.7	balance

(b)

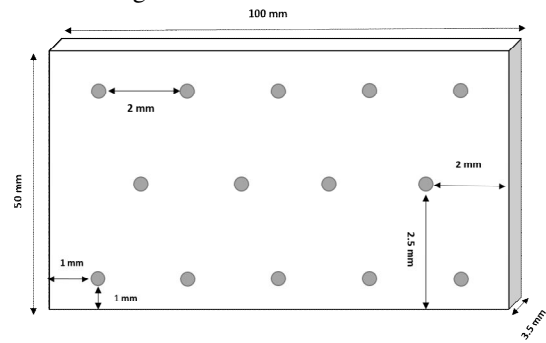
Table 2 shows the influential seawater parameters for corrosion process recorded/maintained for all three experimental conditions.

**Table 2** Influential seawater parameters at field and laboratory based experiments.

Parameters	Units	Polluted (Field)	Natural (Field)	Artificial seawater
Temperature	°C	27±3	27±3	40±3
DO	mg/L	1±0.3	>3.5	3.4±0.75
pH		6.5±0.5	7.5-8.2	7.5-8.2
Conductivity	mS/m	63± 4.8	50-55	60±4
Velocity	m/s	~ 0.3	~ 0.3	~ 0.3
DIN(Nitrates)	mg/L	1.5±0.2	>0.005	>0.005
Sulphates	mg/L	~ 2900	~1900	~1900

## 2.2. Dimensional Metrology Method for Corrosion Measurement

The dimensional metrology (DM) approach is purely based on the measurement of dimensions (test coupons) accurately prior and post exposure to the corrosive environment. This uses a contact metrology technique (with digital micrometers) to measure the plate dimensions before exposure. After exposure, again the measurements of plate thickness were taken at the same predetermined positions, as shown in Figure 1.



**Figure 1** Schematic of DM pattern. Here dots indicate positions of measured prior/post immersion.

After collection of the samples from seawater exposure, the known position and the nearest vicinities were measured for the thickness loss and deepest points. In addition to the DM technique, the standard weight-loss method [4,5] has also been used to calculate corrosion rate/loss and compared to the DM approach. Equations below (1 and 2) refer to the standard weight-loss method.

$$C_R \text{ (mm/yr)} = 87.6 * \left( \frac{\Delta W}{D.A.T} \right) \quad (1)$$

Where  $C_R$  is the corrosion rate,  $\Delta W$  is the weight difference prior/post immersion (in milligrams),  $D$  is the material density in grams/cm<sup>3</sup>,  $A$  is the sample's exposure surface area in cm<sup>2</sup> and  $T$  is the exposure time (hours). Similarly, average corrosion loss is calculated using the following equation:

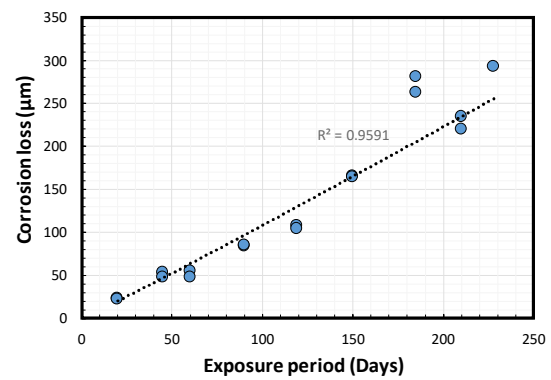
$$\text{Corrosion loss } (\mu\text{m}) = \frac{\Delta W * 1000}{D.A} \quad (2)$$

For all field and laboratory based tests, the rust compounds accumulated on the metal surface during the seawater immersion were characterized using SEM/EDS and XRD.

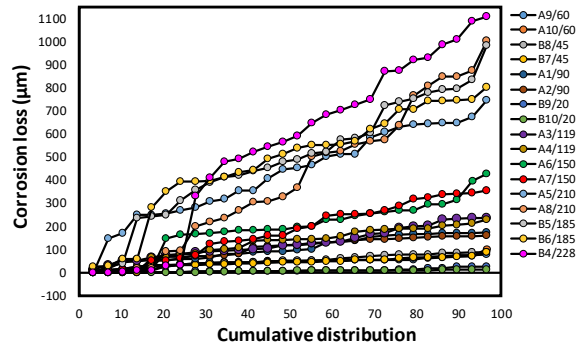
## 3. Results and Discussion

### 3.1 Laboratory-based corrosion test results

In the laboratory-based experiments, duplicate coupons were recovered from 20 up to 228 days of immersion. Figure 2 illustrates the average corrosion loss calculated using equation 2 and Figure 3 shows the cumulative distribution function (CDF) of corrosion loss calculated using the DM approach.



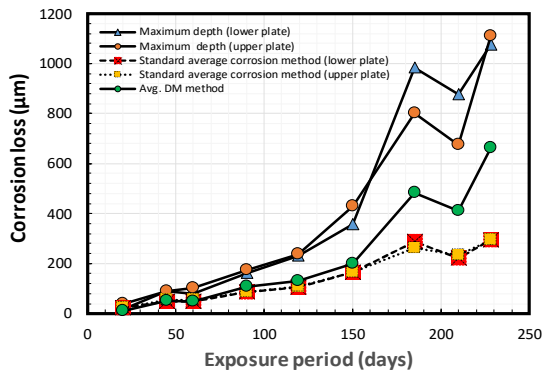
**Figure 2** Average corrosion loss calculated using standard weight-loss method (for laboratory corrosion tests carried out at ~40 °C).



**Figure 3** Cumulative distributions of corrosion loss measurements using the DM approach (legends indicates coupon denomination/immersion period in days).

In this DM approach, the greater the number of measured points prior- and post-exposure the more stable are the incremental trends of corrosion. The DM plot (in Fig. 3) provides a comprehensive information on the corrosion phenomena such as mean corrosion depths, deepest pit depths, their percentage above mean value, probability density, CDF, and a definite trend line classifying the corrosion pattern (i.e. uniform or localised) on either sides of the corroding surfaces (multi-modal pattern of

corrosion). Figure 4 demonstrates a comparative analysis for corrosion loss calculated using DM approach and standard weight-loss method. It shows maximum corrosion depth points (orange and blue markers) and mean corrosion depths (green markers) calculated using DM approach; whereas, red and yellow markers represent corrosion losses calculated using standard average weight-loss method.

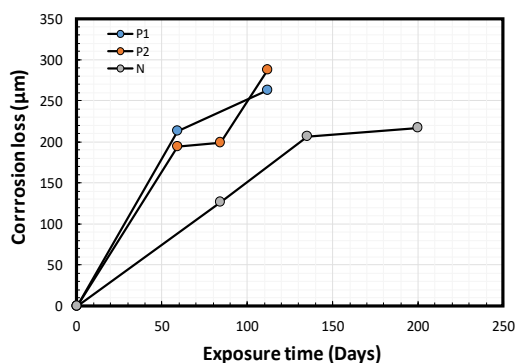


**Figure 4** Comparison of corrosion loss parameter calculated using the standard average corrosion method.

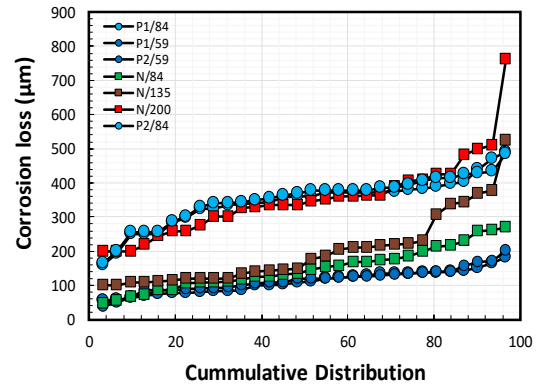
In the laboratory experiments, a corrosion test with similar seawater conditions (salinity/conductivity, pH, flow velocity) was repeated at a seawater temperature of  $18.6 \pm 2.8$  °C for 210 days. The experimental results revealed that both the mean corrosion losses and the maximum corrosion depths were around 4 times higher for a seawater temperature of  $\sim 40$  °C than those observed with a mean temperature of  $\sim 18.6$  °C.

### 3.2 Field corrosion test results

Figures 5 and 6 represent the corrosion loss for both seawater sites (clean natural seawater and polluted seawater) in the Arabian Sea calculated using the standard weight-loss and DM methods, respectively.



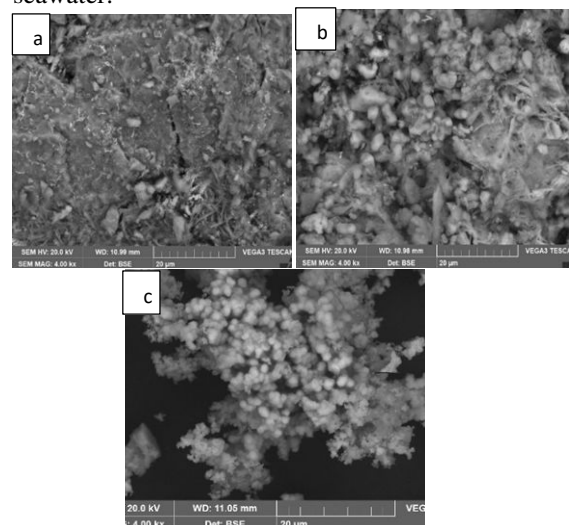
**Figure 5** Standard average corrosion loss calculated in the natural seawater (N), and polluted seawaters (P1, P2)



**Figure 6** Corrosion loss (DM approach) in natural seawater site (N) and pollutant-rich seawater site (P1, P2). The above graphs indicate considerably higher corrosion losses observed in the pollutant-rich seawaters than in the clean natural.

### 3.3 Characterization of rust product

Figure 7 illustrates SEM micrographs for the corrosion product accumulated on the steel coupons submerged under the three different seawater conditions (as outlined above). The EDS results show high sulphur (S) content ( $\sim 2.7$  wt.%) in the corrosion product on the coupons in the pollutant-rich seawater site, whereas a lower S content appeared in the corrosion product collected in the natural seawater site ( $\sim 0.77$  wt.%) and an even lower level was found in that formed in the artificial seawaters of laboratory-based conditions ( $\sim 0.16$  wt.%). In the X-ray diffraction (XRD) analysis, the presence of typical rust phases were observed in all environmental conditions. Additionally, aragonite, calcite, other carbonates/calcareous compounds and silicon oxides were also detect in the corrosion layers; predominantly in the polluted and natural seawater.



**Figure 7** SEM micrographs of corrosion products (Fe/O-rich globules, spongy globules, and distinct phases) formed in: a. natural seawater, b. pollutant-rich seawaters, c. artificial seawater (laboratory).

### 3.3 Discussion

The rate of corrosion is significantly different between the open natural seawater conditions and the pollutant-rich seawater; despite availability of similar seawater temperature, velocity, salinity level and immersion depth. However, some other influential corrosion accelerating factors, such as DO, DINs and pH level were found to be quite different at both field experimental sites. According to previous studies, DO has a direct relationship to the corrosion rate, with its lower concentration in the pollutant-rich seawater favouring a lower corrosion rate. The difference in the pH level is not very significant between both field experimental sites (6.9-8.2); with the available literature suggesting that pH level ranging between 4-10 does not directly affect the rate of corrosion [6,7]. The potential factor is the presence of high DINs (nitrates) in polluted seawater (1.5 ppm). In addition to the high DIN content, presence of significantly high sulphur can be the contributory factors towards accelerated corrosion rates. The EDS results also confirm the presence of high sulphur contents in the corrosion deposits settled in the polluted seawater site.

The average corrosion rates recorded for the clean natural seawater site (~0.4-0.55 mm/yr.) and that in the simulated laboratory conditions (0.4±0.7 mm/yr.) were quite comparable. Whereas in the polluted seawater sites the average corrosion rates ranged 0.87-1.32 mm/yr. for an exposure period up to 112 days. Although known biological activities were not present in the laboratory-based experiments and a difference in the seawater temperature (10 °C) also existed between the field (natural seawaters) and laboratory based experimental conditions. Further, a remarkable corrosion rate difference observed in laboratory tests conducted at 40 °C and 18.6 °C seawater temperature (4 times higher at 40 °C) provide a reason that the corrosion rates in the field environments of Arabian Sea should be significantly higher at a seawater temperature of 40 °C than those recorded in current study at 27-30 °C. As seawater temperatures in the ship tanks, pipelines and equipment (operating in the Arabian Sea) can reach as high as 40 °C. The thickness loss measurements using DM provides a novel approach to collect a useful data set which would otherwise be missing/underestimated with the conventional procedures.

### 4 Conclusion and future research avenues

This research study concludes following:

Higher corrosion damage rates were recorded in the polluted seawater site of Arabian Sea than in the natural seawater conditions under similar seawater temperatures (27-30 °C), salinity, flow velocity, and

pH level. This is mainly attributed to the presence of high DINs (nitrates) levels.

In EDS analysis, the presence of high sulphur levels were observed in the corrosion product accumulated in the polluted seawaters, which has a vital role particularly during the long-term (anaerobic) phases of corrosion.

As compared to the standard weight-loss method, the dimensional metrology approach provides a superior capability to measure various corrosion damage parameters simultaneously and an opportunity to carry out in-depth statistical analyses/prediction modelling for general as well as localized corrosion.

Under similar environmental conditions and seawater specifications in the laboratory-based experiments, 4 times higher corrosion losses (mean corrosion and maximum depths) were recorded at a seawater temperature of ~40 °C than those observed at a seawater temperature of 18.6 °C. These results revealed that the seawater temperature is the most critical parameter in determining the rate of corrosion of submerged steel structures.

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