# STUDY OF MARINE STRUCTURAL CORROSION USING CORROSION COUPONS IN LUMUT AREA

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**ABSTRACT** The corrosion rate in marine environments affects economic interest since the loss of steel in marine structures has impact on structural safety and performance. With emphasis to maintain existing structures in service, there is increasing interest in predicting corrosion rate at a given location for a given period of exposure. Corrosion allowances are prescribed for structural members by standards based on the corrosion protection provided, expected rate of corrosion and service life of structure. There are no studies to determine the appropriate corrosion allowance for marine steel structures in Malaysia. The research objectives are to determine the nature and rate of corrosion and the effect of differences in the immersion depth and microalgae on the corrosion rate. Two sets of corrosion coupons of Type 3 Steel consisting of mild steel were immersed in seawater at Lumut in Malaysia. The corrosion rate of the coupon is estimated based on the material weight loss with time. The corrosion rate is controlled by oxidation in short term and bacterial activity in long term. Corrosion rate in the immersion zone is observed to be more than in the splash zone. The results are also compared with code prescriptions and discussed.

(Keywords: rate of corrosion, uniform corrosion, pitting, corrosion coupons, marine structures.)

# INTRODUCTION

Corrosion is a problem considered during design and maintenance of land based as well as marine steel structures. Corrosion allowances are prescribed for structural members by different standards such as BS 5950[1], EC3[2], Norsok-M001[3], API RP2A WSD[4], and DNV[5]. With the increasing emphasis to maintain existing structures in service for longer periods of time to defer replacement costs, there is increasing interest in predicting corrosion rate at a given location for a given period of exposure once the protection is lost. Moreover for already corroding structures, the present and future expected rates of corrosion are important for predicting remaining safe working life of the structure. The reduction in corrosion allowance can signify large savings. Alternatively, structures may still be safe at the end of the design life.

Corrosion coupons is a preferred tool for monitoring corrosion since they provide accurate results at a reasonable cost, are easy to use and can provide general information that is quantitative and visual. Though different types of coupons have been used (strip coupons, disc coupons, rod coupons, coupons with applied stress etc), the strip coupons give most accurate results and have been used in this work [6].

There were many empirical field investigations on the corrosion of steel in marine environment. Field trials are recommended to assess the likely corrosion rates at the site of interest. Laboratory tests cannot replicate the corrosion that occurs under actual field conditions since the corrosion process is non linear in time. It cannot generate the marine bacteriological process involved in corrosion in real seawaters.

The main objective of the research is to study the nature and rate of corrosion in marine steel structures in Malaysia. The sub-objectives of the study are to determine (1) the nature of corrosion and identify the factors affecting corrosion, (2) the rate of corrosion and compare the rates of corrosion in different zones and with the limits in the codes of practice and (3) the effect of microalgae on the corrosion rate. Sea water at Lumut in Perak, Malaysia was chosen for the experiments due to its proximity to UTP and many industries located there. Corrosion coupons were installed corresponding to atmospheric zone, splash zone and immersed zone using a steel frame. The nature and rate of corrosion at different zones were determined by determining the loss of weight of the steel coupons every three months over a two year period. The corrosion rates were compared with the rates prescribed in the codes.

# LITERATURE REVIEW

The literature review is organized into the sections: General, Measurement of Corrosion loss and rates, Process of immersion corrosion, Studies on corrosion rates, Factors affecting rate of corrosion and Code Provisions on corrosion rates.

#### General

Malaysia, lying between latitudes <sup>1</sup>/<sub>2</sub> ° and 7 ° N and longitude 100 ° and 119 <sup>1</sup>/<sub>2</sub> ° E, has tropical climate. The average temperature is 27.5 ° C and average rainfall is 2409 mm. The mean relative humidity is 62.6%. Lumut located on the northwest shores of Peninsula gains importance from the location of Royal Malaysian Navy, Naval shipyard, Marine Terminal, Industrial Park and the various industries located there. At the location of the experiment on the coast at Lumut, the climate can be classified as "marine tropical" [7][8][9].

Corrosion rates are classified as low, moderate, severe and very severe as shown in **Table 1** [6].

Table 1 Classification of corrosion rates (in mils per year or mpy)[6]

| Classification        | Low      | Moderate        | Severe          | Very Severe |
|-----------------------|----------|-----------------|-----------------|-------------|
| Corrosion rate (mpy)  | <1.0     | 1.0 - 4.9       | 5.0 - 10.0      | >10.0       |
| Corrosion rate (mmpy) | < 0.0254 | 0.0254 - 0.1245 | 0.1270 - 0.2540 | > 0.2540    |

Marine structures have varying environments from the total immersion, tidal zone, splash zone and marine atmosphere zone. The most severe corrosion occurs in the splash zone where corrosion rates are generally more than twice of those in the immersed portion. Above the splash zone protection can be maintained by a range of coatings. The immersed areas are protected by cathodic protection. Maintenance of effective corrosion control is more difficult in the splash and inter-tidal zones. The variation of intensity of corrosion of an unprotected steel structure in seawater with position is shown in Figure 1. The spray and splash zone above the mean high tide level is the most severely attacked region due to continuous contact with highly aerated sea water and the erosive effects of spray, waves and tidal actions.

# Measurement of Corrosion loss and rates

Corrosion loss is determined using the weight loss measurement. The simplicity of measurement offered by corrosion coupon makes it the basic method of measurement in many corrosion monitoring programs. There are many evidences in the corrosion literature that coupons can provide accurate corrosion estimates and that size is not a significant variable within one exposure environment [10][11][12]. This can then be expressed in several ways:

(1) Percent weight change is calculated as:

$$\%\_wt\_change = \frac{Original\_wt - Final\_wt}{Original\_wt} \times 100 \dots (1)$$

(2) The metal loss in mm can be calculated using expression

$$Metal\_loss = W \times \frac{0.01}{DA} \dots (2)$$

(3) Loss of metal thickness per unit time, given by the following expression

$$mm / yr = W \times \frac{87.6}{DAT} \dots (3)$$

W = weight loss in milligrams; D = metal density in g /cm<sup>3</sup>; A = area of sample in cm<sup>2</sup>; T = time of exposure of the metal sample in hours.

(4) Loss of metal thickness per unit time can be expressed using Engineering Units of mils per year. A mil is one thousandth of an inch.

W = weight loss in milligrams; D = metal density in g /cm<sup>3</sup>; A = area of sample in square inches; T = time of exposure of the metal sample in hours.

(5) Weight loss in milligrams per square decimeter per day (mdd) is given by

where T is the exposure time in days

W = weight loss in milligrams; A = area of sample in  $cm^2$ .

(6) Weight loss in grams per square metre per year

$$Wt \_ loss(gm / m^2 / yr) = mdd \times 36.5 \dots (6)$$

#### **Process of immersion corrosion**

On exposure of steel surface, a complex mix of bacterial, nutrient and environmental effects act on it. The corrosion process takes a few days to become established and this is called Phase 0. This phase makes very little contribution to corrosion loss. An equilibrium condition develops over the corroding surface with the corrosion being controlled by the rate of arrival of oxygen at the corroding surface, which is limited by the rate of oxygen diffusion possible from the water adjacent to the corroding surface. Rust layers are still very thin. Though the corrosion loss at this stage (called phase 1) is slightly non-linear function of time, it can be

modeled by a linear function of time. The corrosion by-products tend to reduce the rate of oxygen supply to the corroding surface at phase 2. Phase 3 occurs when the anaerobic conditions are developed. The capability for the oxygen to reach the corroding surface reduces due to the increasing thickness of the rust layer thus allowing localized anaerobic condition to develop. This provides conditions under which sulphate-reducing bacteria (SRB) can flourish under the right nutrient conditions. SRB attack steel through their waste products the (metabolites), principally H<sub>2</sub>S, producing FeS in the process. As a result, the rate of corrosion now depends on the rate of metabolism which in turn depends on the rate of supply of nutrients [13]. Long term anaerobic condition will eventually lead to a near-steady-state situation. This situation develops over the corroding surface with the rate of corrosion dependent on the rate of supply of nutrients [14] and the loss of rust layer through erosion and wear. This is known as 'Phase 4'.

### Studies on corrosion rates

Corrosion rates as high as 0.9mm/year have been reported at Cook Inlet, Alaska and 1.4mm/year in the Gulf of Mexico. Cathodic protection in this area is ineffective because of lack of continuous contact with seawater (the electrolyte) and thus no current flows for most of the time [15]. **Figure 2** shows the essential features of corrosion loss – exposure time model for immersion corrosion and pitting. Five phases (Phase 0 to Phase 5) are identified [16][17].



**Figure 3** shows the weight-loss data obtained at Taylors Beach near Newcastle, converted to the equivalent one-sided corrosion. The widely used non linear monotonic function (whereby oxidation controls the corrosion process from the instant of first exposure indefinitely) does not fit the data. The non-linear, best fit trend is shown together with the best fit linear trend and the power law trend. The power law c=At<sup>B</sup> is widely used and is referred to as a natural 'law'. The increased scatter of data points with time and the phases corresponding to the model are to be noted [18].

**Figure 4** shows the corrosion loss with time for AISI 1020 steel exposed in the Panama Canal Zone (PCZ). This figure can be related to **Figure 2** at the exposure period (ta) which is around 3 years exposure [18]. The average corrosion loss (Ca) is around 0.25mm for the half tide data and it is much lower for immersion corrosion (around 0.05mm). The Ca is around 0.16mm for ta approximately 5 years for the coastal atmospheric data at Christobel while for the inland site it is around 0.12mm. For phase 3 and 4 to establish, ta indicates that it takes more time as the site is further away from the sea.



**Figure 5** shows the same data points for two atmospheric sites (Christoble and Meraflores) with the best fit linear and power law relationship. It is seen that both the linear and the power law functions are not responsive to subtle changes in the trends corresponding to each data set shown with grey circles [18].

Corrosion in insulated coupons at different levels was measured over 3 years at the transport wharf for the Shengli oil field in the Chengdao Sea. The total corrosion losses were plotted as shown in **Figure 6**. Using **Figure 2** for guidance, trend lines have been plotted. As the distance from the fully immersed environment increase, hence both ta and ca increases. For the first two years or so the corrosion is under diffusion control thus there is little difference in ta for the exposure conditions [19].



## Factors affecting rate of corrosion

The effects of various factors on corrosion losses are discussed below:

The differences in salinity of seawater are very little between the major oceans with an average salinity level typically in the range 30-35 parts per thousand. Water salinity has relatively little direct effect on corrosion rate, at least in the short term demonstrated in laboratory experiments by Heyn and Bauer (1910) and Mercer and Lumbard [20] in very carefully conducted experiments. According to DNV-RP-B401, the major seawater parameters affecting cathodic protection in situ include salinity [5].

The relative acidity of the solution is probably the most important factor in aqueous corrosion. The range 4-10 pH has little effect on the early rate of corrosion including in seawater. It may have a modest effect on the rate of metabolism of the bacterial and marine growth (fouling) that commences, typically immediately on immersion of steel in seawater. The rate of metabolism is the principal corrosion action of bacteria. At low pH the evolution of hydrogen tends to eliminate the possibility of protective film formation so that steel continues to corrode but in alkaline solutions, the formation of protective films greatly reduces the corrosion rate. Hence, the greater the water alkalinity, the slower the rate of bacteria attacks [21][22]. Therefore the rate of corrosion tends to reduce with higher pH values at the corroding surface.

Small changes (say < 0.5%) in alloys used in steel should have zero or negligible effect on the

degree of corrosion that occurs while oxygen diffusion controls the corrosion process according to corrosion science theory [15]. More specialized steel with larger alloy compositions will have a lower initial rate of corrosion particularly for alloying elements such as chromium, molybdenum and aluminium and to a lesser extent for nickel, silicon, titanium and vanadium [23][24]. Carbon content has essentially no effect on initial rate of corrosion [24].

Microorganisms attach to metals and colonise the surface to form biofilms producing an environment at the bio film/metal interface in aquatic environments and reduces the diffusion of oxygen thus reducing corrosion rate. The environment is very different from the bulk medium in terms of pH, dissolved oxygen, and organic and inorganic species and leading to electrochemical reactions that control corrosion rates. Microorganisms can accelerate rates of partial reactions in corrosion processes and shift the mechanism for corrosion [25][26].

The general fouling organisms along the Lumut coast are plankton, benthos, algae, bryozoans, barnacles and mussels. Evaluation conducted at Lumut coast on September 2010 by Tenaga National Berhad Research Sdn Bhd in collaboration with Universiti Teknologi Malaysia identified 36 species of phytoplankton during high tide and 42 species during low tide. The most common phytoplankton species were Thalassiosira sp.and Ceratium furca. A total of nine groups of zooplankton comprised of Phylum Cnidaria, Phylum Ctenophora, Phylum Chaetognatha, Phylum Mollusca, Phylum Annelida, Phylum Athropoda, Phylum Echinodermata, Phylum Chordata and Phylum Ectoprocta were found in the course of the study. In terms of benthos, a total of 6 phylum, 4 family and an approximately about 118 genus been sorted out and identified. Six phylum identified were Annelida, Crustacea, Mollusca, Echinodermata, Sipuncula and Vertebrata. Generally there was not much difference from the species list recorded during the previous ECMP (2007) study.

# **Code Provisions on corrosion rates**

The corrosion rates of carbon steel for one year of exposure on test sites situated in temperate, sub tropical and tropical marine sites with general chloride deposition rates (> 100 mg/m<sup>2</sup> day) is shown in **Table 2**[27].

| Table | 2 ( | Corrosion | rates : | for | carbon | steel | for | one | vear | of | exposur | e in | differen | t climate | regions | [27 | 1 |
|-------|-----|-----------|---------|-----|--------|-------|-----|-----|------|----|---------|------|----------|-----------|---------|-----|---|
|       |     |           |         |     |        |       |     |     | J    |    |         |      |          |           |         | L   |   |

| Climate      | Corrosion rate |             | Extreme      |
|--------------|----------------|-------------|--------------|
|              | (µm/year)      | (mm/year)   | (µm/year)    |
| Temperate    | 30 - 70        | 0.03 - 0.07 | Approx. 100  |
| Sub tropical | 40 - 170       | 0.04 - 0.17 | Approx. 250  |
| Wet Tropical | 80-700         | 0.08 - 0.70 | Approx. 1000 |

ISO 12944-2 [28] has placed the atmospheric zone in high corrosion category with corrosion rate of unprotected steel in the range of 80 - 200 µm per year (3 – 8 mils per year) and mass loss of 650 - 1500 g/m<sup>2</sup>. The corrosion rates are even higher in the splash zone at 200 - 500 µm per year (8 – 20 mils per year). The corrosion rate for unprotected steel in the immersion zone is in

the range 100 -200  $\mu m$  per year (4 – 8 mils per year) [29].

EN 12500 [30] has quantitatively classified the corrosivity of an environment on the basis of mass loss of standard flat specimens (rectangular shape 50 x 100m) based on one year of exposure (**Table 3**).

Table 3 Mass loss  $(g/m^2)$  for one year field test exposure in five corrosivity classes [30]

| Corrosiveness category | C1       | C2     | C3      | C4      | C5        |
|------------------------|----------|--------|---------|---------|-----------|
| Description            | Very low | Low    | Medium  | High    | Very high |
| Carbon Steel           | ≤10      | 10-200 | 200-400 | 400-650 | 650-1500  |

BS 6349-1-2000 Code of Practice for Maritime Structures classifies exposure of an area of steel in marine environment into vertical zones[31]. The notional average and upper limit values of corrosion for exposed, unprotected structural steels in temperate steels in temperate climates in mm/side/year is given in **Table 4**.

Table 4 Notional average and upper limits for corrosion rates in (mm/side/year) for different zones in temperate climate (BS 6349-1-2000)

| Zone                       | Average | Upper Limit |
|----------------------------|---------|-------------|
| Atmospheric (in the dry)   | 0.04    | 0.10        |
| Splash zone (above MHWS)   | 0.08    | 0.17        |
| Tidal Zone (MLWS and MHWS) | 0.04    | 0.10        |
| Intertidal low water zone  | 0.08    | 0.17        |
| Continuous immersion zone  | 0.04    | 0.13        |

# METHODOLOGY

The corrosion loss has been measured under field exposure conditions. Laboratory experiments mainly use artificial seawater in which it is difficult to generate the biotic marine conditions. The experiment is confined to corrosion in relatively shallow seawaters at Lumut, Perak. The depth is not expected to have huge impact on corrosion loss and microbiological effect is expected to be of importance.

Corrosion coupons of Type 3 Steel (mild steel) were fabricated from a Chinese fabricator (sample 1) and a Japanese fabricator (sample 2). The coupons were stamped for identification. At atmospheric and fully immersed zone, 3 inches strip coupons (73x22x3.8mm) were installed. At the tidal zone, 6 inches strip coupons (152mm x 22mm x 3.8mm ) were installed since the tide level is likely to fluctuate more than 3 inches. Table 5 shows the characteristics of seawater. The specimens were cleaned; polished and mounting holes were drilled. They were secured to mild steel frames using bolts and nuts, isolated from the mild steel racks with washers and thick rubber. The mild steel racks were installed on 30 March 2010 to reinforced concrete beam approximately 3.0 m below mean low tide so that the lowest test specimens were totally immersed (Figure 7A and 7B). The coupons are being evaluated quarterly for two years and simultaneously the sea water samples were taken to test for the salinity and pH. The coupons on retrieval are photographed and weighed together with the dense mat of fouling organisms which occurred on exposure of coupon. The coupons are then kept in the oven for 24 hours. The coupons are re-weighed and cleaned of any attached debris, deposits, and fouling organisms with sand paper. The coupons are visually inspected, and then photographed to show the surface conditions. Percentage weight reduction of the samples in different zones with time is evaluated. Weight loss method was used to determine the corrosion rates of the coupons. The corrosion loss of the coupon in mm with time in years is also estimated.

#### **RESULTS & DISCUSSION**

The following results of the field corrosion experiments are presented.

- (1) Parameters of the experiment including the characteristics of sea water
- (2) Physical condition of the frames and coupons
- (3) Percentage weight reduction, Corrosion loss (mm) with time and Corrosion rate (mm/year)

Parameters of the experiment:

The experiment is conducted in seawater at Lumut, Malaysia over a two year period. The characteristics of seawater are obtained by laboratory analysis (**Table 5**). The density of steel is taken as 7.86g/cc [32].



Table 5 Characteristics Of Seawater At Lumut

| Characteristic          | Minimum | Maximum |
|-------------------------|---------|---------|
| Surface temperature (C) | 27.4    | 33      |
| Salinity(ppt)           | 31      | 35      |
| pH                      | 8.2     | 7.8     |

Physical condition of the frames and coupons :

The surface condition of the samples was studied to understand the nature and intensity of corrosion. For the two sets of sample (sample 1 and 2), the observation was done for atmospheric zone, splash zone and immersion zone. **Figure 8** show the frames of sample 1 on retrieval from the testing area. At 3 months, the frame was covered mainly by barnacles and at 6 months, the coupons at tidal were densely covered by barnacles, plankton, algae, and bryozoans. At 9 months, the coverage of barnacles, plankton and algae is lesser compared to at 6 months. The nature of the surface of the coupons collected at 6 months did not seem to differ from the coupons collected at 3 months. At 12 months, bacteria like structures appeared attached to the surfaces of the tidal and submerged coupons. The bacteria were orange in color. It was difficult to differentiate amorphous inorganic deposits from bacteria. The coupons were covered by barnacles and algae at certain surface area. At 15 months and 18 months, the surfaces of the coupons were extensively removed, exposing thinner coupon. Thick fibrous materials were entrapped and attached to the coupons.



Figure 9 show the frames of sample 2 on retrieval from the testing area. At 6 months, the coupon was covered mainly by barnacles and plankton at tidal zone. At 12 months, bacteria like structures appeared attached to the surfaces of the tidal and submerged coupons. The bacteria were orange in color. At 15 months, dense

plankton, barnacles and algae covered the coupons at tidal and submerged zones of the frames. Identical condition occurred at 18 months. Some of the coupons exposed were covered with black deposits and some appeared to be in bluish/green deposits. However, the coupons were mostly dull.



Figure 10 shows the sample 1 at atmospheric zone which have been cleaned of the marine growth. At atmospheric zone, the coupons of mild steel 1 exposed were golden/brown. Other predominant features observed include rust-like deposits scattered throughout the coupon surface.

A lesser amount of deposits formed around the punched hole than on the surface exposed to the environment. The surfaces of the coupons showed that the corrosion pattern at atmospheric is essentially free from pitting and showed signs of uniform corrosion.



Figure 11 shows the coupons of sample 2 at atmospheric zone with identical observations as in sample 1.

**Figure 12** shows the sample 1 at splash zone which have been cleaned of the marine growth. At 3 months, the coupons showed signs of small

pits and with time more small pits formed. Large pits are observed at 9 months and 12 months. The thickness of the coupons reduced and rectangular shape was lost. At 18 months, coupons were mostly eaten up therefore the size of coupons were smaller compared to the original samples.



Figure 11 Cleaned coupons of sample 2 of Atmospheric zone at 6, 12, 15 and 18 months



Figure 13 show the coupons of sample 2 at splash zone. At 6 months, the formation of pit is lesser compared to coupons collected at 12 months. At 12 months, dark and golden brown

rust deposits were clearly visible on the pits. Overall the rate of corrosion is slower than in sample 1.



**Figure 1**4 show the sample 1 from immersed zone. The coupons at 3 months were still in rectangular shape, with small pits scattered on the surface. The coupons became thin and had small holes which became closer and deeper. At

9 months, the coupons were smaller indicating the start of severe corrosion. At 12 months, the coupons were badly corroded. The corrosion is very aggressive as indicated at 15 and 18 months. Nearly 70% of the coupons were gone.



**Figure 15** show the sample 2 from immersed zone. The samples show increasing trend of corrosion at 6 months and 12 months. The coupons become thin, deeper pits develop and shape changes. At 15 months, larger pits were developed. Few portions of the coupons were

lost. Other predominant features observed include rust like deposit mostly in the pits region. At 18 months, the coupons were thinner and smaller than the original size. Rust like deposits were observed in the pits region.



# Percentage weight reduction, Corrosion loss (mm) with time and Corrosion rate (mm/year)

Equation 1-6 shows how the values are calculated. **Table 6** and **Table 7** show the percentage weight reduction (column 8), thickness loss due to corrosion with time

(column 9) and corrosion rate for sample 1 and sample 2 respectively expressed in different units (column 10-13). The initial and final measurements of the corrosion coupons are given in column 2-6 and column 7 respectively, and time in column 1.

| $T_{11} (O_{1} 1) (C_{1} 1) (C_{1} 1)$ |                         |                          | · · · · · · · · · · · · · · · · · · · | 1.1   |
|--|-------------------------|--------------------------|---------------------------------------|-------|
| I apple by alciliation of perce        | entage weight reduction | Corrosion loss with time | e and corrosion rate for san          | nniei |
| Tuble o Calculation of pere            |                         |                          |                                       | IDICI |
|  | 0 0                     | ·                        |                                       |       |

| Time        |             | Initi | ial Measu     | rements       |                            | Final       | weig       | Metal  |        | Corrosi | on rate |         |
|-------------|-------------|-------|---------------|---------------|----------------------------|-------------|------------|--------|--------|---------|---------|---------|
| TIME        | wt          | thick | breadt<br>h   | length        | area                       | wt          | ht<br>loss | loss   |        | Corros  | on race |         |
| mths        | <b>(g</b> ) | (cm)  | ( <b>cm</b> ) | ( <b>cm</b> ) | ( <b>cm</b> <sup>2</sup> ) | <b>(g</b> ) | %          | mm     | mmpy   | mpy     | mdd     | g/m²/yr |
| 1           | 2           | 3     | 4             | 5             | 6                          | 7           | 8          | 9      | 10     | 11      | 12      | 13      |
|             |             |       |               | Atmosp        | heric zone                 |             |            |        |        |         |         |         |
| 3           | 31.67       | 0.284 | 2.446         | 6.736         | 38.156                     | 31.47       | 0.65       | 0.0069 | 0.0279 | 1.10    | 6.01    | 219.7   |
| 7           | 30.46       | 0.274 | 2.393         | 6.776         | 37.453                     | 30.31       | 0.47       | 0.0049 | 0.0099 | 0.39    | 2.14    | 78.0    |
| 9           | 31.63       | 0.285 | 2.455         | 6.800         | 38.674                     | 31.45       | 0.54       | 0.0057 | 0.0086 | 0.34    | 1.86    | 67.7    |
| 12          | 31.14       | 0.288 | 2.439         | 6.728         | 38.092                     | 30.97       | 0.55       | 0.0057 | 0.0057 | 0.22    | 1.22    | 44.6    |
| 15          | 31.63       | 0.282 | 2.469         | 8.507         | 48.185                     | 31.59       | 0.11       | 0.0010 | 0.0008 | 0.03    | 0.17    | 6.1     |
| 18          | 31.56       | 0.284 | 2.437         | 8.432         | 47.284                     | 31.32       | 0.76       | 0.0064 | 0.0043 | 0.17    | 0.94    | 34.2    |
| Splash zone |             |       |               |               |                            |             |            |        |        |         |         |         |
| 3           | 65.30       | 0.290 | 2.437         | 13.565        | 75.421                     | 61.63       | 5.61       | 0.0618 | 0.2503 | 9.86    | 53.9    | 1969.8  |
| 7           | 64.70       | 0.283 | 2.359         | 13.555        | 72.968                     | 56.40       | 12.82      | 0.1447 | 0.2930 | 11.54   | 63.2    | 2305.6  |
| 9           | 65.95       | 0.290 | 2.424         | 13.470        | 74.519                     | 45.14       | 31.55      | 0.3552 | 0.5397 | 21.25   | 116.3   | 4246.6  |
| 12          | 63.83       | 0.286 | 2.427         | 13.555        | 74.953                     | 48.45       | 24.10      | 0.2611 | 0.2608 | 10.27   | 56.2    | 2052.0  |
| 15          | 65.19       | 0.283 | 2.441         | 11.837        | 65.852                     | 42.20       | 35.28      | 0.4443 | 0.3600 | 14.17   | 77.6    | 2832.6  |
| 18          | 64.38       | 0.288 | 2.428         | 11.835        | 65.678                     | 12.62       | 80.40      | 1.0026 | 0.6769 | 26.65   | 145.9   | 5326.6  |
|             |             |       |               | Immer         | sion zone                  |             |            |        |        |         |         |         |
| 3           | 31.28       | 0.283 | 2.391         | 6.784         | 37.647                     | 26.04       | 16.75      | 0.1771 | 0.7173 | 28.24   | 154.6   | 5644.8  |
| 7           | 31.66       | 0.277 | 2.450         | 6.759         | 38.208                     | 26.61       | 15.93      | 0.1679 | 0.3401 | 13.39   | 73.3    | 2676.2  |
| 9           | 32.49       | 0.286 | 2.435         | 6.830         | 38.549                     | 20.25       | 37.68      | 0.4040 | 0.6138 | 24.17   | 132.3   | 4829.6  |
| 12          | 31.09       | 0.288 | 2.436         | 6.721         | 38.013                     | 15.95       | 48.69      | 0.5066 | 0.5060 | 19.92   | 109.1   | 3981.6  |
| 15          | 31.28       | 0.283 | 2.435         | 6.772         | 38.203                     | 13.03       | 58.35      | 0.6079 | 0.4925 | 19.39   | 106.2   | 3875.5  |
| 18          | 31.54       | 0.279 | 2.435         | 6.739         | 37.938                     | 12.69       | 59.76      | 0.6320 | 0.4267 | 16.80   | 92.0    | 3357.8  |

| Time             |        |       | initial |               |                            | Final   | weight | Metal  | Corrosion rate |       |           |         |
|------------------|--------|-------|---------|---------------|----------------------------|---------|--------|--------|----------------|-------|-----------|---------|
| mtha             | wt     | thick | breadth | length        | area                       | wt      | loss   | loss   |                | Corro | sion rate |         |
| muns             | (g)    | (cm)  | (cm)    | ( <b>cm</b> ) | ( <b>cm</b> <sup>2</sup> ) | (g)     | %      | mm     | mmpy           | mpy   | mdd       | g/m²/yr |
| 1                | 2      | 3     | 4       | 5             | 6                          | 7       | 8      | 9      | 10             | 11    | 12        | 13      |
| Atmospheric zone |        |       |         |               |                            |         |        |        |                |       |           |         |
| 6                | 50.24  | 0.435 | 2.286   | 7.418         | 42.348                     | 50.05   | 0.39   | 0.0059 | 0.0120         | 0.47  | 2.59      | 94.6    |
| 9                | 49.81  | 0.436 | 2.319   | 7.271         | 42.086                     | 49.7    | 0.22   | 0.0033 | 0.0044         | 0.17  | 0.95      | 34.5    |
| 15               | 50.48  | 0.442 | 2.319   | 7.271         | 42.205                     | 50.44   | 0.08   | 0.0013 | 0.0010         | 0.04  | 0.22      | 8.2     |
| 18               | 49.86  | 0.436 | 2.325   | 7.377         | 42.760                     | 49.79   | 0.15   | 0.0022 | 0.0015         | 0.06  | 0.31      | 11.5    |
| Splash zone      |        |       |         |               |                            |         |        |        |                |       |           |         |
| 6                | 106.74 | 0.435 | 2.243   | 11.08         | 61.291                     | 99.69   | 6.61   | 0.1464 | 0.2964         | 11.67 | 63.91     | 2332.7  |
| 9                | 106.45 | 0.438 | 2.325   | 15.400        | 87.139                     | 85.1    | 20.06  | 0.3118 | 0.4210         | 16.57 | 90.76     | 3312.6  |
| 15               | 107.15 | 0.477 | 2.325   | 15.400        | 88.530                     | 82.92   | 22.61  | 0.3482 | 0.2821         | 11.11 | 60.81     | 2219.7  |
| 18               | 106.61 | 0.437 | 2.325   | 15.400        | 87.099                     | 76.95   | 27.82  | 0.4331 | 0.2924         | 11.51 | 63.05     | 2301.2  |
|                  |        |       |         |               | Im                         | mersion | zone   |        |                |       |           |         |
| 6                | 49.78  | 0.433 | 2.233   | 7.283         | 40.752                     | 42.1    | 15.42  | 0.2397 | 0.4855         | 19.12 | 104.67    | 3820.3  |
| 9                | 50.45  | 0.434 | 2.321   | 7.387         | 42.712                     | 33.18   | 34.24  | 0.5146 | 0.6948         | 27.36 | 149.80    | 5467.7  |
| 15               | 49.91  | 0.436 | 2.321   | 7.387         | 42.760                     | 29.19   | 41.52  | 0.6166 | 0.4995         | 19.67 | 107.69    | 3930.8  |
| 18               | 50.12  | 0.434 | 2.324   | 7.387         | 42.762                     | 25.39   | 49.35  | 0.7359 | 0.4968         | 19.56 | 107.11    | 3909.6  |

Table 7 Calculation of percentage weight reduction, corrosion loss with time and corrosion rate for sample 2

#### **Percentage weight loss**

Figure 16 shows the percentage weight loss at different zones with time. The graph indicates that over the period of observation the weight loss is negligible for atmospheric zone and that the corrosion in the immersion zone is more than in the splash zone. The presence of black deposits (Figure 9) and pitting corrosion is typical of corrosion due to Sulphate Reducing Bacteria (SRB) which is predominant at the immersion zone.

#### **Corrosion loss (mm)**

The profile for corrosion losses (mm) of sample 1 and sample 2 for 18 months of exposure in the seawater is shown in **Figure 17**. The corrosion loss for the immersion zone is higher than that for the splash zone for both samples. For sample 1, the splash zone shows an increase towards the second year over the immersion zone. For atmospheric zone, the corrosion losses are very small compared to the other two zones.



Figure 16 Percentage weight loss at 6, 15 and 18 months for sample 1(left) and sample 2 (right)



Figure 17 Corrosion loss (mm) for sample 1 (left) and sample 2 (right)

#### **Corrosion rate (mm/year)**

#### Atmospheric zone:

At the atmospheric zone, the surface of mild steel experiences uniform corrosion. For sample 1, the maximum corrosion rate was 0.0279 mm/side/year and for sample 2 it was 0.012mm/side/year. This is lesser than the upper limit of 0.10 recommended by BS 6349-1-2000[31] for temperate climate (**Table 4**). Comparing with Table 2, the corrosion rate is less than the values for wet tropical region (0.08 - 0.70 mm/year) [27]. The values of corrosion rate in mils per year (mpy) in column 11 of Table 6 and Table 7 can be compared with the values in ISO (1998), where the range of 3 - 8mpy is classified as "high corrosion category". The mass loss  $(g/m^2/year)$  in column 13 can be checked with the classification in EN 12500[30]. The atmospheric corrosion falls under "low category"  $(10 - 200 \text{ g/m}^2/\text{year})$ .

Splash and immersion zones:

During the exposure period, fouling was mainly caused by algae and barnacles. Figure 18 (left) shows that for sample 1 corrosion rates ranged from 0.4 to 0.7 mm/year at the immersion zone. Figure 18 (right) shows that for sample 2 the corrosion rates ranged from 0.5 to 0.7 mm/ year at the immersion zone during the study period of 18 months. These are higher than the upper limits in BS 6349-1-2000[31] for immersion zone in temperate climates (0.13 mm/side/year) which is to be expected for a tropical zone. Figure 18 (left) for sample 1 show the distinctive change in corrosion behaviour at the theoretical time, ta as marked in Figure 2. In this case ta is around 6 months exposure for both immersion and tidal zones. This is shown much later for sample 2 in Figure 18(right) for both immersion and tidal zones for which t<sub>a</sub> is estimated at around 15 to 18 months. The parameter C<sub>a</sub> is around 0.422 mm/ year. This is slightly greater than the corresponding value for tidal corrosion 0.346 mm/ year for sample 1.



Figure 18 Corrosion rate (mm/year) for sample 1 (left) and sample 2 (right)

In Figure 18 (left), the corrosion rate increases a little during the first 3 months for both tidal and fully immersed zone due to moderate dissolved oxygen levels and salinity (35ppt) of the water. As corrosion continues, the corrosion products (rust) form on the corroding surface and the rate of oxygen diffusion through it will control the corrosion rate. The corrosion rate declines slightly from 3 to 6 months implying the protective nature of corrosion products and biomass during exposure. A dense coverage is created by organisms over the substrate which reduces the diffusion of oxygen, thus reducing corrosion rate. The decrease in the cumulative corrosion rate is attributed to the biofouling acting as a barrier between metal and the seawater, thereby reducing the oxygen diffusion to the metal surface [25]. As the dense coverage is built up, it becomes increasingly difficult for oxygen to reach the corroding surface. This allows the development of anaerobic conditions [18]. This provides conditions under which sulphate- reducing bacteria (SRB) can flourish under the right nutrient conditions. SRB attacked the coupons through their waste products, principally H<sub>2</sub>S producing FeS in the process [18]. As a result, the rate of corrosion now depends on the rate of metabolism which in turn depends on the rate of supply of nutrient [18]. This constitutes phase 3(shown in **figure 2**). The photographs of the coupons at immersion zone clearly show that they were badly attacked by SRB.

Figure 18(right) shows the corrosion rate increasing linearly upto 9 months of exposure. The coupons on exposure at the sea, is invaded by a complex mix of bacteria and nutrients. The corrosion process takes a little time to become fully established and the rate of corrosion is controlled by the rate of arrival of oxygen at the corroding surface [18]. Then there is a thin build up of corrosion products on the corroding surface as corrosion continues. Oxidation takes place therefore the corrosion rate increases [16]. Figure 18b show that ta is approximately 15 to 18 months and C<sub>a</sub> is around 5.7mm/year. Evidently, t<sub>a</sub> indicates that it takes more time to establish corrosion conditions similar to sample 1. Sample 1 only took 6 months for phase 3 to commence. This relationship does not appear to exist for sample 2. There may also be other influences involved such as the surface rust being more permeable for sample 2.

# **Comparison of corrosion rates**

**Table 8** shows the comparison of the minimum and maximum corrosion rate in mm per year for the different zones obtained from the study with values recommended in BS 6349-1-2000[31] provided in **Table 4** and those reported by [27] in **table 2**.

| Zones       |     | Experimental Co | prrosion rate | Comparison with                 |               |  |  |  |
|-------------|-----|-----------------|---------------|---------------------------------|---------------|--|--|--|
|             |     | Sample 1        | Sample 2      | BS 6349-1[31]<br>(from Table 4) | Table 2[27]   |  |  |  |
| Atmospheric | Min | 0.0008          | 0.0010        | low                             | low           |  |  |  |
|             | Max | 0.0279          | 0.012         |                                 |               |  |  |  |
| Splash      | Min | 0.2503          | 0.2821        | higher                          | Rates compare |  |  |  |
|             | Max | 0.6769          | 0.4210        |                                 | with sub      |  |  |  |
| Immersion   | Min | 0.3401          | 0.4855        | higher                          | tropical and  |  |  |  |
|             | Max | 0.7173          | 0.6948        |                                 | wet tropical  |  |  |  |

Table 8 Comparison of corrosion rates (mmpy)

**Table 9** compares the corrosion rate in mils peryear (mpy) for the different zones with valuesrecommended in Table 1.

Table 10 shows the corrosion rate in mass loss per year  $(g/m^2/year)$  for the different zones compared with values recommended in Table 3 by EN12500.

| Zones       | Ex  | perimental Cor | rosion rate | Comparison with |
|-------------|-----|----------------|-------------|-----------------|
|             |     | Sample 1       | Sample 2    | Table 1         |
| Atmospheric | Min | 0.03           | 0.04        | Low             |
|             | Max | 1.10           | 0.47        |                 |
| Splash      | Min | 9.86           | 11.11       | Very severe     |
|             | Max | 26.65          | 16.57       |                 |
| Immersion   | Min | 13.39          | 28.24       | Very severe     |
|             | Max | 19.12          | 27.36       |                 |

Table 9 Comparison of corrosion rates (mpy)

| Table | 10 | Com | parison | of | corrosion | rates | $(g/m^2/year)$ |
|-------|----|-----|---------|----|-----------|-------|----------------|
|-------|----|-----|---------|----|-----------|-------|----------------|

| Zones       | Experimental Corrosion rate |          |          | Comparison    |
|-------------|-----------------------------|----------|----------|---------------|
|             |                             | Sample 1 | Sample 2 | with Table    |
|             |                             |          |          | 3[30]         |
| Atmospheric | Min                         | 6.1      | 8.2      | Low to Medium |
|             | Max                         | 219.7    | 94.6     |               |
| Splash      | Min                         | 1969.8   | 2219.7   | Very high     |
| _           | Max                         | 5326.6   | 3312.6   |               |
| Immersion   | Min                         | 2676.2   | 3820.3   | Very high     |
|             | Max                         | 5467.7   |          |               |

# CONCLUSION

The physical conditions of the coupons were studied over a period of two years. The coupons at the atmospheric zone were free from pitting and showed uniform corrosion, which was mild in nature. The coupons at the splash zone showed pitting corrosion which increased with time. The thickness of the coupons was reduced and often the shape was modified. The coupons at the immersed zone also showed pitting corrosion, more severe than at the splash zone. The shapes too were lost. The immersion corrosion was more severe than in the splash zone. The weight loss studies confirmed the findings of the visual observations. Figure 18 shows trends that are consistent with the model shown in Figure 2 for marine immersion corrosion. It is seen corrosion is oxygen diffusion controlled and then by microbiological action. The controlling process changes with time and the bacterial action and the supply of nutrient governed the oxygen diffusion. The process of marine immersion corrosion is complex and non-linear. The experimental values also show that corrosion rate in immersion zone is higher than that in the splash zone which is contrary to expectations. The causative factor for this is the SRB corrosion which is verified by the presence of black deposits and pitting corrosion. The corrosion rates were compared with code and other published values. **Table 8** shows that the corrosion rates at the atmospheric zone were low compared to BS 6349 and Tidblad et al (2000). The rates for immersion and splash zone are higher. **Table 9** shows that the corrosion values observed are low for atmospheric zone whereas they are very severe for splash and immersion zones. The corrosion rates are comparable to those given for sub- tropic and wet tropical zone. On comparison with EN 12500 values **in table 10**, the experimental values indicate that the atmospheric zone falls in low to medium class; the splash and immersion zone falls in very high corrosion class.

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