REVISTAMATĒRIA

V.27 N.02

ISSN 1517-7076 articles e13166, 2022

Corrosion of Carbon Steel in Mauritian water bodies

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ABSTRACT

Carbon steel is a commonly used metal in water applications in Mauritius. However, the corrosion resistance of steels and effectiveness of corrosion prevention methods in Mauritian water bodies are unknown. This study is performed to investigate the corrosion behavior of S235 carbon steel in the local tropical waters using various corrosion monitoring techniques. Specimens of the metal are subjected to a simple laboratory immersion test under ambient conditions according to ASTM G31. The coupons are immersed in three distinctively different waters. Upon removal after specific time intervals over a 3-month period, the mass loss, thickness loss and surface roughness are duly evaluated. Mass loss and thickness loss variation with time of immersion are obtained in the form of the power law function. Regarding the surface roughness parameters measured, it is observed that they change logarithmically with corrosion loss due to increasing thickness of the rust layer. A general deterministic model in terms of Rp and Rq is successfully stemmed using Genetic Programming to forecast the corrosion rate.

Keywords: Carbon steel; Marine Corrosion; Weight loss; Surface Roughness; Genetic Programming.

1. INTRODUCTION

Corrosion has deleterious effects on metal structures in contact with water bodies, such as ships, submerged pipelines, and steel pilings amongst others. The unchecked effects of this type of corrosion can come swiftly, leading to severe and costly consequences of failure [1]. Effects of marine concentrated corrosion is causing major difficulties in protection of steel piles in various ports [2, 3]. Another major concern regarding marine corrosion phenomena is the degradation of metallic components in marine devices used to capture renewable energy in the form of offshore wind and ocean wave energies [4]. In fact, it is estimated that the total cost of marine corrosion worldwide is between USD 50 - 80 billion every year [5]. Marine corrosion studies have been carried out extensively along the African coast, in the Mediterranean and in Bermuda, situated in the North Atlantic Ocean [6, 7]. However, any research on marine corrosion for tropical regions, especially near the Tropic of Capricorn, is scarce.

Mauritius is a small island in the Indian Ocean, having 1865 km^2 land area, with 330 km of coastline. The climatic conditions are characteristic of a typical tropical island. Previous research on corrosion in Mauritius has been primarily focused on atmospheric corrosion and little or almost no attempt has been made to investigate how steel corrodes in the local seawater and river water. In fact, this is not to be ignored given that the island is gearing towards another economic sector – the Ocean Economy. The expansion of the port, which is turning into a regional maritime hub, is one amongst the myriad of examples. Such projects require sound use of metals, especially steel.

Relying on data from other countries may lead to overdesign or even under-design of steel structures, due to improper allowances being applied, leading to serious failures. Mauritius, with its tropical climate, may prove to exacerbate the marine corrosion problem. Additionally, it has been identified that Proteobacteria are the predominant bacterial microorganisms found in the Mauritian seawater [8]. All seawater environments have unique characteristics based on several parameters specific to the properties of the water [9]. The latter can vary in terms of its chemical composition, oxygen content, temperature, salinity, pH and biological activity. Bhandari et al. [10] reported that the pH of seawater or fresh water is due to the carbon dioxide equilibrium with the atmosphere and the presence of ions such as hydrocarbonates,

Corresponding Author: Yashwantraj Seechurn Received on: 22/02/2020 Accepted on: 14/02/2022

10.1590/S1517-707620220002.1366

carbonates and undissolved carbonic acid. All these parameters have an impact on the corrosion rate and corrosion mechanism. Hence, corrosion behaviour of steel varies significantly based on location and given that steel is heavily used in water applications in Mauritius, an understanding of its corrosion behaviour in the Mauritian water bodies is imperative.

Although there is no formal categorization of the Mauritian coast, the adjoining sea zones can be broadly classified, based on the inherent activities, as marine-touristic, marine-fishing/agricultural and marine-industrial. Development of new industrial zones around the capital, Port Louis, and the mushrooming of hotels along the coastline, have increased the risk of water contamination [11-13]. Given that metal traces such as chromium, nickel, copper, zinc, cadmium, lead have been identified in the industrial zone catchment area, and nitrates and phosphates in the touristic/agricultural zone, their consequent impact on corrosion rate is not to be ignored.

During the initial phase of seawater corrosion, immediately after the metal is first exposed, its surface is populated by bacterial colonies, forming a biofilm in which anaerobic niches may form. This leads to the formation of γ – FeOOH, which is a thin, flaky and poorly adherent rust layer [14]. As the time of immersion progresses, a thicker layer, Fe_3O_4 starts to develop. This consequently reduces the rate of oxygen diffusion from the water to the metal interface in a second stage of the corrosion process. The combination of these two stages leads to an almost linear model. However, owing to reduced oxygen diffusion to the inner cathodic sites in the Fe matrix, a reduced corrosion rate is eventually expected. The power function (Equation 1), also known as the bi-logarithmic law, is widely used to predict the corrosion behavior in various metallic materials even after long exposure times [15].

$$P = At^n \tag{1}$$

Where P is the mass loss, t is the time of exposure, A and n are constants

The value of n does not majorly affect first year corrosion but rather corrosion in successive years where its contribution becomes increasingly essential. In fact, the value of n serves as a diagnostic tool to indicate the nature of the relationship: linear (n = 1 or approaching 1), parabolic (n = 0.5), cubic (n = 0.33) and so on. As a rule, n should always be less than 1. Values of n > 1 occur practically as exceptions, due to outliers in weight loss determination [15]. Equation 1 is a mass-balance equation demonstrating that the diffusion process is rate determining, and this rate varies according to the diffusive properties of the layer separating the reactants [16].

The characteristics of the corrosion products on the surface of the metal would also have a direct effect on the surface roughness of the metal. Surface topography offers vital information on the corrosion behavior of materials in corrosive environments and can be explained by a myriad of parameters such as the amplitude, motif, spacing and hybrid parameters. The amplitude parameters such as Ra (arithmetic average height), Rq (root mean square roughness), Rz (ten-point height) and Rv (maximum depth of valleys), are commonly used to gauge the extent of corrosion as a function of surface roughness [17]. Analysis of the surface roughness of the corroded metal would consequently enable the quantification of corrosion rate. Very few studies have been conducted where the surface roughness parameters are utilized as a tool to assess the corrosion rate.

To model the amount of corrosion through variation in surface roughness, symbolic regression could be used. The latter is a type of regression analysis that utilizes Evolutionary Algorithm to explore mathematical expressions to find the model that best fits a given data set, both in terms of accuracy and simplicity [18]. The process to solve complex problems by symbolic regression was developed by Koza [19], who used Genetic Algorithm in so-called Genetic Programming. The latter has been meekly used in corrosion studies. A notable study is that of Marref et al. [20], in which a preliminary universal atmospheric corrosion model for steel was developed in MATLAB and later refined using the Eureqa Artificial Intelligence software. Such a corrosivity model can enormously facilitate the task of selecting material, protections systems and maintenance intervals.

In this study, a simple immersion test was used, which provide the finest, quickest and most cost-effective method of screening, for providing accurate results which mimics natural surroundings. To forecast the corrosion rate values for carbon steel structures submerged in any type of water body in Mauritius, the changing surface roughness of the base metal was also studied.

2. MATERIALS AND METHODS

Seawater and river water were sampled throughout Mauritius. Then based on the requirements of ISO 11130 [21], three distinctively different locations (Figure 1) were chosen, which are described below.

- Mont Choisy: Pure marine seawater with pH 8.42, salinity of 37 ppt and temperature of 25.1℃;
- Port Louis: Marine-industrial seawater with pH 8.19, salinity of 41 ppt and temperature of 25.1℃;
- Vacoas: Rivière du Rempart river, from an agricultural and industrial region, with pH 7.22, salinity of 1.5 ppt and temperature of 25.4℃.

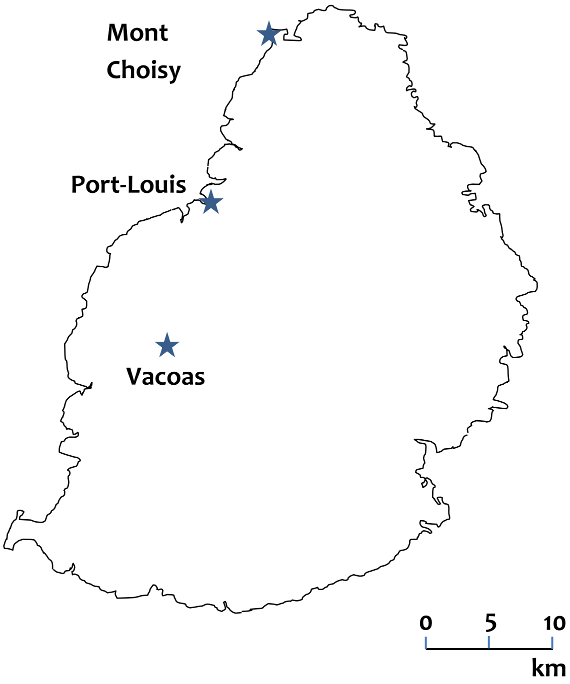

Figure 1: Map of Mauritius showing the Seawater and River water sites.

S235 carbon structural steel plates, with composition shown in Table 1, were prepared according to ASTM G1-03, ISO 8407, ASM Metals Handbooks and a methodology established by the National Institute of Chemistry of New Zealand [22-25]. The coupons of size 90 x 40 x 1.8 mm were all sheared from the same carbon steel sheet. The metal specimens were first cleaned with 10% w/v of sodium hydroxide for five minutes to remove all inorganic and hydrophilic substances from the surface. The deposits were then loosened through rinsing with distilled water before the metals were acid pickled for 60 minutes in 10% w/v of hydrochloric acid. After rinsing the metals again in distilled water, the coupons were re-passivated in 10% w/v sodium hydroxide. Finally, the metal coupons were hot-air dried.

Table 1: Composition of carbon steel exposed.

ELEMENTS	C	Mn	P	S	Si	Ni	Cu	Fe
WT-%	0.26	0.75	0.04	0.05	0.004	0.012	0.55	98.3

By placing the metal coupons on a custom-made wooden mount, one side of the metal was wet-polished manually and progressively using Silicon Carbide paper of grit sizes 320, 600, 800, 1200, 1500 and 2000. The metal coupons were then fine polished using diamond paste of 6 and 1 microns respectively, until a mirror finish was obtained. After degreasing using acetone, the metals were stored in a desiccator prior to immersion.

A Simple Immersion Open Beaker test, as per ISO 11130, ASTM G31-72 and the works of Chuka et al. [21, 26, 27], was devised as the coupons were fully immersed in triplicate batches in the waters from Mont Choisy, Port Louis and Vacoas for a duration of almost three months. Chemically inert High Density Polyethylene containers, having adequate water to satisfy the “solution to specimen area ratio”, were used.

The water was refreshed every 168 hours, and each successive set of specimens were removed after consecutive 15, 30, 45, 55 and 83 days of exposure. All the containers were set up in a room at ambient temperature, with no forced ventilation.

After each removal, the coupons were cleaned according to ASTM G1-03 [22]. The bulky corrosion products were scraped off using a soft bristle brush around which lint-free cloth was tightly wrapped. The coupons were then placed in a solution of hydrochloric acid (sp 1.19) and hexamethylenetetramine for 15 to 25 mins. Post cleaning, the specimens were cooled air dried prior to application of the various corrosion assessment techniques. The specimens were weighed to three decimal places. A blank correction was equally accounted for, and the corrosion rate and thickness loss were calculated using Equations 2 and 3.

$$C_R = \frac{k * \Delta W}{A * t * \rho} \tag{2}$$

$$\text{Thickness Loss (in µm)} = \frac{\Delta W}{A * \rho} \text{ x } 1000 \tag{3}$$

Where, C_R is the Corrosion rate in mm yr^{-1}, k is 8.76 x 10^4 (constant), ΔW is the weight loss in grams, A is the exposed surface area in mm^2, t is the time of exposure in years (yr) and ρ is the density in g mm^{-3}.

Post surface preparation of the metal coupons and prior to immersion, measurements of specific surface roughness parameters (Ra, Rq, Rp and Rv) were taken over 1 mm interval, covering the entire metal surface. The Taylor Hobson Talysurf instrument, set in the positive X direction for a Run-Up length of 0.3 mm at a measurement speed of 0.5 mm/s, was used for this purpose. The same procedure was carried out after each removal over the 83-day period.

Results from the mass loss technique and the surface roughness data were then Genetically programmed on the Eureqa Pro beta version .84 Artificial Intelligence software to obtain a general corrosion model, in simple parameters for the Mauritian water bodies. It incorporates the advanced island model for parallelization and the Age-Fitness Pareto for selection as improvements to Genetic programming. The island genetic algorithm model prevents premature convergence towards an equation.

3. RESULTS

3.1 Visual appearance of corroded specimens

The color of the corrosion products formed on the surface of the plates immersed in the two different types of seawater were both red brown (Figures 2 and 3). This is a characteristic of iron (III) compounds. Upon scraping off the bulky layer, grey and black patches covered the metal surface, consequently inferring the existence of Sulphur Reducing Bacteria (SRB) in the seawater. Regarding the specimens submerged in the river water, they differed from the aforementioned plates in terms of the color of their rust layer, which was brownish orange with no grey-black blotches (Figure 4). However, absence of dark patches doesn’t necessarily imply a shallow concentration of SRB microorganisms, since occurrence of SRBs also depends on very specific conditions such as the depth of the collected water, which may affect the content of inorganic/organic compounds capable of destabilizing their metabolism, presence of other microorganisms, etc.

Figure 2: Polished side of metal coupons immersed in Mont Choisy seawater (1st Removal to 5th Removal from left to right).

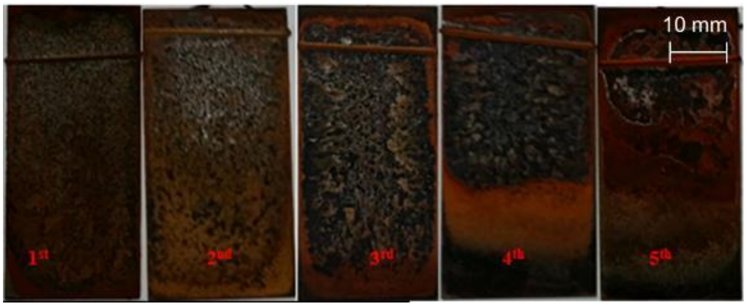

Figure 3: Polished side of metal coupons immersed in Port-Louis seawater (1st Removal to 5th Removal from left to right).

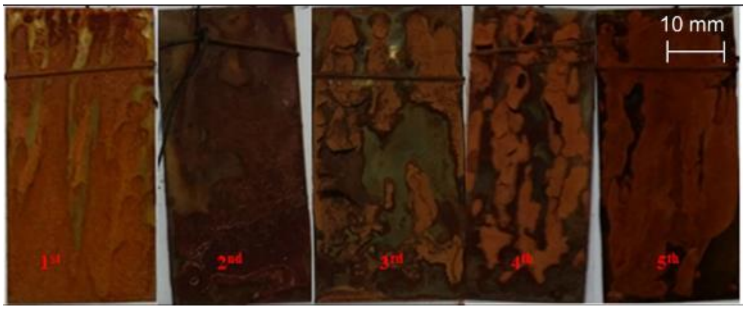

Figure 4: Polished side of metal coupons immersed in Vacoas River water (1st Removal to 5th Removal from left to right).

3.2 Mass-Loss Analysis

The Mass Loss Technique is the best known and most straightforward of all uniform corrosion-monitoring techniques, whereby the substantial loss of material, due to corrosion or erosion, is measured by physical means. Upon application of Equations 2 and 3, the graphs shown in Figures 5, 6 and 7 were obtained, with more than 80% of the total variation in the values successfully explained. The graphs in Figures 5 and 6 fitted the power law, with mass loss and thickness loss increasing as time progresses. Based on the power law equations, a decreasing corrosion rate is expected, as shown in Figure 7. The mass loss, thickness loss and corrosion rate therefore rank in the following order (from highest to lowest): Vacoas, Port Louis and Mont Choisy.

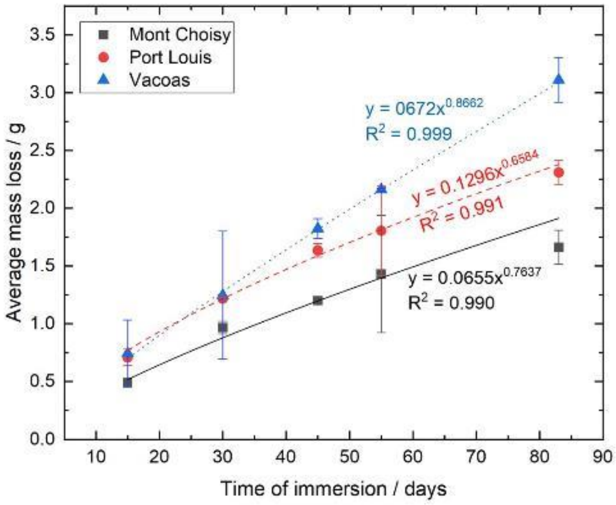

Figure 5: Graph representing the average mass loss in grams of the immersed coupons over an 83-day period for the three selected locations.

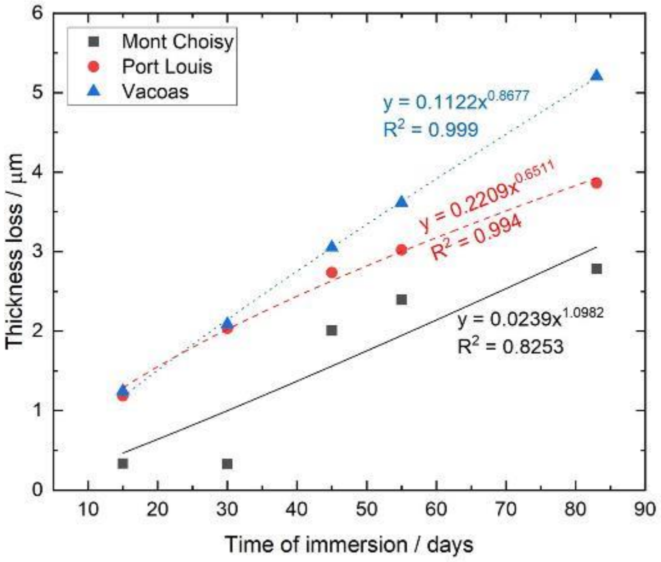

Figure 6: Graph representing thickness loss in μm of the immersed coupons over an 83-day period for the three selected locations.

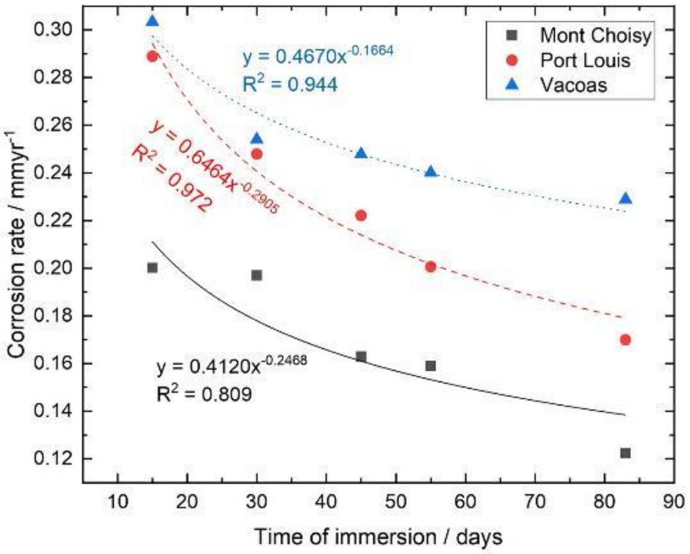

Figure 7: Graph representing corrosion rate in mm/yr. of the immersed against over an 83-day period for the three selected locations.

3.3 Variation of Surface Roughness with Corrosion loss (Thickness loss)

Both Ra and Rq vary logarithmically with corrosion loss, as confirmed by the high R^2 values in Figures 8 and 9. This implies that during the initial weeks of immersion, there is a rapid increase in the surface roughness, followed by slow growth, which can be explained in terms of the thickness and porosity of the corrosion products formed on the metal surface. During the early weeks of removal, the rust layer was still thin, inferring that it could not protect the base metal from the immediate damaging effect of oxygen diffusion. As the metal corroded, the irregularities on the surface became deeper, most probably due to the continuous process, which proceeded down the pores in the rust layer, but at a much-reduced rate.

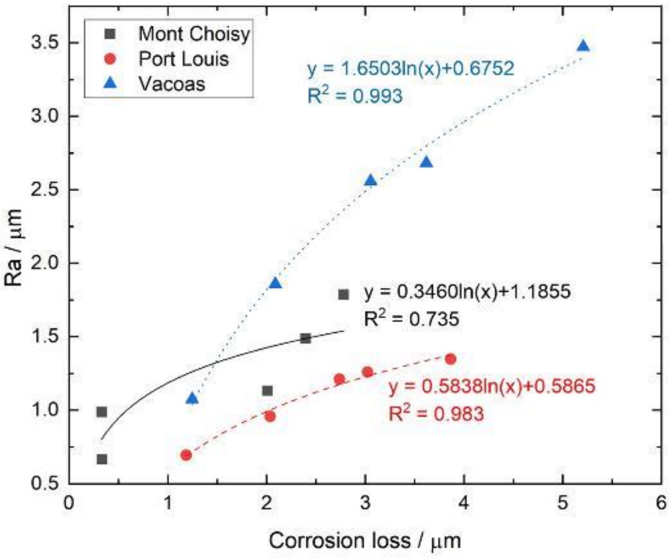

Figure 8: Graph of Ra vs. Corrosion loss, representing change in surface topography, with Ra measured at 10 mm intervals along the length and breadth of the metal coupon.

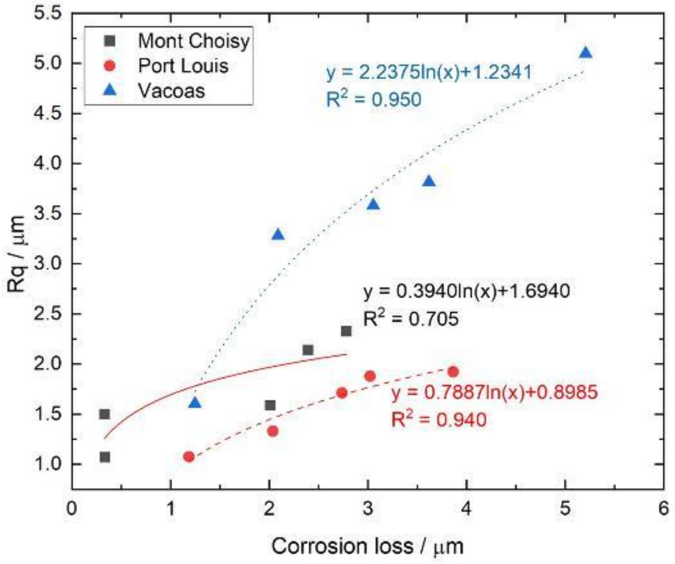

Figure 9: Graph of Rq vs. Corrosion loss, representing change in surface topography, with Rq measured at 10 mm intervals along the length and breadth of the metal coupon.

As the time of immersion progresses, the surface becomes bumpier. Upon comparing the individual logarithmic equations for Rp and Rv (Figure 10 and Figure 11), it was found that for the seawater sites (Mont Choisy and Port Louis), the equations for Rv have significantly higher constants than the equations involving Rp. This implies that more valleys than peaks are being formed.

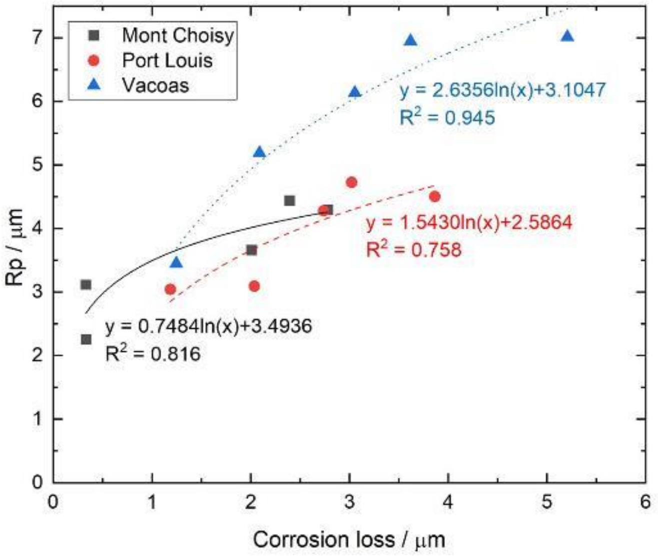

Figure 10: Graph of Rp vs. Corrosion loss, representing change in surface topography, with Rp measured at 10 mm intervals along the length and breadth of the metal coupon.

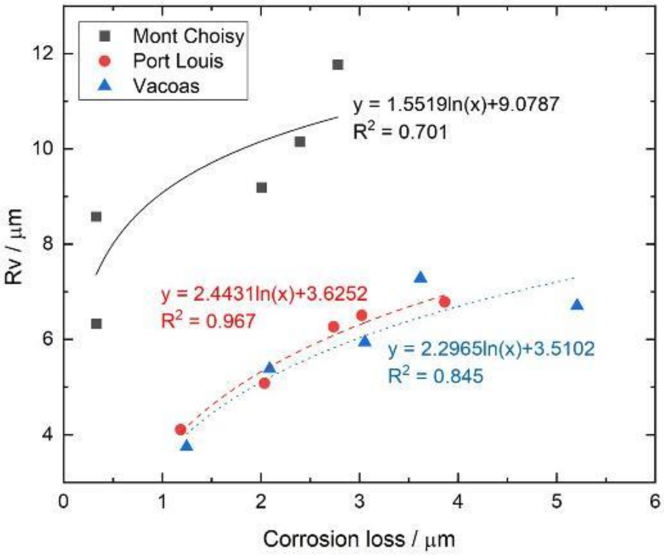

Figure 11: Graph of Rv vs. Corrosion loss, representing change in surface topography, with Rv measured at 10 mm intervals along the length and breadth of the metal coupon.

3.4 Genetic Programming and Corrosion Model

Since Ra is less sensitive to peaks and valleys, the input consisted only of Rp, Rv and Rq and the unsmoothed/unfiltered mass loss data. The target expression for a global model with the desired formula building blocks was also entered. The search for the most appropriate formula was conducted for 3 hours 30 minutes until 100% confidence convergence and 97.8% stability were achieved. In total, 470 billion formulae were evaluated against a progress plot. The best possible solutions are determined by two factors: their complexity (size) and their accuracy (fit) on the validation data. A Pareto chart listed 13 solutions as they were ranked by accuracy and complexity. Three solutions were preliminary chosen where the right balance between complexity and accuracy was observed. The 'Evaluate and Predict' command tool was used to determine the results of mass loss using the available surface roughness parameters. The final regression and Goodness of fit revealed Equation 4 as the most suitable model, which was later replaced in the traditional corrosion rate equation (Equation 5). Rv was not used since the Artificial Intelligence software inferred significant multicollinearity between Rv and another variable.

$$\text{Mass Loss} = 1.42\sin(\mathrm{R}_q) + 0.158\mathrm{R}_p\mathrm{R}_q - 1.13 \tag{4}$$

$$C_R = \frac{k*[1.42\sin(R_q)+0.158R_pR_q-1.13]}{A*T*\rho} \quad (5)$$

4. DISCUSSION

A low salinity of 1.5 ppt could explain why the metal coupons immersed in the river water from Vacoas were being consumed the most readily. Phull and Abdullahi [28] reported that DO content follows an inverse relationship with salinity. A low salinity implies a high concentration of DO, which has a good correlation with corrosion rate [27]. Hence, despite the waters of Port Louis and Mont Choisy being more concentrated in chloride ions (Cl^-), the mass loss and corrosion rate were lower because of their inferior DO content in comparison to the river water. It should be noted that factors such as pH, presence of other electro active species, the material of the electrode, etc. are also used to evaluate the corrosivity of a certain medium. In this study of carbon steel, DO is the key factor. Moreover, the river water could be having a low Methyl Orange (MO) alkalinity than usual, which infers towards a shallow concentration of carbonate ions in the water. This could have inhibited the formation of a protective passivating calcium carbonate layer, subsequently fostering the build-up of corrosion products. The river water was sourced from an industrial-agrarian region, which indicate the presence of corrosion enhancing ions especially nitrates from agricultural leach off [29]. Nitrate ions are thermodynamically strong oxidizers and have been documented to augment uniform corrosion rate [30].

Unusually, the coupons immersed in the Port Louis seawater, which has a higher salinity and lower DO content, recorded the second highest corrosion loss instead of those submerged in the Mont Choisy seawater. This phenomenon could be explained by the presence of suspect ions in the Port Louis water. The seawater sample was collected at 25 m from the harbor, which is also the discharge point of a canal containing polluted water from all the neighboring regions. In contrast, sample of the Mont-Choisy seawater was taken only a few meters from a sandy shore very far from pollution sources. Consequently, presence of ions such as nitrates, bromides, or iodides in sufficiently high concentration in the Port-Louis water could have increased the electron mobility and thus the rate of rusting of the metal plates immersed in the Port Louis seawater.

A hypothesis set to find out whether the corrosion rate values of the coupons from the three sites correspond to the known values of 0.17-1.06 mm/year for seawater, and 1.00 mm/year for freshwater [31-33], proved that all lie within the accepted range at a P-value of less than 0.05 for a confidence interval of 95%. Furthermore, a two-tail two sample t-test at 95% confidence interval was used to compare the corrosion rate values of the three sites. Statistical significance was obtained for the corrosion rate values between Mont Choisy and Port Louis, and Mont Choisy and Vacoas. However, there was no statistical significance between the values for coupons immersed in Port-Louis seawater and Vacoas river water. This could be attributed to the regions from where the water was collected. The Port Louis seawater is replete with effluents from the adjoining regions. The same could be said about Rivière du Rempart river with numerous rivulets containing effluents and industrial wastes flowing through numerous residential and industrial regions. Hence, similar ions from the various industrial wastes could be present in the seawater and river water, contributing towards their almost similar corrosion rate.

The Ra and Rq values are highest for the coupons immersed in the river water. The elevated concentration of DO content in the freshwater caused the immersed specimens to be corroded (and thus roughened) the most, tailed by those dunked in the Mont Choisy seawater and eventually those in the Port Louis seawater. Given that Ra is the arithmetic mean deviation of the assessed profile, this implies that the coupons submerged in the Mont Choisy seawater had more prominent peaks or valleys than those from Port Louis. As corrosion progresses, the surface becomes rougher with time of immersion and upon comparing the individual logarithmic equations for Rp and Rv (Figures 10 and 11), it was found that Mont Choisy seawater produced the deepest valleys, followed by that from Port Louis and eventually that from Vacoas. Carbon steel is also subjected to pitting corrosion when immersed in seawater and this occurs instantly due to the absence of a passive film. The valleys could be associated to pits, which grow significantly deeper with higher pH level [29, 30, 34]. The latter causes oxygen to be adsorbed more readily at the anodic sites of the steel, subsequently enhancing pit development [29]. Any pit formation on the plates immersed in the Vacoas water would therefore be less prominent due to its low pH. Additionally, both the seawaters have significantly higher chloride concentration than the river water, which further compounds pitting formation and propagation. The Fe^{2+} matrix attracts Cl^- ions present in the water causing the corrosion attack to proceed through the available pores in the rust layer, thereby producing pits of increasing depth. However, the subsequent slow increase in the various Rp and Rv values could be justified in terms of the slow pit growth owing to the "competition" for cathode space within the Fe^{2+} matrix.

Eventually, Equation 5 was experimentally validated by immersing S235 carbon steel plates of the same dimensions in seawater collected from another region (Pointe aux Biches). Water from this region is characteristic of the typical seawater surrounding Mauritius and is known to have pH 8.14 and a salinity of 33.9 ppt [8]. The maximum difference between mass loss obtained from the model and the measured mass loss was 3.6% with a standard deviation of 0.5810. This reinforces the validity of Equation 5 as a general model to predict corrosion rate of carbon steel in all Mauritian water bodies.

5. CONCLUSIONS

Uniform corrosion was observed on all carbon steel specimens subjected to a three-month simple immersion test in water sampled from three different sites in Mauritius (Mont-Choisy and Port-Louis seawaters and Vacoas river water). The mass loss and thickness loss graphs follow the bi-logarithmic law with n approaching 1. Low salinity and correspondingly high DO content accounted for the higher corrosion rate of the plates immersed in the river water. All the surface roughness parameters (Ra, Rq, Rp and Rv) also follow a logarithmic trend as time of immersion progresses. The thickness and porosity of the rust layer, which later impact on the oxygen diffusion rate, could be attributed for this phenomenon. Genetic programming was successfully applied using the Eureqa Artificial Intelligence software to obtain a generalized corrosion rate model in terms of Rp and Rq for the entire Mauritian water bodies, which was then successfully validated using seawater from another location. Thus, by simply using a portable roughness analyzer, a corrosion rate can be obtained for any submerged carbon steel structure in Mauritius.

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