AN INVESTIGATION OF CORROSION BEHAVIOR OF ALUMINUM AND STAINLESS STEEL IN MARINE ENVIRONMENT OF KARACHI HARBOR

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Copyright Statement

Dedicated to my beloved parents, supportive wife and adored daughter for his unwavering guidance, motivation and teachings since my childhood which led me to this remarkable achievement.

Abstract

Corrosion costs trillion of dollars every year to world economy. Among all type of corrosions, atmosphere corrosion is considered as most destructive. Very less wok in field of corrosion has been carried out in field of corrosion in Pakistan. Karachi is considered backbone of country economy and the hub of industrial activities along with main trade gateway for international shipping; thus there is a dire need to determine corrosion rate especially of high valued locations at Karachi.

In view of above, a new location inside Karachi harbor i.e. dockyard has been selected for ascertaining atmospheric corrosion of Aluminium and stainless Steel by complying ISO and ASTM norms. Corrosion behaviour of Stainless steel and Aluminium will be studied after exposing for one year at Karachi harbour (dockyard) which is a key points having high value installation like ships, defence assets, ship building industry and others. Different atmospheric condition and content of corrosive agents will be measured periodically for one year at site of test. Using ISO 9223 standard corrosion rate will be determine by method of mass loss. Finally statistical corrosion models will be developed for Stainless steel and Aluminium using bivariate and multivariate approaches as function of time and atmospheric corrosive agents

Keywords: Corrosion, Karachi harbour, rate of corrosion, model for corrosion, Alumium, Stainless Steel, Marine corrosion

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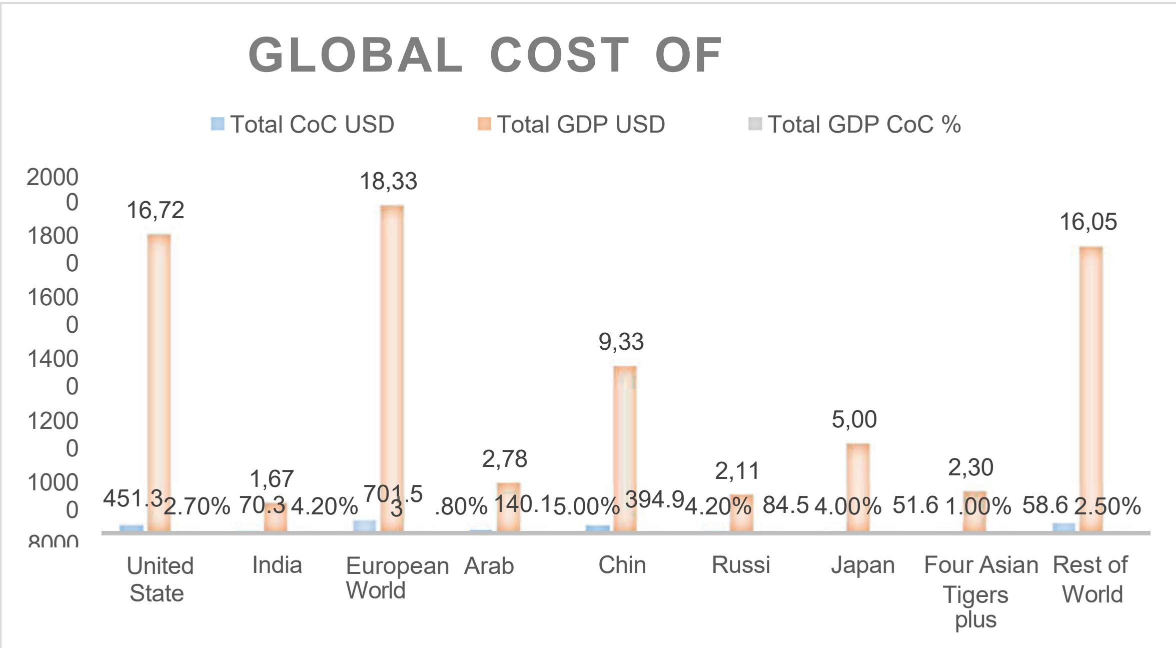
CHAPTER 1

INTRODUCTION

Corrosion is an irreversible electrochemical or chemical reaction of metal with its environment which results in degradation of its properties. The word "corrosion" comes from a Latin word "Corrōdere" which meant "to chew away". The common example of corrosion is formation of rust on iron or metallic surface. [1].Since ancient times, many scientist studied corrosion and its mechanism. Plato (427-347 BC) work regarding corrosion is considered as oldest. Georgius Agricola (1494-1555) defined corrosion and suggested that by applying tar layer on the surface of metal corrosion phenomena can be avoided. [2]

NACE international studied economic impact of corrosion all around world. According to NACE international's IMPACT report, Corrosion costs are estimated to be in the range of US$ 2.5 trillion, or 3.4 percent of world GDP. With effective corrosion control method this number can be decreases by 15-35% of the total cost around $375 Billion -$875 Billion annually globally. In this study cost of safety and environmental consequence due to corrosion are not added to overall cost. [3]



Effect of corrosion on economy has been studied by Jeffery Didas, according to study Pakistan can save PKR 270-380 Billion every year by using adopting different corrosion prevention methods. [4]

1.1. Form of Corrosion

Metal tends to react with elements to make them more chemically stable. Like in case of uniform corrosion a regular film is produced at whole surface and metal is corroded at similar rate. Visual observation is being used for classification on corrosion. [5] Wet corrosion can be divided into following based on its appearance. [6]

a. General corrosion/uniform corrosion

b. Pitting corrosion

c. Intergranular corrosion

d. De-alloying

e. Galvanic Corrosion

f. Crevice Corrosion

There are different type/form of corrosion depend upon following:

a. Corrodent's nature

b. Corroded Metal's appearance

c. Corrosion Mechanism

1.1.1 General /Uniform corrosion

General corrosion (Uniform corrosion) is most commonly observed of corrosion in environment which is caused by electrochemical or chemical reaction on the exposed surface of the metal having regular layer of oxide. It can be easily can be predicted and therefore it can be manage and can be prevented by different technique. [6] [7]

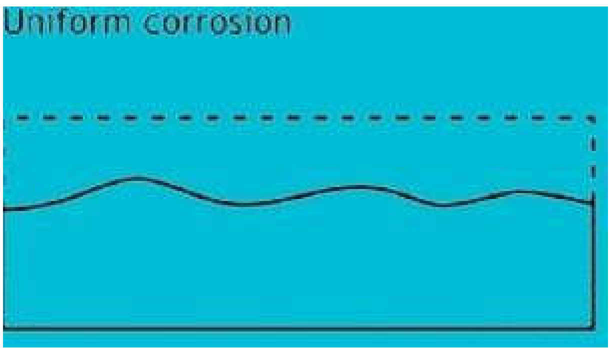


Figure 1.1 Uniform corrosion

1.1.2 Pitting Corrosion

Pitting corrosion occurs on a certain area due to galvanic reaction. Normally small hole or cavity is present on surface of metal which may lead to pitting due to pitting corrosion. It is very difficult to predict which make pitting one of most dangerous type corrosion as compare to other corrosion type. This kind of corrosion is difficult to predict but can be prevent by applying layer of paint. [6] [7] [8]

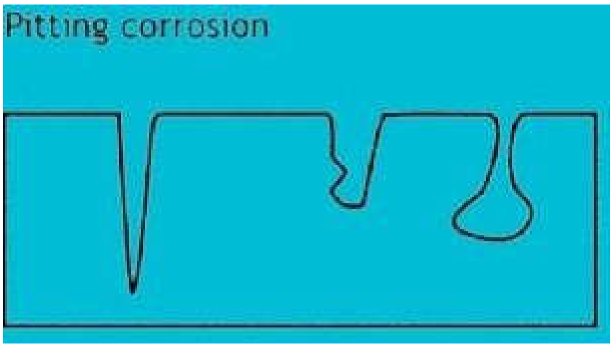


Figure1.0-2 Pitting Corrosion

1.1.3 Intergranular Corrosion

Intergranular corrosion occurs in the grain of the metal due to existence of impurities. Few impurities existing in metal may cause reduction of metal around boundary of grain which decrease mechanical properties of the metal. It is also called exfoliation. This type of corrosion normally occurs in passive alloys. It normally occur near grain bodies of alloy such as steel. Different heat treatment method are used to prevention of intergranular corrosion [6] [9]

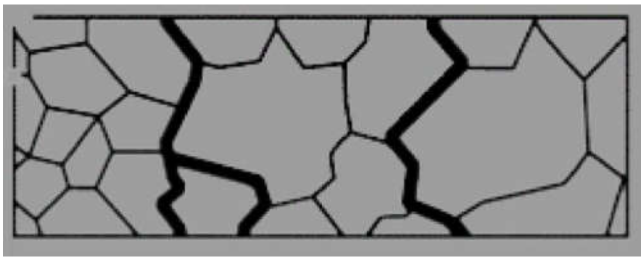


Figure1.0-3 Intergranular Corrosion

1.1.4 De-alloying

De-alloying is also called selective corrosion in which is caused by attack on single element of the alloy which result in dissolving of element. There are different metals such as carbon, nickel, cobalt, zinc are exposed to selective corrosion which result in dissolving of elements. In different alloys every element is having different corrosion potential as compare to other elements. Element having less corrosion potential is mostly exposed to De-alloying. Different heat treatment method are used to avoid de-alloying. [1] [10]

1.1.5 Galvanic Corrosion

Galvanic corrosion is occur which two electrochemically two dissimilar metal comes in together in the corrosive environment. In this process one metal turns as anode and while other acts a cathode. The metal which as anode get corroded and metal act as cathode is protected. Hence electrolysis reaction occurs which result in degradation of the metal. It is also called bimetallic corrosion. This type of corrosion common near sea and petroleum industry. [11]

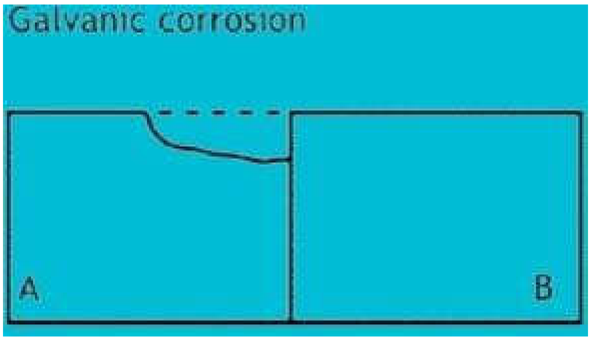
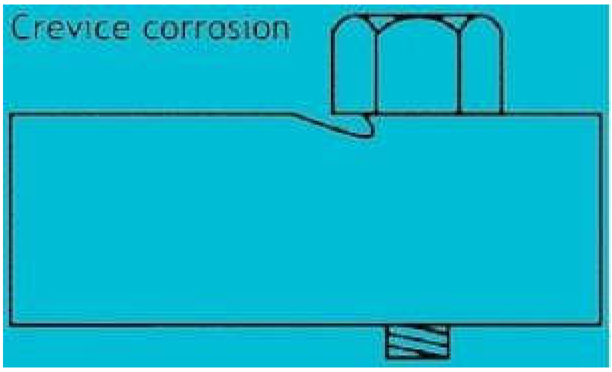


Figure1.0-4 Galvanic corrosion

1.1.6 Crevice Corrosion

Crevice Corrosion mostly occurs at stagnant micro-environment where there is ion difference at surface of metal and having limited supply of oxygen. This type of corrosion is normally overserved in shielded area i.e. areas under gasket, washer or bolts. Cathodic protection is used to prevent the metal from crevice corrosion. [11] [12]



1.2 Categorization of corrosion process

Corrosion process can be divided into following on basis of process: [13]

a. Chemical corrosion

b. Electrochemical corrosion

1.2.1 Chemical Corrosion

Chemical corrosion is a natural process in which chemical reaction occurs between metal and environment to form chemically more stable state such as oxide, sulphide, hydroxide etc. chemical corrosion usually occurs places like metal under stressed condition or isolated areas. There are two type of chemical corrosion i.e. dry corrosion and wet corrosion. Wet corrosion occurs in moist environment which dry corrosion occurs in dry climate. [14]

1.2.2 Electrochemical corrosion

Electrochemical corrosion occur when two dissimilar metal react with each other in presence of electrolyte medium. Electrochemical corrosion can be divided into following: [15]

1. Immersion Corrosion
2. Underground corrosion
3. Atmospheric corrosion

1.3 Atmospheric corrosion

Atmospheric corrosion phenomena occurs only when electrolyte is present as external condition. [16] This type of corrosion is mostly commonly of corrosion which result in degradation of metal when it reacts with atmosphere and cause heavy financial loses. [17] It is ultimate important to calculate corrosion rate and its calculated expect life of metal before using that material in that particular environment. [18] Atmospheric corrosion is mostly occurs when metal are exposed to moist atmosphere especially in presence of aggressive gas. It is mostly occur in industrial sites and coastal areas. [19] It cause heavy financial loses and service life of material in that particular areas. Atmospheric corrosion is global issue and having serious impact on civil construction sites, industrials sites and all other engineering structures near coastal line and industrial areas. [20] Atmospheric corrosion is process of electrochemical reaction metal with it environment. The factor which effect corrosion rate are temperature, humidity, salinity, sulphur content, time of exposure and content of gas like oxygen, carbon dioxide , sulphur dioxide , nitrogen dioxide and other which effect overall speed of reaction. [21] [22] [23]

1.3.1 Type of atmospheric corrosion on bases of environment

Atmospheric corrosion on bases of environment are as follow: [24]

1. Urban environment

2. Rural environment
3. Industrial environment
4. Marine environment

1.3.1.1 **Urban**

Urban atmosphere mostly consist of SO_X and NO_X compounds. Emission due to domestic fuel and motor vehicles are the main source of pollution in urban environment. Urban environment is having strong corrosive agent such as sulphide oxide and nitride oxide which cause corrosion on surface of metal. [25]

1.3.1.2 Rural

Rural environment consist of strong aggressive agents. Primary destruction agents are miniscule quantity of SO_x, moisture, NH_3, CO_2 and humidity. Organic and inorganic compound are also present in this environment but mostly they do not contain chemical pollution. Mostly urban environment consist tropical or dry atmosphere which is very sever atmosphere due to very less rainfall or high humidity conditions. [26] [27]

1.3.1.3 **Industrial**

Industrial atmosphere consist of strong corrosive agent such as SO_x, NOx, smog and acidic rain. Other agent like NH3, chlorides, phosphates and hydrogen sulphates may also be present in traces. When these agents accumulates on surface of metals, the relative humidity decrease upto 60%. [28]

1.3.1.4 **Marine**

Marine environment is very destructive environment for materials consist of high relative humidity in air and having high sodium chloride precipitations. The factor which effect marine corrosion are as follow: [29]

1. Wind and its direction
2. Topography of shore
3. Wave action
4. Relative humidity

5. **Distance from coastline**

Shore wind carries marine fog and droplets having high precipitations of salt which cause high corrosive on surface of metal if relative humidity is greater than 55%. The region above the sea surface, where heavy sea sprays and splashes occur, is also included in the marine atmosphere. [30]

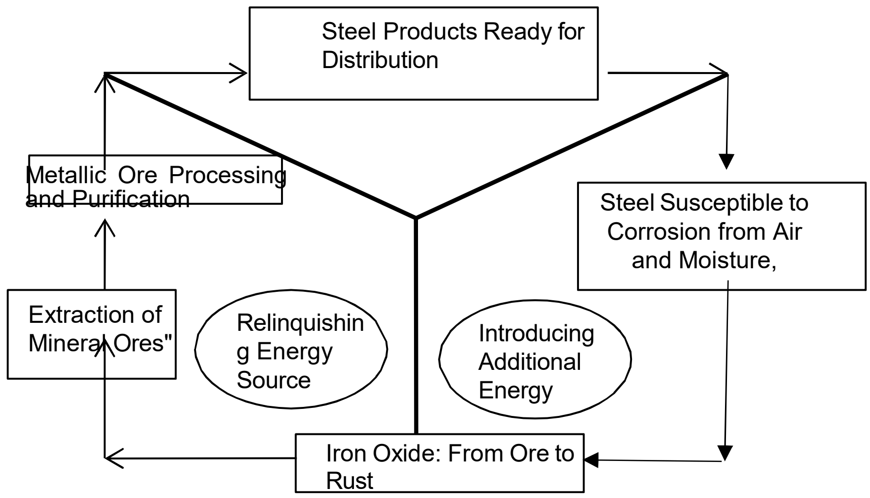


Figure 1.1.3-1 CORROSION CYCCLE OF STEEL

1.4. Factors Influencing Corrosion

1.4.1. Factor affecting atmosphere corrosion

There are many pollutants available in atmosphere which affect atmospheric corrosion. When metal are exposed to atmosphere, there are many factors such as humidity, SO_2, Cl^{-1} and temperature which may affect the corrosion rate of metals. [31][35]

1.4.2. **Sulphur Dioxide**

Sulphur Dioxide is produced from serval sources i.e. combustion of fossil fuel in engines, volcanic eruption and from different industrial processes. [32] It is one of important reason for atmospheric corrosion. Concentration of SO_2 and its acidic compounds are considered as one of most important and active corrosive agent in atmosphere corrosion. [24] Around the world there are two type of trend about concentration of SO_2 in air. First are those where concentration of SO_2 is increasing due to industrial emission and second are those areas where its concentration is decreasing by using emission control and use sulphur fuel. [33]

Effect of sulphur Dioxide and corrosion mechanism has been be studied by different researchers. It is been noted that SO_2 reacts with metals only presence of humidity and other participation of pollution. Vernon was the first researcher who observed that there is no significant corrosive due to SO_2 in absence of humidity and other pollutant. It is noted during research that sulphate ion are produced from Sulphur Dioxide in presence humidity and other parameters. These ion further reacts with metals which result in corrosion of metals surface. [34] [35]

1.4.3. Time of Wetness (TOW)

According to ISO standard 9223, TOW is the period when relative humidity in climate is beyond 80% and temperature is beyond zero degree centigrade. Basically it is time when on metal surface is wet due to conductive water. Presence of water creates on surface of metal acts as electrolysis on corroded metals. Temperature is also key factor regarding atmosphere corrosion. Coastal climate is ideal for atmosphere corrosion due to ideal temperature and high relative humidity. [36] [37]

1.4.4. Chloride

Chloride is present in atmosphere which is produced from different industrial emission and from natural phenomena. Chloride is very aggressive agent which can cause extensive corrosion. Chloride naturally produced from natural airborne salinity, which can impact atmospheric corrosion and its function may vary depending on atmospheric climate. It is overserved that at the high moisture condition, chloride ion are generated at fast speed which reduce acceleration of rate of corrosion. [38]

Chloride in coastal area further increase rate of corrosion as compare to other climates/atmospheres. Barton carried out research on rate of corrosion in marine environment and concluded following from his research: [39] [40]

1. Chloride and its species i.e. NaCl, $CaCl_2$ can increase rate of reaction of electrochemical corrosion process and it can cause high corrosion at relative low humidity and other condition by producing electrolysis.
2. Corrosion product nature such as solubility play important role in rate of corrosion.

1.4.5. Temperature

Temperature another major factor in atmosphere corrosion after humidity and pollutant. It has reported that by increase of 10 degree centigrade in temperature theoretically corrosion rate there might be double. Diffusion of metals in high temperature is an vital factor for atmospheric corrosion rate. Due to increase in temperature, following procession occur which effect atmospheric corrosion: [41] [42]

1. Electrochemical reaction rate will be increased.
2. Metallic diffusion process speed will be accelerated.

Due to increase in temperature there will be decrease in relative humidity which result in increased electrolyte surface evaporation. That's result in increase in corrosion rate of metals. [43]

1.4.6. Additional atmospheric containments

There are some additional containments which may contribute in acceleration of atmospheric corrosion. The factors are as follow:

- Hydrogen sulphide
- Hydrogen chloride
- Chlorine
- Nitrogen compounds, in form of nitrogen oxide

It has been discovered that hydrogen sulphide is very aggressive agent for mostly metal. Sulphide ions from hydrogen sulphide react with surface and cause high corrosion on surface of metal. Hydrogen chloride and chlorine in high relative humidity are highly corrosive agents. These agents effect anion part of chloride salts. Mixture of these pollutant make heavily corrosive agents for metal. [44] [45]

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1.5. The Economic Consequences of Corrosion

Given the detrimental effects and damages caused by corrosion, it is unsurprising that the associated costs are substantial. Extensive research conducted over the past two decades has indicated that the direct annual cost of corrosion to an industrial economy ranges from approximately 3% to 6% of the country's Gross National Product (GNP) [12]. Corrosion significantly weakens metal materials and polymers, thereby impacting the quality of the country's metal production [5]. Experts suggest that corrosion is a process of converting the metal back to its original constituents, emphasizing the need to address and mitigate this phenomenon.

Pakistan experiences an annual loss of $3 billion due to corrosion in infrastructure, domestic settings, and industries. Moreover, the corrosion challenge adds to the costs of power generation, transmission, and distribution in the country. The corrosive nature of seawater, with its high concentration of dissolved salts, poses a significant risk to steel, infrastructure, and marine environments as well as surrounding properties. Ongoing efforts are being made in various industries to develop and implement solutions aimed at reducing corrosion and preventing degradation of properties in marine environments [11].

1.6. The Basis for the Study

The following factors were considered during the selection process for the locations:

- Metal being tested
- Climate
- Proximity to pollutants
- Geographic location

After careful consideration of multiple locations, the West Wharf of Karachi Harbor was chosen for the corrosion analysis. However, the selected site poses challenges due to its proximity to significant installations and structures such as the Pakistan International Container Terminal (PICT), Karachi International Container Terminal (KICT), Karachi Shipyard & Engineering Works (KS&EW), and Naval Property. As a coastal area, the site is expected to have a high chloride content. Additionally, the corrosion assessment needs to take into account the presence of SO_4^{-2}, the impact of merchant and naval vessel effluents, coal dumping operations on the Eastern Ghats, and the inflow of industrial waste from Layari and Malir into the Karachi harbor, which further contributes to the site's pollution from waste materials.

1.7. Study Objectives and Goals

The study aims to achieve the following objectives:

- To assess the corrosiveness of Karachi harbor water by employing the weight loss method outlined in the ISO 9223 standard, using suspended metal coupons.
- To gather data on pollutant concentration and weather conditions through the weight loss method.
- To establish mathematical models that can measure the corrosiveness of the Karachi harbor water channel (specifically, West Wharf) by analyzing the concentration of marine pollutants.

1.8. Thesis Framework

Chapter 2 provides an extensive review of the existing literature relevant to this research study, incorporating background knowledge and previous research conducted on the subject matter.

Chapter 3 focuses on the experimental aspects of the study, detailing the materials and equipment employed in the research.

Chapter 4 presents the mathematical model developed for Stainless Steel, while Chapter 5 discusses the mathematical model formulated for galvanized steel.

Chapter 6 concludes the study by summarizing the findings and presenting recommendations based on the experimental results, thereby suggesting areas for future research.

CHAPTER 2

LITERATURE REVIEW

2.1 Corrosion in Marine Environments

Marine corrosion, particularly in steel structures, is a complex phenomenon characterized by multiple corrosion processes arising from the interaction between the metal matrix and the aquatic environment. The relationship between these factors is influenced by various elements such as temperature, dissolved oxygen, pH, and salinity [46]. The oceans have experienced significant temperature fluctuations due to global warming, making it crucial to continuously monitor and assess the implications of this changing climate. Structural materials used in applications like vehicles, offshore wind turbines (OWTs), and oil and gas platforms need to undergo corrosion resistance testing [47]. Carbon steels are widely produced (~1.8 billion tonnes globally in 2018) and are cost-effective, which is why they are commonly used in marine operations. They also possess favorable mechanical properties [48]. These steels are primarily susceptible to uniform corrosion and have been extensively studied in various marine environments over the years. Researchers have developed models to accurately understand their corrosion behavior and estimate their lifespan with reasonable precision [49].

2.2 Key Aspects of Marine Corrosion

The phenomenon of marine corrosion involves a complex interplay of chemical, biological, and physical factors. Comprehending the impact of each parameter and element is crucial for optimizing the construction of metal structures and machinery employed in marine settings [48].

Furthermore, it is essential to enhance anti-corrosion techniques and ensure the durability of materials. Localized corrosion, in particular, represents a subtle process of oxidation that can significantly undermine the long-term integrity of metal structures [50].

2.3 Determinants of Marine Corrosion

In marine environments, the corrosion of steel structures is impacted by various factors [50]. These factors can be classified into three categories:

1. Physical factors: These include sea water temperature, water velocity, surface moistening, suspended solids, and water pressure.
2. Chemical factors: This category comprises dissolved oxygen (DO), CO2 (carbon dioxide), SO_4^{-2} (sulphate), pH, pollutants, and carbonate solubility.
3. Biological factors: These factors involve the presence of bacteria, biomass, pollutants, and marine organisms that can contribute to corrosion processes.

2.4 Marine Fouling

Fouling refers to the growth of marine plants and animals on marine vessels and structures. Certain organisms, such as barnacles, flourish on smooth surfaces, causing them to become rough. For instance, the hull of a ship can be likened to soft paper transforming into a gritty surface, akin to sand [25].

Foul organisms can be classified into two categories: microorganisms and microsystems. The "soil" layer primarily consists of bacteria, fungi, protozoa, and single-celled organisms, with bacteria and diatoms being particularly significant [51]. The microsystem consists of algae and animals, with red, brown, and green algae being the most prevalent forms.

2.4.1 The Impact of Marine Fouling on Sea Vessels

The West Wharf of Karachi Harbor exhibits a significant presence of green algae, along with a multitude of microorganisms. Consequently, fouling development on painted steel surfaces of sea vessels submerged in seawater follows a general sequence. Initially, a layer of sludge containing bacteria and diatoms covers the surface. Subsequently, weed growth occurs from spores trapped in the mud [52].

The most common types of weeds found on ships are green and brown algae. Eventually, during the second stage of fouling, animal larvae attach themselves. Weed growth is primarily observed on areas of the vessel exposed to sunlight, while green species tend to coexist with brown weeds near and below the waterline. Animals predominantly inhabit the underside of the hull, as they face competition from weeds on the sides. This is where the corrosion of ships commences, weakening their structural integrity [53].

The accumulation of fouling organisms progressively increases the drag resistance of the vessel's hull through the water, reaching critical values. Failure to remove the fouling results in even the smallest rise in seawater causing a hydrodynamic drag on the ship's hull, surpassing the roughness caused by corrosion on the plating [54].

Furthermore, apart from the increased abrasion resistance caused by the roughness effect, the presence of shell-bearing organisms, if left unchecked, can damage the underlying paint films by cutting into the coating with their shells, eventually penetrating it. Fouling, therefore, has both direct and indirect effects on corrosion. Bacterial activity, especially in coastal areas and harbors, has a direct impact on the contamination of water, particularly due to the degradation of steel by sulphate-reducing bacteria under anaerobic conditions [55].

2.5 Prior Investigations on Marine Corrosion

In the past few years, atmospheric corrosion has received a lot of attention, and a lot of study has done into understanding the factors and causes of corrosion. Different method are being used for investigation relationship of corrosion rate with its environment parameters and that model is further compare with experimental results. [56] There are basically two type of model being used for corrosion. [57]

- **Mathematical model/ Theoretical model** Mathematical modelling is obtained by using different mathematical equations, graphs, diagrams, plots and other mathematical relations/formula to obtain a representation of actual corrosion model. It is mostly used for investigation of corrosion. The most advantage of mathematical model is that predication and response factors of corrosion are free from specification error and measurement uncertainty. Thus, more accurate theoretical models are obtained in this case. [56] [57]

- **Empirical models/ statistical model** Empirical models are drawn from experimental data. Mostly data is obtained from basis of experimental data which might be having observation error, experimental error and measurement error. It explain how a system against any type of response. It does not provide any information about any component of the system. [56] [57]

- **Machine learning based model** Machine learning has been used to calculate overall corrosion rate of certain areas. The benefits of using of machine learning is that very few limitation for considering external condition and variable. It is easy to solve in machine learning due to less solving of regressive factor solving. Currently more work is being carried out on machine learning technique and model. [59]

These model are being used to predict corrosion rate in function of time and Sulphur Dioxide, chloride, time of wetness and other parameter are independent variable. Stability of model is obtained by using different statistical approached and mathematical expressions.

Qiyue Zaho and his team studied long term effect of industrial and marine atmosphere on Aluminium alloy. During the research weight loss method and mechanical property method was used to understand the behaviour of Aluminium alloy during 5 years and then draw model for future behaviour. Result shows that mechanical properties of alloy has been changed due to pitting and intergranular corrosion. [59]

Abdul Waris established mathematical model to study atmosphere corrosion particular microbiological influenced corrosion rate. Model consist of corrosion causing parameter, relation between different corrosion causing parameters and response of these causing parameter on corrosion. The result shows that bacteria are causing iron oxidization which also result in methanogens are the primary causes of this type of corrosion. This model helps to predict corrosion rate in petroleum industry. [60]

Alessandro studied galvanic steel by creating statistic mathematic model. The model consist of canonical macro ensemble on laboratory scale to study life of galvanic steel in particular conditions. Research consist of creating a theoretical modelling foundation and comparing its result with qualified experimental device like Canonical macro ensemble. And predicting corrosion rate and useful life of galvanic steel. [61]

Zhang created a mathematical model when aluminium alloy surface was exposed to aggressive environment. The process and effect of formation of oxide layer on alloy surface and ion concentration which result in pitting was studied. A mathematical model was established which then verified to experimental data by comparing method. The result shows that pitting observed on metallic surface was due to release of ion due to strong environmental effect. Moreover, three dimensional morphology was created by process of image processing method. [62]

Yuhang Wang has carried research on EH 36 steel in marine and industrial climate for different active and inactive inclusion. Ca, Mg and Al are added in EH steel 36 to achieve different desired result. During study it was noted that stress matrix of active inclusion was higher than yield point which cause localized corrosion which propagate quickly as expose to marine environment. [63]

Xueyu studied HSSS steel in marine environment for stress corrosion cracking by using mechanical-electrochemical testing apparatus.

Lu Zhang studied behavior of Cr-AL alloy steel in construction industry by creating equitant circuit model which help to predict behavior of steel and corrosion rate of steel. By using this machine learning technique accurate result is obtained without solving complex equation in mathematical model. [64]

Zibo used Random Forest based Machine learning approach for monitoring of corrosion of carbon steel by using corrosion sensor. Different external corrosive agent such as humidity, chloride, Sulphur dioxide are kept as considered as key factors. RF model predict the instantons corrosion at any time. So any point of time corrosion rate can be obtained by providing environmental conditions. [65]

Wainda carried out research on corrosion on tropical environment of Thailand and draw corrosion map base on model with chloride distribution on structural steel. Research was carried out from costal line upto 5 KM to understand corrosion rate and chloride effect on it keeping wind as dependent variable. On bases of model, corrosion map is obtained which can help to predict corrosion rate any place or time on coastal line. [66]

Luchun Yan used machine learning tool for study of corrosion rate model. Empirical model has limitation of being used on limited certain factors and climates due to regression analysis of factors. Yan used machine learning tool for modeling of corrosion rate. Result shows that machine learning tool efficiently analyze corrosion behavior without involving complex multiple factors of regression analysis. [67]

Yupend Diao collected data of low alloy steel in oceanic climate and establish corrosion model using machine learning and predict the corrosion rate of alloy. Machine learning based model is having better accuracy. During the study chemical composition of alloy and external environment are used as external factors. [48]

Ya-Jun studied corrosion rate based on support vector machines. 3D scanner were used to get corrosion condition data. Different external parameters are obtained through numerical method. These parameter were used to optimize support vector machines. Results show that two vector support machines are required accurately calculate corrosion rate of steel. [68]

Wang carried out research on prediction corrosion rate of bulk carrier marine ship. Ship are moving from different waters having different concentrations and environment so they are exposed to heavy atmosphere corrosion. During the research, ship survey data along with experimental data has been analysed by using machine learning algorithm. This gave minimum 82% accurate result with absolute error difference of 0.10mm. [69]

Reza and his team carried out modelling of carbon steel by using machine learning (Random forest method) to calculate corrosion rate. Measurement has been carried out by corrosion rate as time dependent. Moreover during study corrosion inhibiters were added in different time frame and quantity. The results shows that corrosion rate as function of time depend on amount and time of inhibiters. Moreover, overall corrosion depends on external corrosive agents. During the experiment best results were achieved using Random Forest method of machine learning and overall model for corrosion rate is also generated by Random Forest method. Overall corrosion rate sensitivity is precisely calculated trough this model. [70]

In recent years, there has been an increasing interest in the field of marine corrosion, with extensive research conducted to understand its mechanisms and causes.

Muntazir Abbas et al. [71] conducted a study to analyze the impact of marine environmental conditions on the corrosion-induced degradation of steel structures. The research also focused on developing prognostic models for marine corrosion phenomena and their influence on asset reliability, health assessment, inspection intervals, and overall maintenance strategies. Due to the significant variability of environmental factors, the corrosion of marine steel structures exhibits considerable variation across different immersion zones. The research advocates for a comprehensive inspection and maintenance approach for maritime infrastructure, incorporating dynamic prediction models integrated with online/offline structural health monitoring (SHM) software or adjusting inspection intervals based on the severity of climate conditions.

Yikun et al. [72] emphasized that existing corrosion prediction models are primarily based on historical data or calculations of corrosion failure, while physical models are based on the latest corrosion stages. Achieving precise corrosion prediction is challenging due to the highly complex environmental conditions and the scattered nature of available evidence.

Previous research has proposed linear and deterministic models for corrosion estimation. However, recent studies have suggested non-linear and probabilistic approaches. Southwell was the first researcher to recommend two linear and bilinear corrosion models for steel structures [73].

Rajput et al. [74] conducted experimental investigations to study the corrosion progression properties of steel submerged in fresh and saltwater at low temperatures. Three types of steel were tested under varying corrosive conditions and temperatures. The mass loss procedure was employed to measure the steel thickness. The results revealed that the highest rate of corrosion progression occurred when the steel was submerged in seawater at room temperature.

Sundijano et al. [75] conducted an assessment of corrosive behavior on Stainless Steel at the north coast of Java and Bali (Tol Mandara) on the south coast. The corrosion resistance of Stainless Steel was evaluated after exposure for up to one month in seawater test solutions from the Muara Baru, Suramadu, and Tol Mandara sites. The main parameters affecting the corrosion rate of steel in marine water were salinity, dissolved oxygen (DO), pH, and temperature. The study considered these parameters and observed that the corrosion of Stainless Steel was primarily caused by dissolved oxygen (DO) in all test solutions, with a decrease in DO magnitude over time. Conductivity, salinity, and dissolved solids remained relatively consistent throughout the exposure period. The higher salinity of the solutions in the three natural seawaters played a crucial role in inducing the corrosion risk of Stainless Steel. Additionally, a decrease in dissolved oxygen levels indicated a reduction process in all test solutions. The morphology of the corroded Stainless Steel samples tended to be uniform after exposure in all test solutions.

Dogancan et al. [76] proposed a timely biofouling growth model that enables the prediction of the impact of biofouling on the resistance and effective evaluation of ships on a daily basis. The model initially utilized data from antifouling coating testing to forecast the performance of layers over time, considering the operating profile and shipping route. Biofouling growth estimates over time were converted into equivalent heights of sand roughness based on equivalent literature values. The model was validated using operational data from a 176 m tanker over one year. The predicted frictional resistance change for the 176 m tanker was approximately 32 percent, and the findings were compared and verified against real data. The increase in effective power for the vessel was measured at approximately 25 percent. The model's estimates were found to be consistent with those provided by a ship operator for ship efficiency studies.

Yangfan Li et al. [77] summarized recent studies on the mechanisms of marine-induced corrosion (MIC) and marine biofouling.

2.6. Corrosion rate and atmospheric corrosivity

Corrosion rate is defined as measurement of amount of corrosion produced on unit surface area of certain metal in certain period of time. Corrosive rate is very useful tool in designing systems for measuring amount of damage occur due to corrosion on system.[81] By calculating corrosion rate life prediction of any material while designing any system. There are serval parameter or factor on which corrosion rate depend upon are as follow: [82]

- Time period of wetness
- Chemical composition of material and its properties
- Nature and amount of pollutant
- Temperature
- Thickness of passive film formed on surface of metal
- Electrolysis nature and composition

Term atmospheric corrosivity is defined as ability of atmosphere react with metal and cause corrosion on unit surface of material of any system or sub system. [83] It is very important to calculate to atmospheric corrosivity while designing any system having strong corrosive agents. [84] To calculate atmospheric corrosivity is vital for:

- Signifying materials
- Suggesting corrosive protection technique
- Suggesting maintenance routine to get complete life of any material[85]

2.7. Fundamental approaches for classification of corrosivity

It is ultimate important to obtain relationship between different atmospheric corrosive agents and corrosive rate in order to get a draw a model for study of atmosphere corrosion. The fundamental approaches for classification of corrosivty are as follow:

- The ISO methodology: Different ISO standard also known as ISO CORRAG are available for study and analysis of corrosion. [86]
- On basis of PACER LIME Algorithm is study of corrosion by making a relationship between pollutant and moisture content in air. It is mostly used for marine environment and for corrosion study of aircrafts. [87]
- Rate of Corrosion as function of time corrosion is studied as function of time of exposure in environment. [88]
- Direct measurement of atmospheric corrosion: which is further divided into following methods.[89]
    - Corrosion specimen
    - Electrochemical atmospheric corrosion sensor
    - Alternative technologies for atmospheric corrosion sesnoring

As discussed earlier corrosion modelling helps researcher to predict future effect of corrosion on material. Different approached/ method are used for modelling i.e. Mathematical model, statistical model and machine learning modelling. [56,57] As studied earlier prediction model of corrosion rate as function of time with independent function like sulphide, chloride, TOW etc. are used to construction of modelling. In this study statistical modelling will be used for modelling of corrosion rate by studying bivariate and multivariate approaches. Corrosion model can only be constructed after complete understanding of mechanism of corrosion and factors that affect corrosion. [92]

Corrosion protection method can only be developed after detail considerate of corrosion and products formed as result of corrosion. [93] Different analytical techniques are available for characteristics of products formed as result of corrosion.

- Scanning electron microscopy (SEM) is study by generating surface image of any material by using electronic beam. It provides microscopic image of material which help us to get morphology of material. It is commonly used method in analytical method for analysis and examination of material up to 10 nm. The electron are emitted from filament and focused at a single point by mean of set of lenses. These electron hit the material and return back certain characteristic (topography) which show the nature and electronic image of material. The intensity of beam can be varied depending on nature of material.[94]
- Fourier Transform infrared absorption spectroscopy (FTIR) used infrared spectrum which is emitted by range of different solid and liquids to identify chemical bond between materials in form of infrared spectrum. Different high resolution spectra data has been collected by mean of spectrometer from range of different spectrum range. Data collected by this method is raw and scattered. Thus, Fourier transform is used for analysis of each spectra. [95]
- Energy dispersive X-ray spectroscopy (EDS) uses X-ray radiation to find out elemental identification on surface of species. Beam of electron is focused on the sample material. As electron hit the atom at ground level, electron is emitted from base level and jumped to upper energy level. During this process a hole is created at lower level of energy. To fill this hole, electron from higher energy level jumped to lower level to fill the gap. During this process energy is released in from of x-ray. Every element is having its own energy. Energy released during this process is plot in spectrum which is further studied for every element. [96]
- X-ray diffraction method uses diffraction of X-ray to find out phase identification of corrosion and its products formed. Metal having specific crystalline structure and phase angle. In this technique X-ray beam are focused on crystalline structure of metal and angle of X-ray diffract is measured. These diffract angles are compared to database of that structure before exposed to corrosion and scaling. Moreover, it is also used to find out inorganic corrosion product in composition of elements.[97]

Bivariate and Multivariate model is used for modelling of system for corrosion using any above analytical method. [37], [38] Bivariate model is used when two variable which depend upon each other from data sample achieved through analytical approaches. Among these variable one is dependent of other variable. Bivariate uses different techniques like correlation coefficient, regression analysis and scatter plot. In case of corrosion, normally bivariate corrosion model using any one of above technique between corrosion rate and time of exposure of metal to specific environment. That model can predict rate of corrosion in different exposure time in future. [99][101]

Multivariate modelling or analysis is used when more than two variables from data set are studied by using different statistical methods to get a predictive behaviour of corrosion. There are different method for multivariate analysis such as multiple regression analysis, MANOVA, factor analysis, additive tree, factor analysis. In multivariate modelling different variables or factors which are independent from each other i.e. Chloride content, sulphur content, time of wetness but they are dependent on final outcome for example rate of corrosion. [100][101]

2.8. Scope of the Current Research Study

Extensive experience and multiple exposure systems have demonstrated that marine corrosion is a very diverse process from place to place. Studies around the world have shown that marine corrosion rate is dependent on the testing of steel, the location, the environmental contaminant, pH, dissolved oxygen, salinity, and microbiological growth. For the assessment of Stainless Steel and galvanized steel corrosion, the new site was chosen, i.e. the Karachi Port (West Wharf). It is worth noting that the marine corrosion of any metal at the chosen location has not yet been identified. In reality, it is closer to critical plants and facilities that include the international container terminal of Pakistan (PICT), the container terminal in Karachi (KICT), the shipyard and engineering facilities in Karachi (KS&EW), the naval facilities and the possible existence of contaminants (and) that make the site newer for the project.

CHAPTER 3

METHODOLOGY

3.1 Approach and Methodology

The present evaluation was conducted to determine the corrosive propensity of Karachi Harbor (West Wharf), a crucial hub for transportation activities, ship construction, and repair practices. This assessment was carried out using mass disaster and toxic substance center assessment, following the guidelines outlined in the ISO9223 standard. Throughout the study, the operational methods were modified as follows:

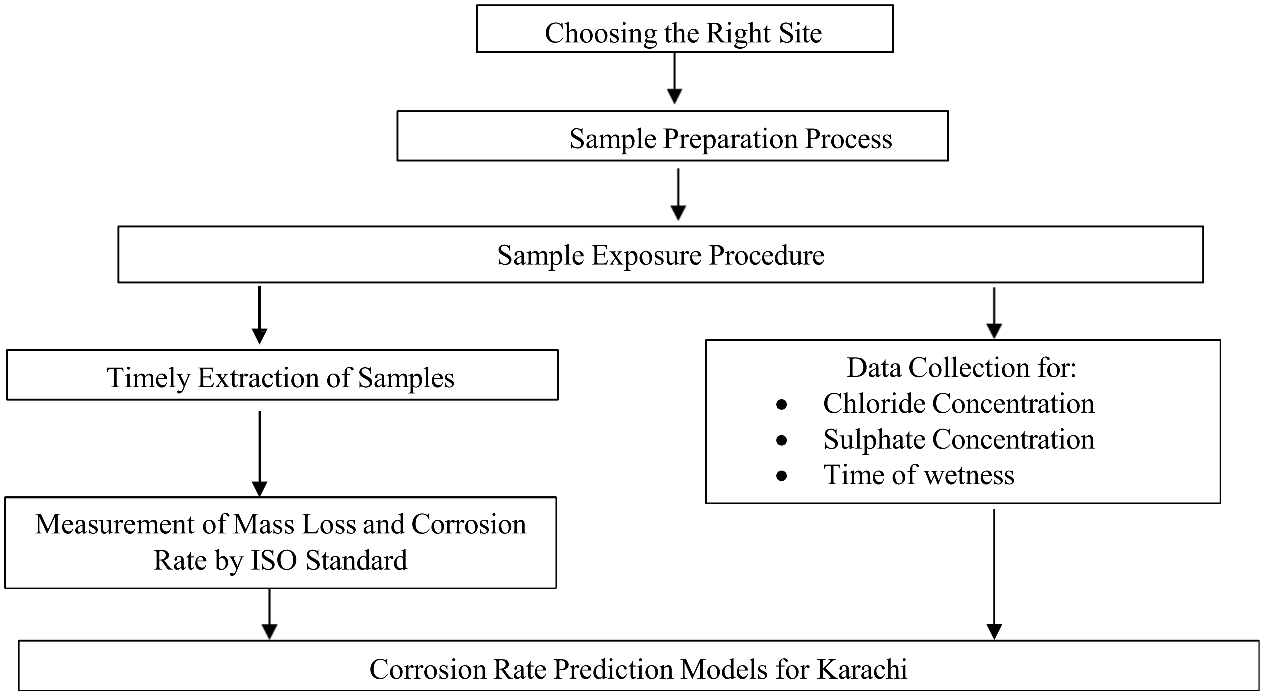

Figure 3.1 Approach and Methodology for research work

Figure 0-1

3.1.1 Selection Criteria for Material

Stainless steel is a type of steel that contains less than 1.2% carbon and is widely used worldwide due to its desirable properties such as ease of manufacturing, weldability, availability, and affordability. On the other hand,

For the direct study, test coupons of commercial grade Stainless Steel Type 316 (also called marine grade and alumium were selected, measuring 103 x 152 x 3 mm. The ASTM G50 standard was followed for the preparation of the test coupons. In the laboratory, the coupons were cleaned and degreased using acetone (C_3H_6O) and then dried using hot air. The initial mass of the test coupons was recorded in accordance with ASTM G1 using an AFD 1000 electronic precision balance. The prepared test coupons were securely packed in airtight bags and sent to the test station for experimentation. The chemical composition of both materials is documented below:

3.2 Selection of Experimental Site

Karachi, located along a 70 km shoreline belt between DHA Phase-VIII and Ras Muari, was chosen as the site for testing the coupons and assessing environmental hazards. The specific site selected within Karachi Harbor at West Wharf (24° 82' N 66° 97' E) offers convenient access and serves as a hub for various important infrastructure and developments, including the Pakistan International Container Terminal (PICT), Karachi International Container Terminal (KICT), Karachi Shipyard and Engineering Works (KS&EW), and Naval assets. The impact of marine corrosion on these facilities has significant financial implications for the national treasury.

Considering the marine nature of the site, it was anticipated that the selected location would have a high chloride content. It is crucial to assess the risk at this specific station due to the presence of sulphate ions (SO_4^{-2}), effluents from merchant and sea vessels, coal dumping activities at the east wharf, and industrial waste entering the Karachi Harbor through the Lyari and Malir rivers. These factors contribute to a highly polluted site, making it an ideal and compelling subject for research.

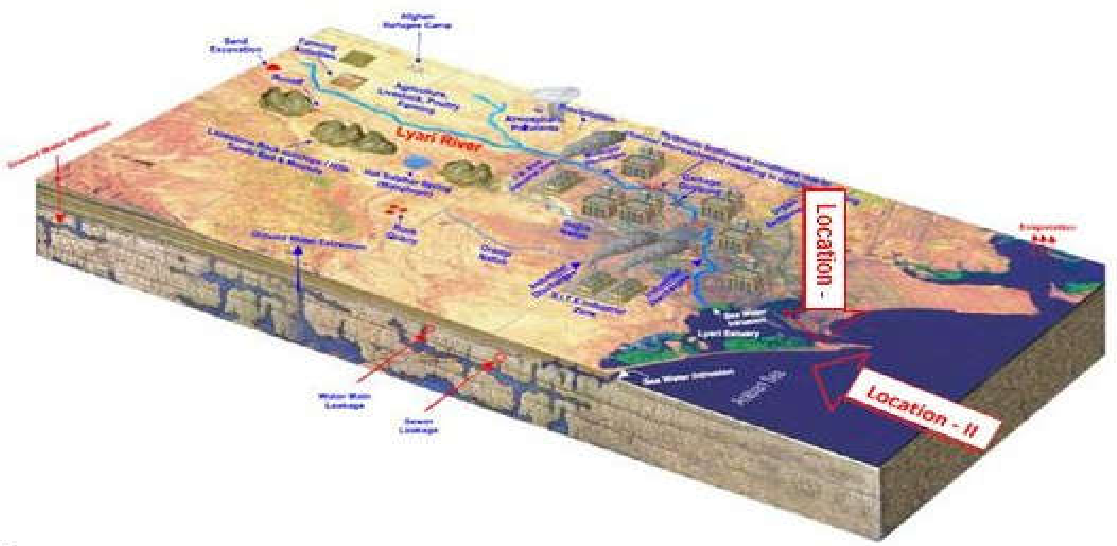

Figure 3.2 Test Site's Geographical Position

3.3 Measurement of Meteorological Parameters

The Karachi Meteorological Office provided the necessary meteorological data for the test site, enabling the generation of monthly insights into the maximum, minimum, and average values of the following parameters:

- Water humidity and temperature
- Rainfall
- Salinity, specifically chloride and SO_4^{-2} content
- Dissolved oxygen

3.4 Assessing the Corrosive Nature of Karachi Harbor's Marine Environment

Under the ISO 9223 standard, the corrosive propensity of the selected test station was determined by evaluating the following key parameters:

- Physical factors including sea water temperature, velocity, surface wetting, suspended solids, and water pressure.
- Chemical factors such as dissolved oxygen (DO), CO2 levels, SO_4^{-2} content, pH, presence of pollutants, and carbonate solubility.
- Biological factors that can influence marine corrosion, such as bacteria, biomass, pollutants, and marine life.

3.4.1 Quantification of Chloride Levels

Wet candle method as prescribed in ISO 9225 was used for determining chloride contents in atmosphere [23]. Following was carried out for preparation of chloride measurement kit:

a. A wooden housing as shown at figure 3-4 was prepared for subsequent placement of conical flask.

b. 350 ml of the reagent water was poured in conical flask. Reagent water was prepared by adding 200 ml of glycerin and 20 drops of octanoic acid in 800 ml of de-ionized water.

c. Wet candles were prepared by wrapping cotton gauze ontest tube covering area of 100 mm^2.

d. “The candle wags affixed in rubber stopper containing center hole, while the wick ends of the gauze were inserted intoflask and the stopper was fixed firmly into the neck of the flask”[23].

e. The flask and prepared candle were thoroughly rinsed with de-ionized water to eradicate any contaminants.

f. The candle was then placed at the selected test site in order to collect the data related to chloride deposition.

g. These candles were removed on monthly basis and deposited chloride was extracted from the candles. The analysis of the deposited chloride was conducted by argentometric titration method i.a.w standard designation G140-02 and ISO 9225. “The amount of chloride deposited was calculated asdeposition weight per unit area per day ($mg/m^2.d$)” [23].

Figure 3-3: Wooden Frame Housing Conical Flask and Wet Candle for Determination of Atmospheric Chloride

3.4.2 Quantification of SO_4^{-2} Levels

Concentration of SO_2 in an atmosphere is a critical parameter forestablishing corrosivity of test site. In this regard, following activity wascarried out for preparation of sulfation cylinders i.a.w ISO 9225 [23] and ASTM D2010/D2010M [24] and subsequent measurement of SO2 concentration:

h. A beaker of 500 ml was selected and 2 g of tragacanth powder was dissolved in 10 ml of ethyl alcohol and 190 ml of deionized water while stirring.

i. Warm the mixture at low temperature till formation of a uniformgel.

j. Add 5 g of PbO_2 slowly with continuous stirring to prepare a lump free paste.

k. Cut a cotton gauze of 100 cm-sq and apply at middle part of glass cylinder (Circumference 10 cm and length 15 cm).

l. Apply the paste uniformly on cotton gauze wrapped around glasscylinder using brush.

m. Prepared candles were then dried in an oven set upto 100 °C forapprox. 1 hour and then cooled down in SO_2 free environment and finally sealed in an air tight bag for onward dispatch to exposure site.

n. When the sulfation candle is exposed, it is enclosed in a shelter to protect it from the rain. The shelter is designed to permit freecirculation of air around the candle.

Figure 3-4: Wooden Frame Housing Sulfation Cylinder for Measuring SO2 Concentration

o. Sulfation cylinders were placed in a wooden assembly andexposed at designated site (25m away from sea).

p. Sulfation cylinders were removed on monthly basis and brought back to laboratory in air tight bags for further lab analysis.

q. “The cotton gauze was removed from the sulfation cylinder andplaced in a 500 ml beaker. Mix 100 ml of deionized water and 5 g of sodium carbonate in the beaker and dissolved it thoroughly by stirring”[23].

r. The mixture was boiled for 30 mins and then cooled down at room temperature. Filtered the mixture by using a Whatman 45 filter paper.

s. “7.4 g of barium chloride was then added to gently boil filtered sulfate ion solution to get precipitate of barium sulfate. The precipitate solution of barium sulfate were filtered by using G-4 sintered glass crucible, dried and weighed. The amount of sulfur dioxide collected bythis method was measured by using gravimetric method and results were expressed as sulfur dioxide deposition rate in milligrams per square meter per day ($mg/m^2.d$)" [24] .

3.4.3 Evaluation of TOW

The period of wetness (TOW) refers to the duration in which the relative humidity remains above 80% at a temperature higher than 0°C [22]. In this study, TOW was determined by calculating the monthly average of temperature and relative humidity (RH).

3.5 Corrosion Modeling for Stainless Steel and Alumium

To assess the complexity and intricacy of climatic corrosion and its contributing factors in marine-related systems, real strategies are commonly employed. Mathematical models are developed to gain a comprehensive understanding of the natural and physical phenomena at play. These mathematical models are then validated through specific evaluations to mitigate potential errors and uncertainties that may impact the outcomes. In this context, these models are formulated as equations or sets of conditions.

These models can be considered as a formal expression of a hypothesis or a test plan that leads to the generation of observed data. Therefore, modeling can be defined as the process of creating a mathematical statement that explains the response of a relevant variable. The independent factors in the models are referred to as explanatory variables, while the dependent factors are known as response variables. These independent factors elucidate the direction of the dependent variables utilized in the mathematical models.

In this analysis, bivariate and multivariate tests were employed to advance the development of corrosion models for stainless steel and alumium. Models were constructed to predict the corrosion rate of the test coupons over time, considering dependent factors such as SO_4^{2-}, Cl^-, and TOW. Finally, the robustness of the models was assessed through heteroscedasticity tests.

CHAPTER 4

BI-VARIATE AND MULTIVARIATE MODELING FOR STAINLESS STEEL

The primary goal of the research was to determine the corrosivity classification of Karachi Harbor (West Wharf) based on the ISO 9223 standard. To assess the corrosiveness of the site, test coupons made of Stainless Steel were exposed to the environment. This section focuses on the analysis of experimental results obtained for the measurement of Cl^-, SO_4^{2-}, and TOW. The collected data is subjected to statistical analysis to observe the fluctuations in the marine pollutant, which is the primary factor contributing to corrosion..

4.1 Assessing the Corrosiveness of Karachi Harbour's Marine Environment

The corrosivity category of the test site was determined through the use of degradation methods and the measurement of pollutant concentrations in the marine environment. The results of these assessments are discussed in detail in the subsequent paragraphs.

4.1.1 Analyzing Marine Pollutants in a Descriptive Manner

Table 4.1, shown below, presents the average fluctuations and the range of deviations in marine pollutant levels. Over the course of 1765.62 periods of wetness, the annual average value of SO_4^{2-} was found to be higher than that of Cl^-. Similarly, TOW exhibited significant variations, accompanied by varying maximum and minimum values of marine pollutants.

Table 4.1: Deviation in marine pollutant with ranges

Pollutant	Average Value	Range
□l^{-}	77.64657	49.79 < □□$^{-}$ < 109.01
□□$_4^{-2}$	152.43353	102.01 < □□$_4$ < 191.10
TOW	1765.62	361.70 < TOW < 5062.26

Table 4.2, presented below, illustrates the dispersion and variability observed in the pollutant data. The greatest variation is observed in TOW compared to other factors, while the deviation in pollutant levels is approximately 1.1077. However, TOW follows a normal distribution, whereas the remaining pollutants exhibit a distribution that is approximately Gaussian.

Table 4.2: Contrasting Measures of Dispersion in Marine Pollutants

Pollutant	SD	Skewness	Kurtosis
□l^{-}	20.260	0.015	1.86
□□$_4^{-2}$	31.87	-0.21467	1.847
TOW	1432.29	1.1077	3.6277

4.1.2 Assessment of Normal Distribution in Marine Pollutants

To ensure the normality of residuals, the Jarque-Bera test was conducted, and the estimated statistics are presented in Table 4.3. The calculated p-value from the Jarque-Bera test confirms the normal distribution of marine water pollutants. These values were obtained through data analysis using E-views.

Table 4.3: Distribution of Marine Pollutants: Normality Assessment

Pollutant	**JarqueBera Value**	**Probability Value**
Cl^{-}	0.9818	0.604
SO_4^{-2}	0.9654	0.691
TOW	2.5369	0.3167

4.2 Quantification of Concentration Levels for Marine Pollutants

The influence of seasonal variations on marine pollutants has been determined at the testing site of Karachi Harbor (West Wharf).

4.2.1 Assessment of Marine Chloride Concentration Levels

The measurement of chloride concentration at the test station of Karachi Harbor West Wharf is depicted in Figure 4.1. The highest deposition of chloride, reaching 108.1 mg/m2.d, was observed during the summer month of August, while the lowest deposition, was 48.97 mg/m2.d occurred in the winter month of January. The average chloride concentration throughout the year was observed to be 77.64657 mg/m2.d.

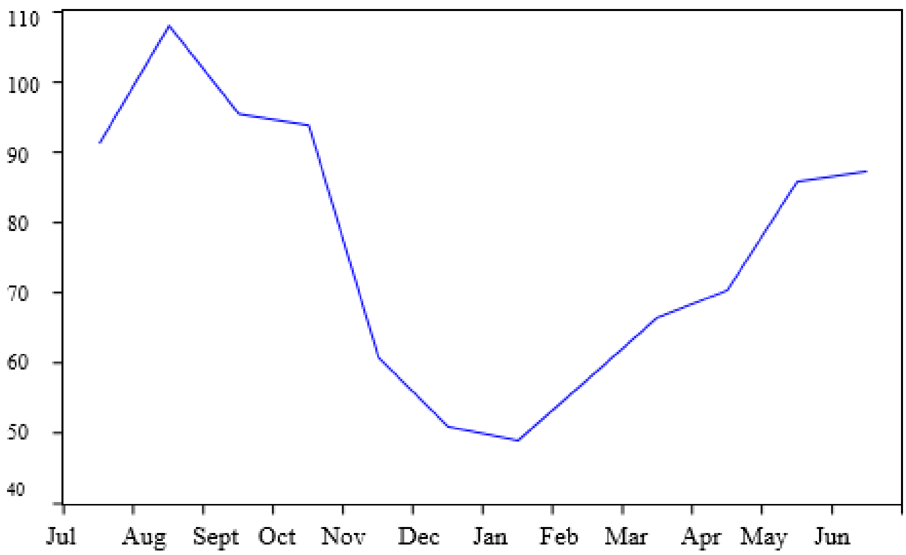

Figure 4.1: Chloride Concentration Analysis at the West Wharf Test Site

4.2.2 Assessment of Sulphate (SO_4^{2-}) Concentration Levels

The measurement of sulphate concentration at the test station of Karachi Harbor West Wharf was conducted from July to May, as illustrated in Figure 4.2. The highest deposition of sulphate, reaching 190 mg/m2.d, was observed in May, while the lowest deposition, 101 mg/m2.d, occurred in January. The annual average sulphate concentration throughout the year was observed to be 151.33 mg/m2.d

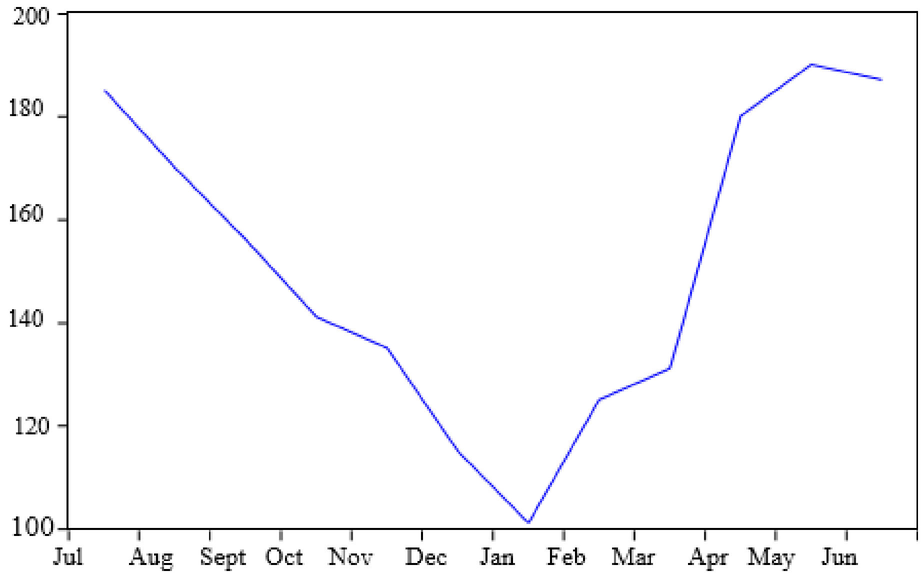

Figure 4.2: Sulphate (□ $□_4^{-2}$)concentration Analysis at The west wharf test site

4.2.3 Evaluation of Time of Wetness (TOW)

TOW (Period of Wetness) is a crucial parameter used to determine corrosion and is greatly influenced by relative humidity, temperature, and the surface characteristics of the specimen. Figure 4.3 presents the TOW values during the exposure period. The maximum TOW recorded during this period was 5026.26 hrs/area in August, while the minimum TOW was 360.07 hrs/area in November and December. The annual average TOW for the current study is calculated to be 1754.27 hrs/area.

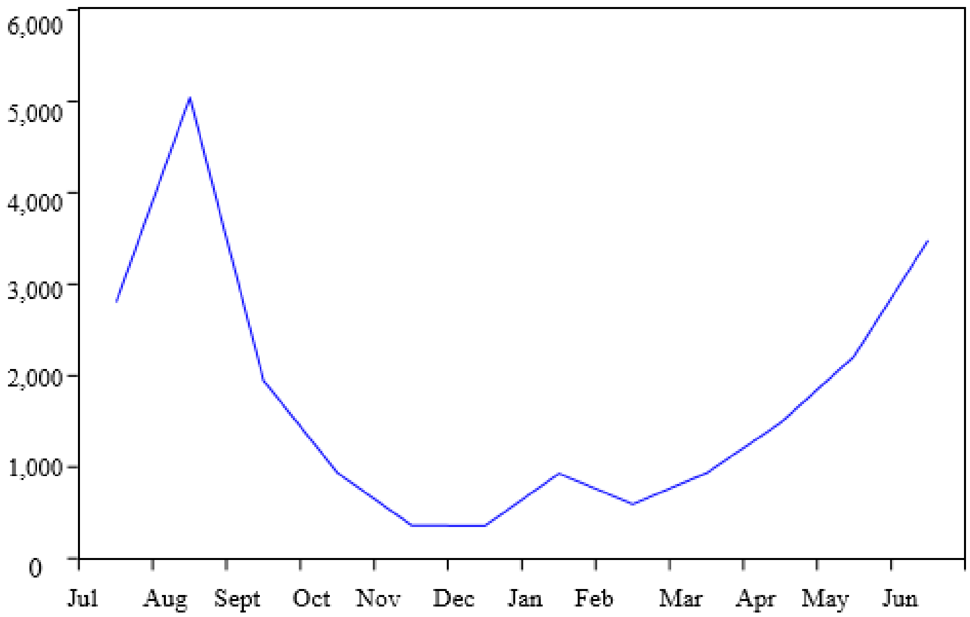

Figure 4.3: Assessment of Wetness Duration at the West Wharf Test Site

4.3 Evaluation of Stainless Steel's General Response to Marine Pollutants

The statistical relationship between corrosion and marine pollutant concentrations, as well as Time of Wetness (TOW), is illustrated in the graph below. The graph depicts the correlation between the corrosion rate of Stainless Steel and Galvanized Steel with the respective observed pollutant variables.

4.3.1 Correlation between Stainless Steel and Pollutants

The correlation between pollutants (SO_4^{2-} and Cl^-) and TOW with Stainless Steel has been determined by calculating Correlation Coefficients. The estimated coefficients are presented in Table 4.4 below. Strong and positive correlations are observed between Cl^- and SO_4^{2-}, Cl^- and TOW, as well as SO_4^{2-} and TOW. However, a moderate positive correlation is found between Stainless Steel and Cl^-. Additionally, a weak positive correlation is identified between Stainless Steel and SO_4^{2-}, as well as Stainless Steel and TOW.

Table 4.4: Correlation coefficients Analysis between the variables for Stainless Steel

	MS	**Cl⁻**	□ □−□ □
□ □−□	0.42		
□ □−□ □	0.16	0.87	
TOW	0.27	0.90	0.84

Figure 4.4 illustrates the graph depicting the relationship between Stainless Steel and chloride ion concentration over time, as well as the Nearest Neighbor Fit. The graph exhibits a curved pattern, with the maximum chloride ion concentration of 4.68 on the Y-axis and the minimum value of 3.89. Similarly, the maximum value of Stainless Steel is 4.60 on the X-axis, while the minimum value is 3.29.

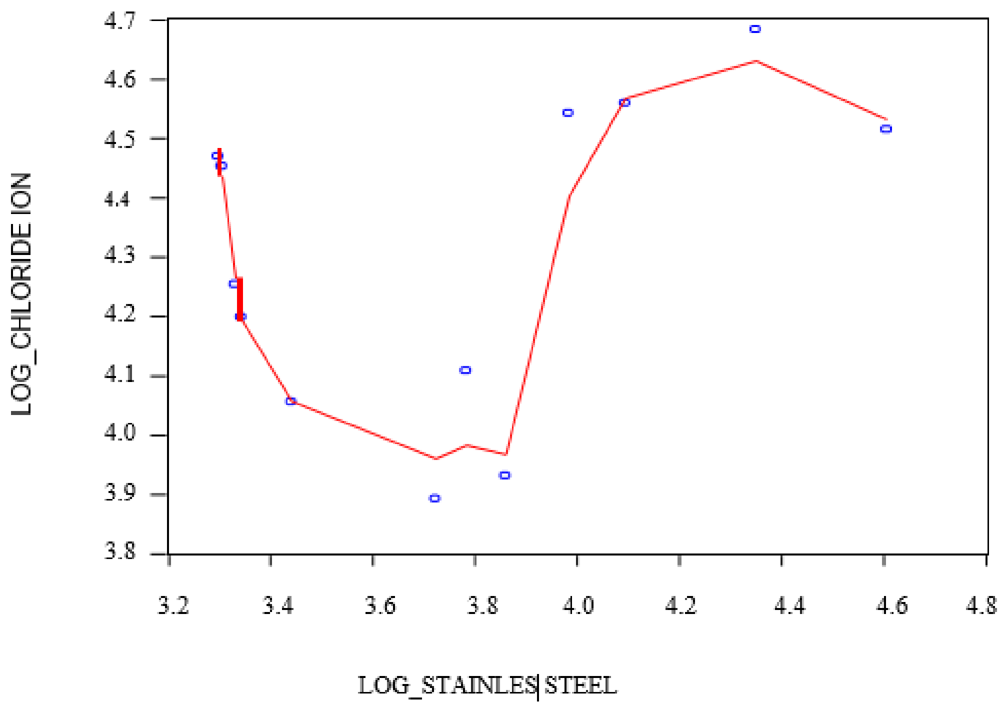

Figure 4.4: Graphical Representation of Stainless Steel versus Chloride Ion Concentration with Nearest Neighbour Fit

Figure 4.5 presents the graph depicting the relationship between Stainless Steel and sulphate (SO_4^{2-}) concentration over time, along with the nearest Neighbor Fit. The graph displays a curved pattern, with the maximum value of Stainless Steel at 4.60 on the X-axis and the minimum value at 3.29. Similarly, the maximum value of sulphate concentration is 5.24 on the Y-axis, while the minimum value is 4.61.

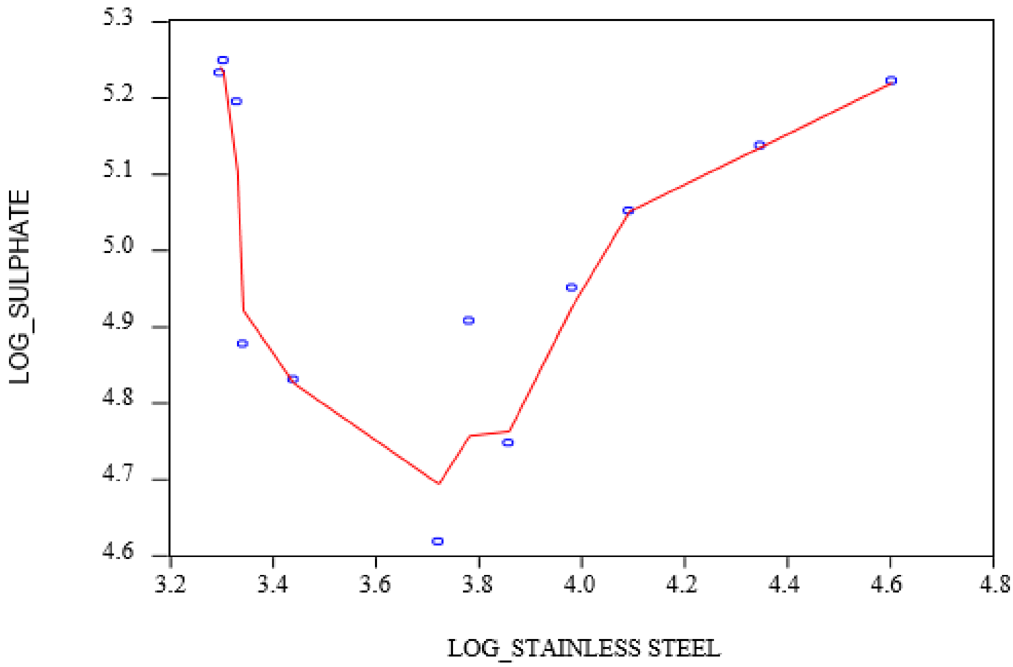

Figure 4.5: Graphical Representation of Stainless Steel versus □□$_4^{-2}$ along with nearest neighbour fit

The graph in Figure 4.6 illustrates the changing relationship between the Time of Wetness (TOW) and Stainless Steel over time. The Nearest Neighbor Fit is used to depict this relationship. The curve on the graph reveals that the maximum value of TOW is 8.52, represented on the Y-axis, while the minimum value is 5.88. On the X-axis, the maximum value of Stainless Steel is 4.60, and the minimum value is 3.29.

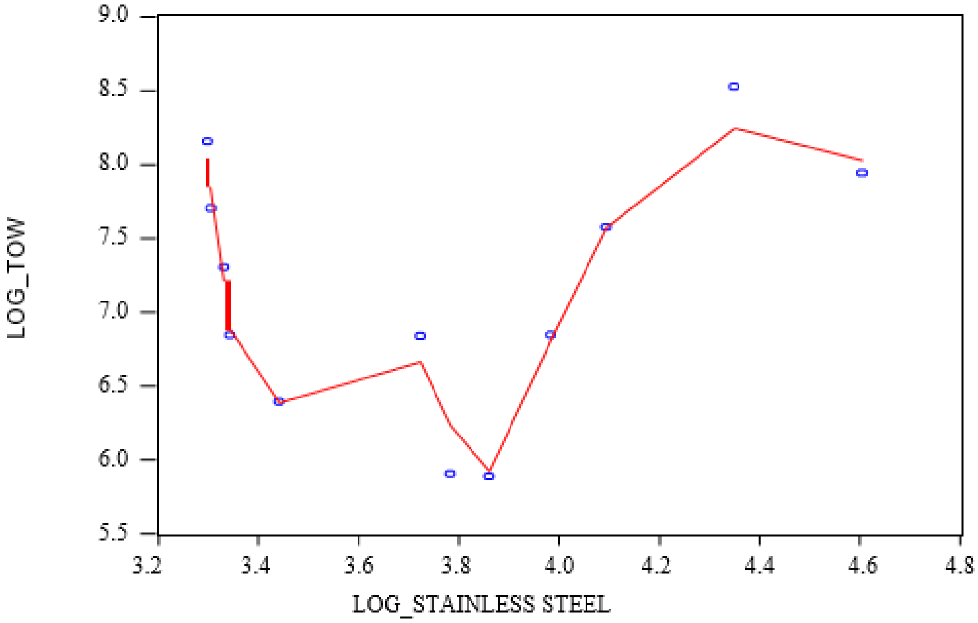

Figure 4.6: Graphical Representation of Stainless Steel versus Wetness Duration with Nearest Neighbour Fit

The graph in Figure 4.6, along with the Nearest Neighbor Fit, illustrates the relationship between Stainless Steel and two marine pollutants, chloride ions (Cl-) and sulphate ions ($□_4□^{-2}$), as well as the Time of Wetness (TOW). This graph depicts a curve

that reaches a maximum value of 8.52 for TOW and a minimum value of 5.88. Additionally, the maximum value for chloride ions is 4.68, while the minimum value is 3.89, and the maximum value for sulphate ions is 5.24, while the minimum value is 4.61. The scattered nature of the graph indicates that TOW has a stronger correlation with Stainless Steel compared to the other pollutants, as its values tend to be higher.

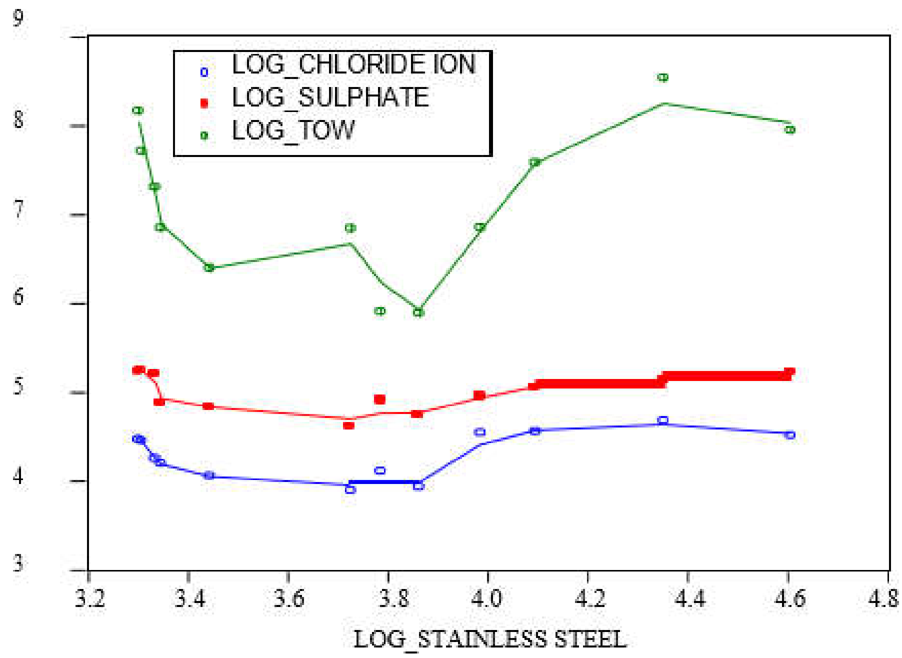

Figure 4.7: Graphical Representation of Stainless Steel versus Marine Pollutants and Wetness Duration with Nearest Neighbour Fit

4.4 Bivariate Corrosion Model for Stainless Steel at Dockyard: Analysis and Findings

The correlation between the observed corrosion rate and the exposure time of the studied material (M□) is captured by the bivariate corrosion rate model for Stainless Steel. The equation derived from the regression analysis, along with important statistical measures, is presented below:

$$\square_{\square} = 57.67 - 6.54\square\square\square\square_{\square}^{2} - 185.2\square^{-\square\square} + \square_{\square} \quad (4.1)$$

Standard Error : (2.42) (0.612) (11.08)

t-stat : (26.32) (-10.7) (16.25)

p-value : (0.011) (0.011) (0.0012)

$R^2 = 0.967$

Here,

□□ = Represents the corrosion accumulated on Stainless Steel

□□ = Represents the rate of corrosion

□□ = Represents the error column vector

R^2 = Represents the Coefficient of multiple determination

Key Measurements for Optimized Model Function

Table 4.5: Key measurements

Estimated Statistical Analysis	**Estimated Quantitative Assessment**
Proportion of Explain Variance	98.780%
Coefficient of Multiple Determination	0.967
Adjusted Coefficient of Determination	0.967
DW-Statistics	1.876
Residual Tolerance	0.00000000012

4.4.1 Assessment of Model Stability

1. The coefficient of determination indicates that approximately 97.8% of the variation in the regression model can be explained by the regressor.
2. The probability plot of residuals displayed below demonstrates that the residuals exhibit a normal distribution.

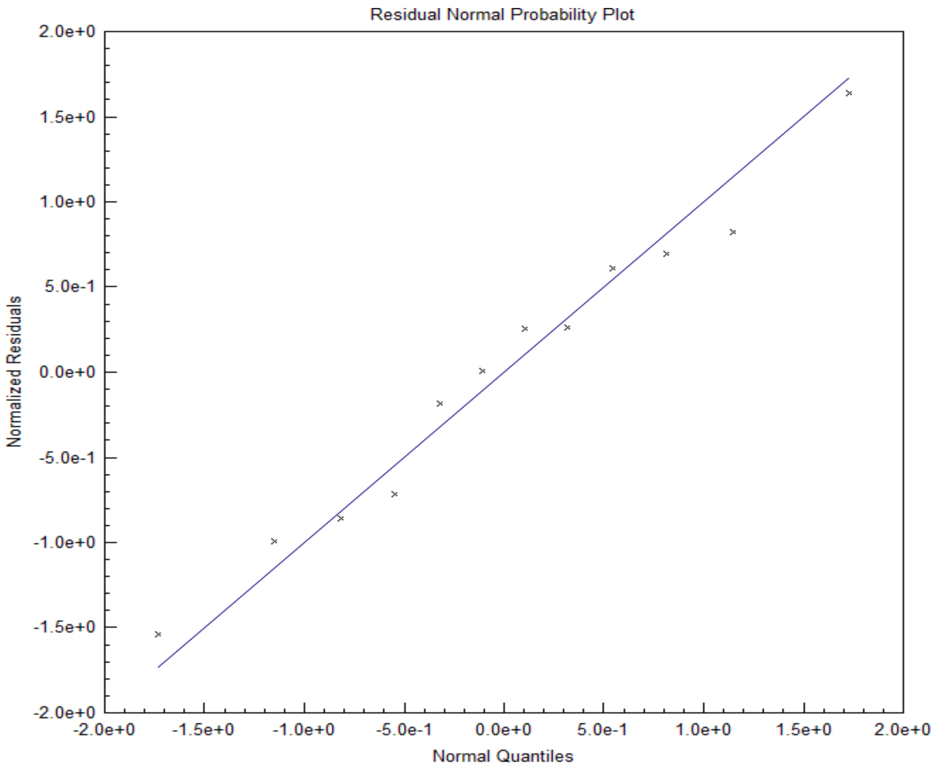

Figure 4.8: Residual normality probability

1. The calculated DW-Stat value of 1.876 indicates the absence of serial correlation.
2. The graphical representation of the actual and estimated values affirms the appropriateness of the constructed models.

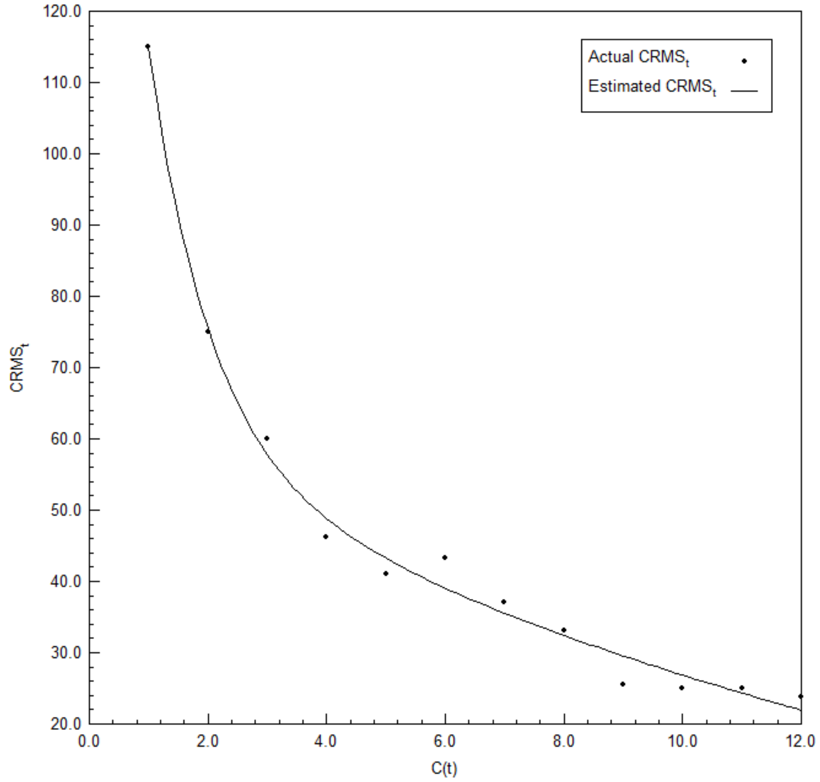

Figure 4.9: Bivariate Model Comparison: Actual and Estimated Plot for Stainless Steel

4.5 Multivariate Corrosion Model For Stainless Steel at Dockyard: Analysis and Findings

Similarly, multivariate relation is developed by regressing corrosion rate of Stainless Steel onto TOW, $\square\square_4^{-2}$ and chloride. The optimized nonlinear empirical relation is as follows

$$\square_{\square} = \square^{0.110+2.79\square_{\square}+1.06\square_{\square}-2.56\square} + \square_{\square} \qquad (4.2)$$

Std Error	: (2.41)	(8.29)	(0.016)	(1.20)
t-stat	: (0.05)	(3.60)	(0.67)	(-2.07)
p-value	: (0.19)	(0.008)	(0.16)	(0.08)

$R^2 = 0.71$

Here,

□□ = Represents the corrosion accumulated on Stainless Steel

□□ = Represents the Chloride deposits

□□ = Represents the Sulphate deposits

□□ = Represents the error column vector

R^2 = Represents the Coefficient of multiple determination

Table 4.6 displays the crucial measurements required for optimizing the model function.

Table 4.6: Key measurements

Estimated Statistical Analysis	**Estimated Quantitative Assessment**
Proportion of Explain Variance	71.24%
Coefficient of Multiple Determination	0.687
Adjusted Coefficient of Determination	0.687
DW-Statistics	2.72
Residual Tolerance	0.0000000011

4.5.1 Assessment of Model Stability

1. The calculated DW-Stat value of 2.72 indicates the absence of serial correlation.
2. The graph depicting the actual and estimated values confirms the appropriateness of the constructed models.

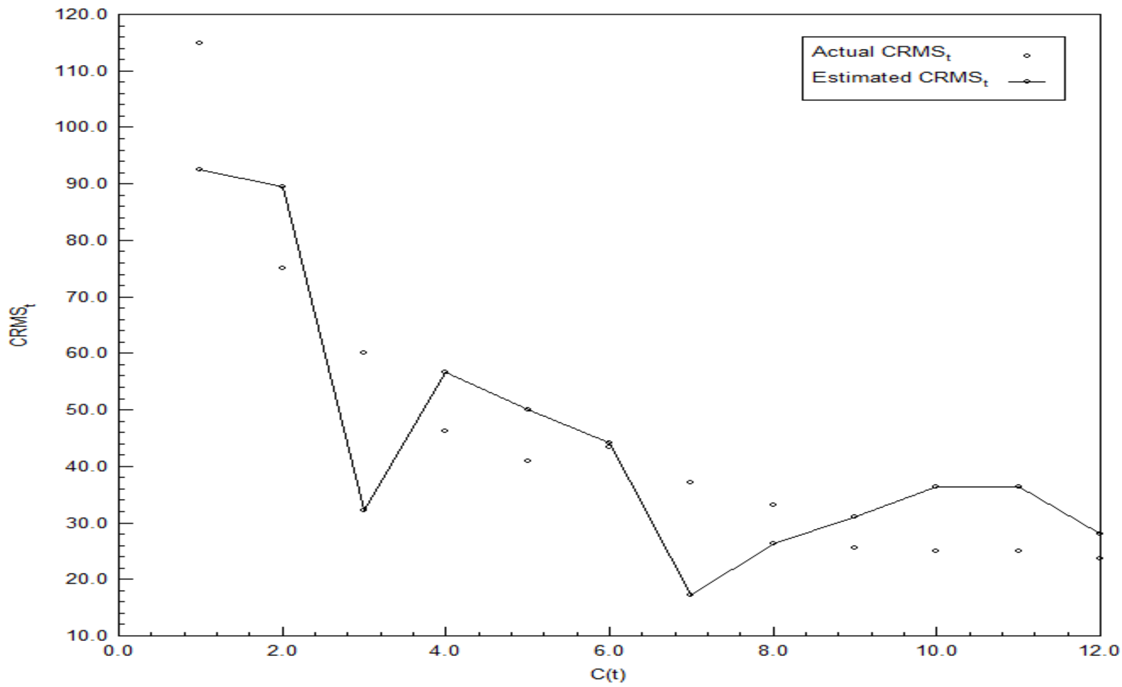

Figure 4.10: Comparison of Actual and Estimated Plots for Multivariate Model on Stainless Steel

CHAPTER 5

BI-VARIATE AND MULTIVARIATE MODELING FOR ALUMINIUM

The primary goal of the research was to determine the corrosiveness classification of West Wharf in Karachi Harbor by applying the ISO 9223 standard. In order to assess the corrosive nature of the location, test samples of Aluminium were exposed. This section presents an examination of the findings derived from the experiments conducted to measure the levels of chloride (Cl^-), sulphate (SO_4^{-2}), and total organic weight (TOW). The collected data for the study underwent statistical analysis to observe the fluctuations in the marine pollutant, which is the primary factor contributing to corrosion.

5.1 Assessing the Overall Behavior of Marine Pollutants using Aluminium

The statistical correlation between corrosion and concentrations of marine pollutants, as well as the Time of Wetness (TOW), is illustrated in the graph presented below. The graph depicts the relationship between the corrosion rate of Aluminium and the corresponding observed pollutant variables.

5.1.1 Correlation between Galvanised Steel and Pollutants

The correlation coefficients were calculated to determine the relationship between pollutants (sulphate (SO_4^{-2}) and chloride (Cl^-) along with Time of Wetness (TOW) and Aluminium. The resulting coefficients are presented in Table 5.1 below. A strong and positive correlation exists between chloride and sulphate, chloride and TOW, as well as sulphate and TOW. However, a moderate positive correlation is observed between Aluminium and chloride. Additionally, a weak positive correlation is identified between Aluminium and sulphate, as well as Aluminium and TOW.

Table 5.1: The correlation coefficients were calculated to analyze the relationship between different variables for Aluminium.

	GS	**Cl^-**	□□$_{□}^{-□}$
Cl^-	0.54		
□□$_{□}^{-□}$	0.1 8	0.82	
TOW	0.34	0.87	0.81

In Figure 5.1, the graph, along with the Nearest Neighbor Fit, illustrates the changing relationship between Aluminium and chloride ion concentration over time. The graph displays a curved pattern, with the highest Aluminium value of 5.01 on the X-axis and the lowest Aluminium value of 3.05. Similarly, the highest Chloride ion value of 4.68 is depicted on the Y-axis, while the lowest Chloride ion value is 3.89.

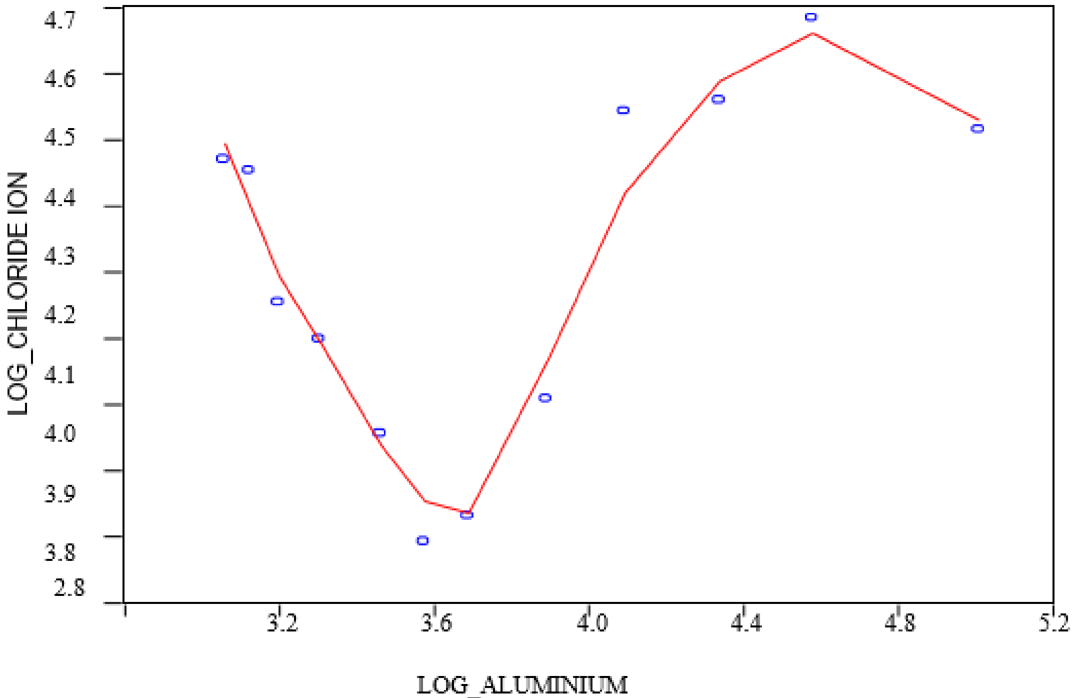

Figure 5.1: Exploring the Relationship between Aluminium and Chloride Ion Concentration: Scatter Plot with Nearest Neighbor Fit

Figure 5.2 displays the graph, along with the Nearest Neighbor Fit, illustrating the changing relationship between Aluminium and sulphate (□□$_4^{-2}$) concentration over time. The graph exhibits a curved pattern, with the highest Aluminium value of 5.01 on the X-axis and the lowest Aluminium value of 3.05. Similarly, the highest sulphate (□□$_4^{-2}$) value of 5.24 is depicted on the Y-axis, while the lowest sulphate (□□$_4^{-2}$) value is 4.61.

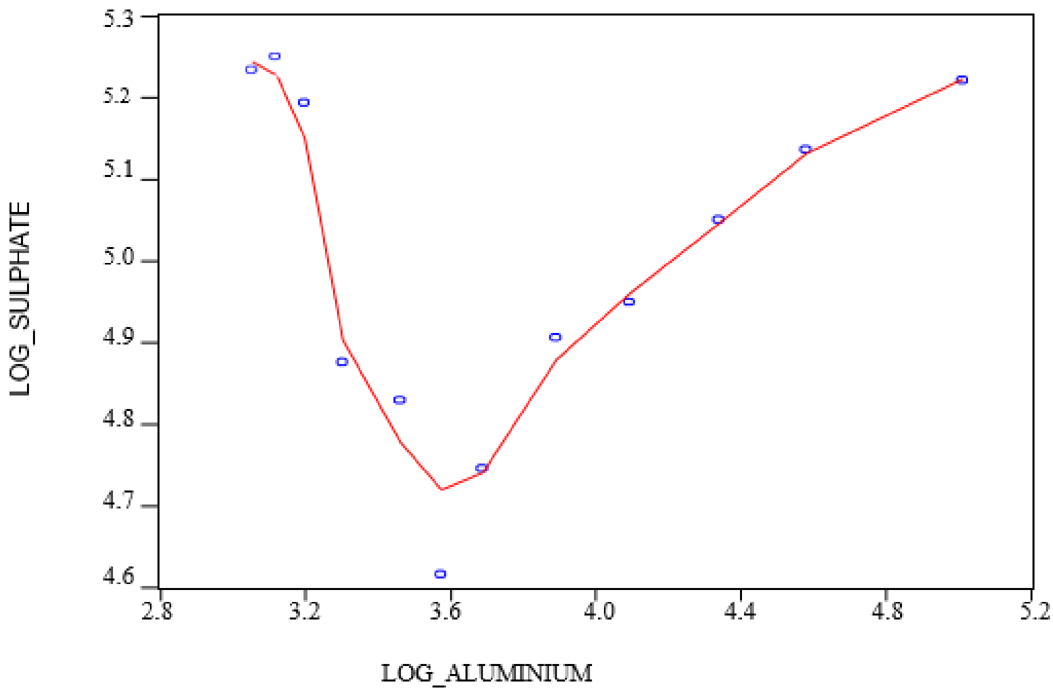

Figure 5.2: Examining the Relationship between Aluminium and Sulphate (SO_4^{2-}) Concentration: Scatter Plot with Nearest Neighbor Fit

Figure 5.3 shows the graph along with the Nearest Neighbor it shows the relationship between Galvanised steel and the Time of wetness changing with respect to time. This graph shows a curve having a maximum value of Aluminium is 5.01 lying on the X-axis and minimum value of Aluminium is 3.05 whereas the maximum value of TOW is 8.52 lies on Y-axis and the minimum value of TOW is 5.88.

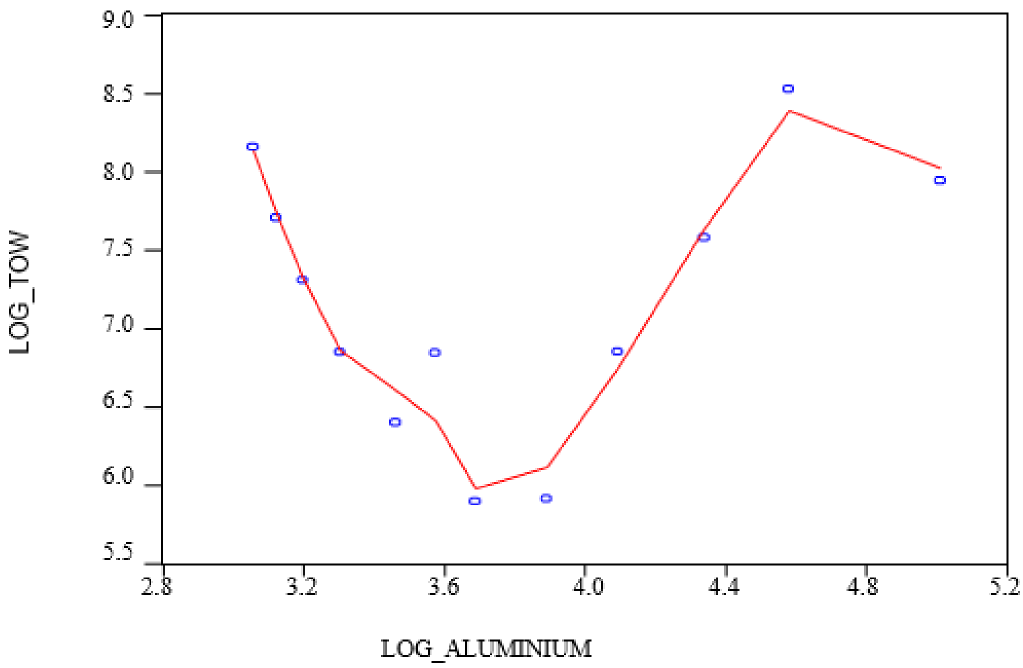

Figure 5.3: Illustrating the Relationship between Aluminium and Time of Wetness (TOW): Scatter Plot with Nearest Neighbor Fit

Figure 5.4 displays the graph, along with the Nearest Neighbor Fit, showcasing the relationship between Aluminium and marine pollutants (sulphate (SO_4^{-2}) and chloride (Cl^-), as well as Time of Wetness (TOW). The graph exhibits a curved pattern, with the maximum TOW value of 8.52 and the minimum TOW value of 5.88. Furthermore, the highest chloride ion (Cl^-) value of 4.68 and the lowest chloride ion value of 3.89 are depicted, along with the highest sulphate (SO_4^{-2}) value of 5.24 and the lowest sulphate (SO_4^{-2}) value of 4.61. The scatter graph indicates that TOW has a stronger correlation compared to the other pollutants, as its values are consistently higher.

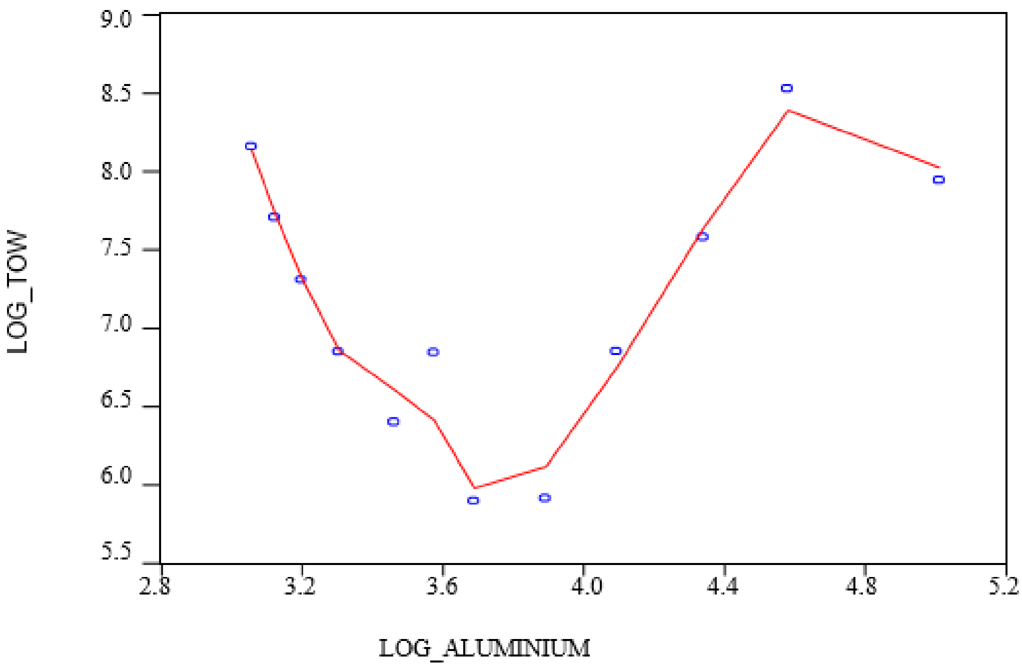

Figure 5.4: Exploring the Relationship between Aluminium and Marine Pollutants (Sulphate, Chloride) and Time of Wetness (TOW): Scatter Plot with Nearest Neighbor Fit

5.2 Bivariate Corrosion Modeling For Aluminium at Dockyard East

The bivariate corrosion rate model for Aluminium is established by performing a regression analysis, relating the observed corrosion rate to the exposure time ($\square_{\square}$) of the material under study. The resulting equation, along with important statistical measures, is presented below:

$$\square_{\square} = 16.41 + 523.12\square_{\square}^{-1.5} - 331.61\square_{\square}^{2} + \square_{\square} \qquad (5.1)$$

Std Error : (1.10) (20.12) (19.05)

t-stat : (16.99) (27.37) (-18.11)

p-value : (0.0012) (0.0012) (0.0012)

$R^2 = 0.98$

Here,

$\square_{\square}$ = Represented the corrosion accumulated on Aluminium

□□ = Represented the rate of corrosion

□□ = Represented the error column vector

R^2 = Represented the Coefficient of multiple determination

"Optimized Model Function: Key Measurements Illustrated in Table 5.2"

Table 5.2: Key measurements

Estimated Statistical Analysis	**Estimated Quantitative Assessment**
Proportion of Explain Variance	80.01%
Coefficient of Multiple Determination	0.80
Adjusted Coefficient of Determination	0.80
DW-Statistics	1.82
Residual Tolerance	0.0000000001

5.2.1 Assessment of Model Stability

The model's stability is achieved by employing error analysis techniques. The optimized model exhibits residuals that are independently and identically distributed. The following steps describe the stability of the model:

1. The coefficient of determination for the bivariate corroded Aluminium model indicates that 80.01 percent of the variance in the dependent variable is explained by the regressor.
2. The estimated statistical measures in Table 5.2 confirm that there is no presence of serial correlation between the error vector column.
3. The residual normal probability plot, as depicted in Figure 5.5, demonstrates that the residuals follow a normal distribution probability.

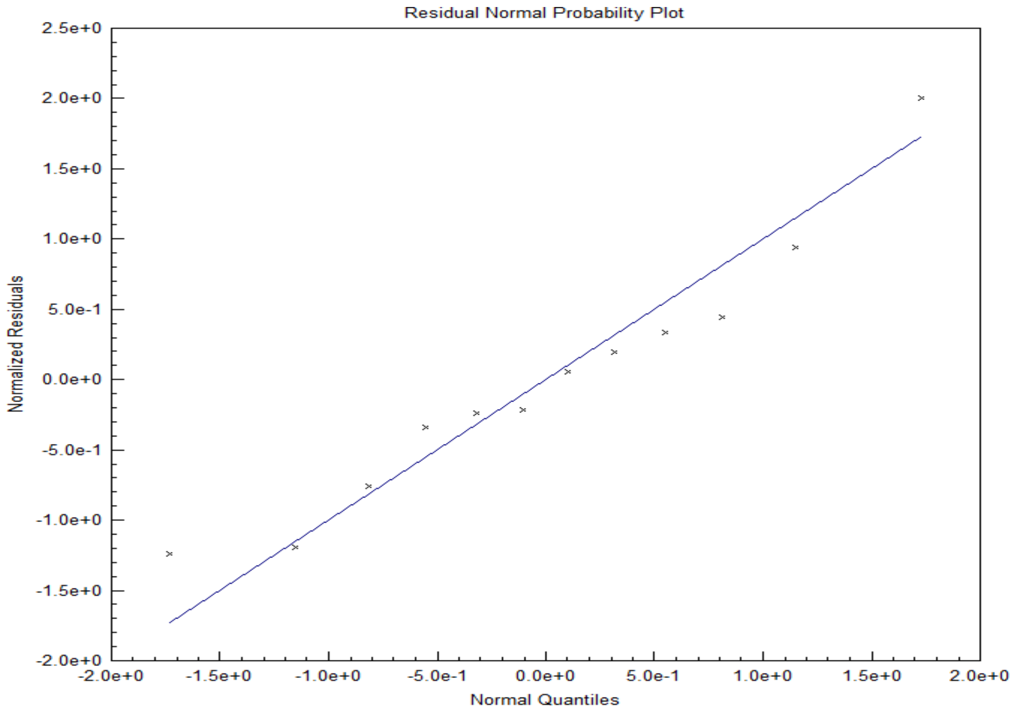

Figure 5.5: The probability of residual normality

1. Both the experimental and simulated plots exhibit similar behaviuor, providing evidence for the effectiveness and credibility of the model.

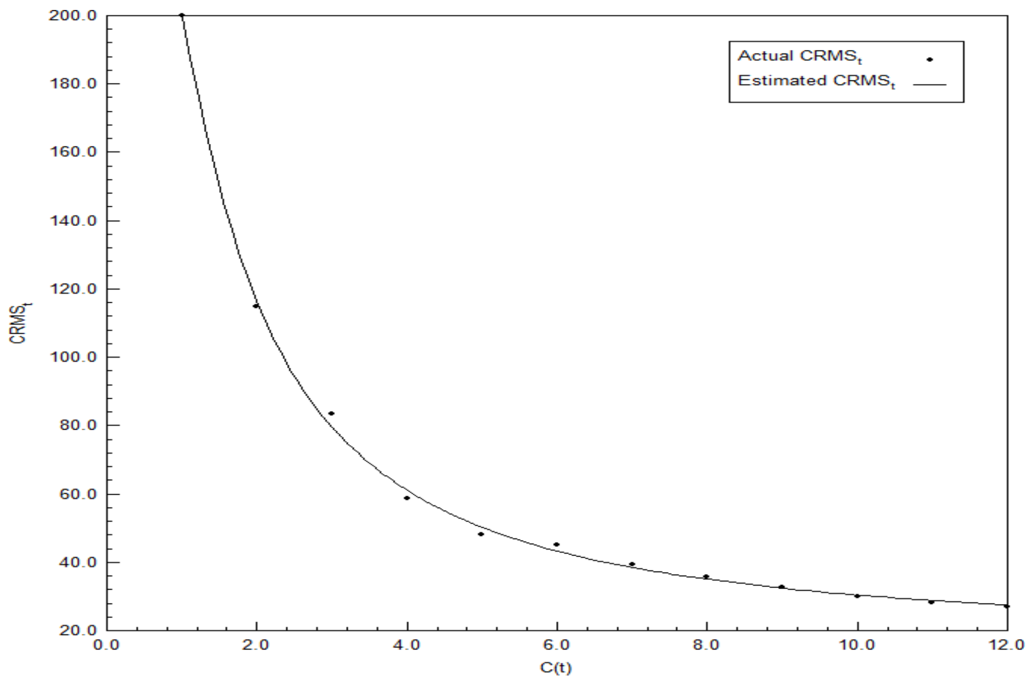

Figure 5.6: "Comparison of Bivariate Model for Aluminium: Actual vs. Estimated Plot"

5.3 Multivariate Corrosion Modeling For Aluminium at Dockyard East

Similarly, a multivariate relationship is established by performing a regression analysis of the corrosion rate of Aluminium with respect to Time of Wetness (TOW), sulphate ($\square\square_4^{-2}$), and chloride. The optimized nonlinear empirical relationship is as follows:

$$\square_{\square} = \square^{-3.47+0.045\square_{\square}+0.033\square_{\square}-4.35\square} + \square_{\square} \tag{5.2}$$

Std Error : (3.61) (1.42) (2.62) (1.8)

t-stat : (-1.6) (4.16) (1.82) (-3.01)

p-value : (0.21) (0.004) (0.16) (0.02)

$R^2 = 0.79$

Here,

$\square_{\square}$ = Represented the corrosion accumulated on Aluminium

$\square_{\square}$ = Represented the Chloride deposits

$\square_{\square}$ = Represented the Sulphate deposits

$\square_{\square}$ = Represented the error column vector

R^2 = Represented the Coefficient of multiple determination

"Optimized Model Function: Key Measurements Presented in Table 5.3"

Table 5.3: Key measurements

Estimated Statistical Analysis	**Estimated Quantitative Assessment**
Proportion of Explain Variance	79.68%
Coefficient of Multiple Determination	0.79
Adjusted Coefficient of Determination	0.79

DW-Statistics	1.91
Residual Tolerance	0.0000000001

5.3.1 Assessment of Model Stability

1. The coefficient of determination indicates that 79.68% of the variance in the dependent variable is explained by the regressor.
2. The residual normality probability plot shown below demonstrates that the residuals follow a normal distribution.

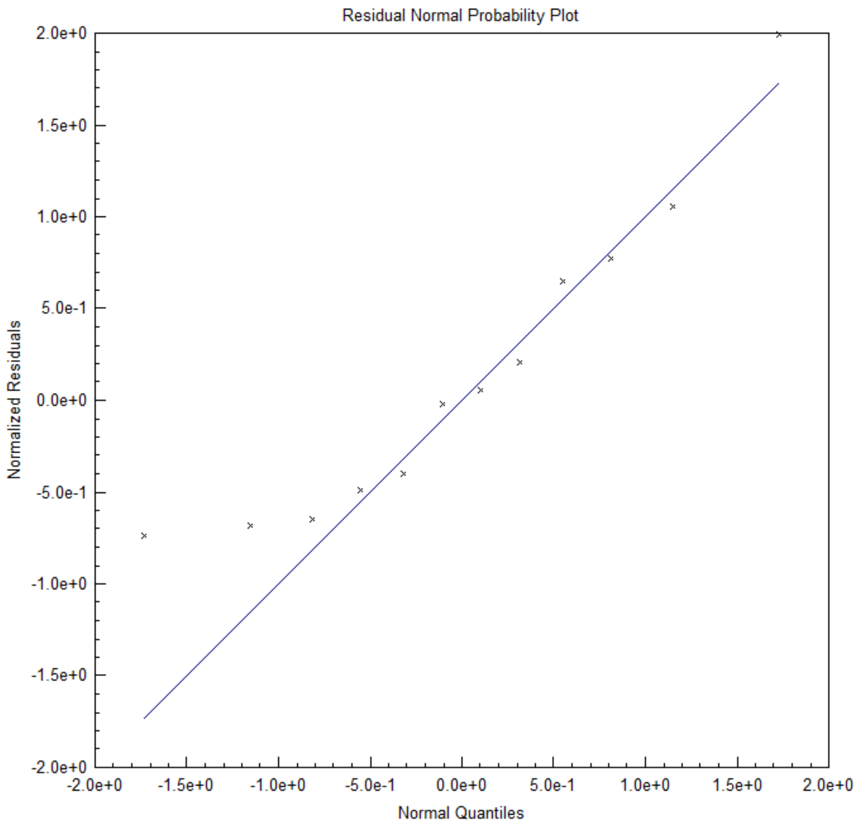

Figure 5.7: Residual normality probability

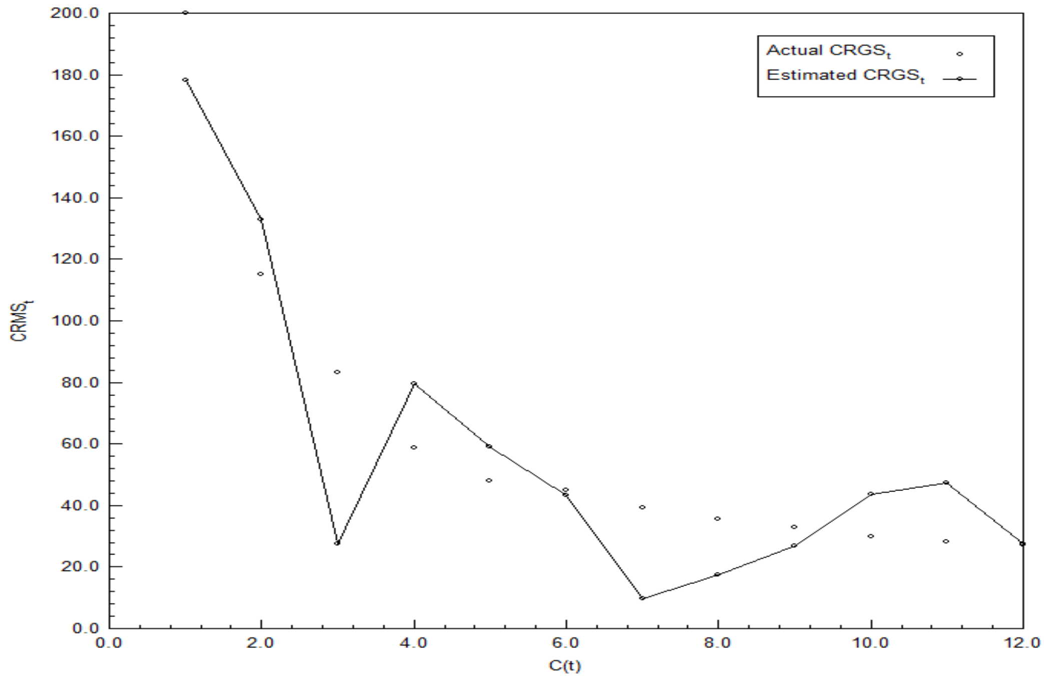

Figure 5.8: "Comparison of Multivariate Model for Aluminium: Actual vs. Estimated Plot"

CHAPTER 6

Summary and Conclusion

Karachi Harbor holds significant strategic importance as a primary trade gateway and due to its presence near key areas such as PICT, KICT, KS&EW, and naval properties. However, the harbor is prone to water corrosion due to the cyclical variations in the Arabian Sea and the presence of toxins, resulting in substantial economic and disruptive effects.

To address corrosion prevention measures for valuable properties in the area, an analysis was conducted to assess the marine corrosiveness at the West Wharf test site in Karachi. Mild and Aluminium test coupons were exposed to ISO 9223 conditions for a duration of 12 months. Several observations were made:

1. Pollutant measurements, including Cl− and SO_4^{-2}) concentrations, as well as TOW (Time of Wetness) concentration, were used to categorize corrosivity at the West Wharf. It was observed that the disparity in TOW was the highest compared to other pollutants, while the remaining pollutants exhibited a roughly Gaussian distribution.
2. Scatter graphs of the correlation coefficient between marine pollutants and Stainless Steel demonstrated that TOW exhibited a stronger correlation compared to other pollutants.
3. Similarly, scatter graphs of the correlation coefficient between marine pollutants and Aluminium revealed that TOW had a stronger correlation compared to other pollutants.

Corrosion models were developed using bivariate and multivariate statistical approaches for both mild and Aluminium. These models will be utilized to predict the corrosion rate of these materials at the West Wharf site.

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Furthermore, the study investigated the impact of marine corrosion and found that Aluminium exhibited greater resistance to corrosion compared to Stainless Steel. It was evident that corrosion resulted from the direct mixing of pollutants into marine water due to industrial and domestic activities. Given the rising levels of these activities, corrosion on both metals is increasing. It is recommended to install treatment plants in these industries and prevent the discharge of effluents into marine water.

6.1 Potential Future Directions:

The present work can be further expanded in the following ways to enhance its scope:

(i) The current study can be extended to evaluate the corrosivity in other maritime, commercial, and urban zones of Karachi, leading to the development of a comprehensive corrosivity map for Pakistan.

(ii) Corrosion rate calculations can be performed for additional materials such as Cu, Cu-Ni, Al, SS, and alloys, as well as for various superstructures, fixed structures, and moving systems in the vicinity of the Karachi port.

(iii) To investigate the long-term effects of corrosion on specific components, exposure times can be extended to 5-10 years, providing more insight into the durability and corrosion resistance of various materials.

(iv) Research and development efforts should be directed towards exploring and producing new protective coatings that offer improved corrosion resistance, specifically designed to safeguard critical properties and facilities against corrosive attacks.

By undertaking these future tasks, the understanding of corrosion dynamics can be further enhanced, leading to the development of more effective corrosion prevention strategies and the preservation of important infrastructure in marine environments.

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