



The Effect of Different Seawater Compositions on  
Surface Condition of Cu-Ni 90 /10

By

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## **Declaration**

None of the material contained in this thesis has been submitted in support of any application for another degree or qualification of this or any other university or institution of learning.

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## **Abstract**

The word corrode is derived from the Latin *corrodere*, which means “to gnaw to pieces.” The general definition of corrode is to eat into or wear away gradually. Whatever the form and the rate, corrosion is a major life deterring factor for all the machinery, equipment and installations. Corrosion however requires environment to complete the chemical reaction. In marine sector, effect and rate of corrosion is manifold primarily due to the harsh environment promoting corrosion. It is therefore imperative to find out the effects of the marine environment on corrosion propagation to reach solution to harness its detrimental effects. In this study, response of Cupronickel 90/10 is being examined after exposure in real time scenarios/conditions at two different sites at coast line of Pakistan having significant difference in seawater composition. The analysis of samples dipped at these two different locations has been done using both weight loss method and optical visualization to determine corrosion rate and surface condition. The results demonstrate that Cupronickel 90/10 being exposed to normal seawater condition has shown great resistance to corrosion in comparison to that being exposed at polluted seawater.

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## Chapter 1

### INTRODUCTION

#### **1.1 Corrosion and its Significance**

Corrosion, a natural occurrence, is applicable to all metals and alloys that engineers have to encounter carefully once dealing with marine applications and offshore machinery [1]. Generally, it is defined as the wear and tear in the materials' properties as an outcome of exposure with the surrounding atmosphere.

Examples for this occurrence is the formation of rust on metals like steel and iron, while, in the non-metallic category phenomena of rubber hardening, swelling in plastics etc are common observations. Experts suggest that corrosion is a reverse extract process, as, if we track back the basic elements; this process is converting the metal to its original components.

Individuals working on materials are suggested to be cognizant of the elementary awareness concerning corrosion and its prevention. The reason is that the corrosion is a natural process, causing harm and damage not only to economic, physical and other resources but a grave impact is also noted in terms of loss to the country's exchequer.

#### **1.2 Corrosive Environment**

Environment has got an important role to play for corrosion. All environments can be considered corrosive up to some extent [1,2]. List of environments considered critical for corrosion is as follows [3, 4]:

- a. Air and humidity
- b. Fresh, distilled, salt and marine water
- c. Natural, urban, marine and industrial atmospheres
- d. Steam and
- e. gases, like chlorine and Ammonia
- f. Hydrogen sulfide, Sulfur dioxide and oxides of nitrogen
- g. Natural fuel gases
- h. Acids and Alkalies

j. Soils



**Figure 1-1; Air and humidity [5]**



**Figure 1-2; Acids and alkides [5]**

It has been noted that that corrosion is having a notable impact which not only impart damages but further play a negative role for the economy of country. At the same time, heavy prices are to be paid for the unexpected failure at any plant / machinery because of corrosion.

### **1.3 Cost of Corrosion**

For the losses incurred because of corrosion there is a cost to pay. This cost is sub divided in two categories. The same are as follows [6].

#### **1.3.1 Direct Costs**

There following two factors have an impact on direct costs;

- a. The design process, manufacturing procedures or production costs being incurred for the material selection, such as the feasibility study conducted for selection of advanced plastics to replace Cupronickel 90/10. Direct costs are also affected while selecting material for anti-corrosive techniques, such as coatings, corrosion inhibitors etc. Costs catering manufacturing processes, production technology being utilized including labor, equipment and raw material will also have a direct impact on the overall cost.

- b. Consistent corrosion enquiry, post corrosion reinstatement, replacement of corroded components, holding cost of raw and finished inventory for replacement and down time observed during the production period comes under direct costs.

### **1.3.2 Indirect Costs**

Indirect cost includes either economic or social cost. This cost consists of any impurities being observed in finished good, seepages / leakages observed in pipes or tanks causing loss of natural resources or resulting in down time of plant / facility. Any damage incorporated to infrastructure or tangible assets such as in production plants will have an indirect cost.

Any country having dependency on industrialization will be highly affected due to corrosion in comparison to the one with less industrialization. The direct and indirect costs will be much higher than presumed for any industrialized country.

The developed countries of Europe being temperate face less effects of corrosion in comparison to Pakistan. The later face grave corrosion losses because of its hot and humid atmosphere. Pakistan, being a developing country has to focus and take precautionary measures to reduce the corrosion costs.

Corrosion, a shattering phenomenon has major financial, significant, and ecological losses as an outcome. In a jointly conducted study for corrosion costs [7-9], the losses encompassed due to erosion were approximately 15.2 percent of the national GDP.

## **1.4 Problem Statement**

At present, the sea ports of Pakistan handle 80% of the cargo (approx. 25 million tons per annum) of the country. These ports are supposed to be considered safe for marine operations but the extent of damage to ship bound / marine related machinery's metallurgy is on the rise as reported by the marine platforms operating in this region on regular basis. Considerable research work across the globe has been done to analyze the impact of seawater on Cupronickel 90/10. However, the evidence of any significant study on the effect of seawater chemistry on this alloy, in detail, was not found for the two main home ports of Pakistan i.e. Karachi and Gawadar / Ormara. This report will focus the same problem area.

## **1.5 Objectives of Research**

The research objectives are as follows:

- a. To determine the effect of different sea water compositions on corrosion rate of Cupronickel 90/10. This will be done by analyzing the sea

water compositions of two different sites at Karachi and Ormara and their impact on the alloy's surface. The impact on Cupronickel 90/10 is studied by observing the surface morphology through optical microscope. The behavior of these samples towards the corrosion resistance is observed.

b. To check the feasibility of the alloy being utilized in marine infrastructure; by estimating the useful life of Cupronickel 90/10. Corrosion rate in each sample is determined by already developed equation to determine the corrosion rate utilizing the weight loss method. In addition, equations to determine weight loss and corrosion rate will be developed for predicting the useful life of Cupronickel 90/10 in these two different locations.

c. To create a significant contribution towards study of corrosion on Cupronickel 90/10 to provide a suitable platform for opening future avenues.

## **1.6 Scope of Research**

The outcome of this research is anticipated to increase the acceptance level of concerned bodies / officials to adapt emerging techniques and alternate products for selection as well as implementation in the concerned areas / infrastructure. It is also expected that this research will elevate the priorities of the concerned authorities for rehabilitation of the polluted harbor. This in turn, will enhance the life expectancy of Cupronickel 90/10 for its safe usage in marine applications. This research is also expected to provide necessary guidelines for the safe usage of Cupronickel 90/10 while its usage in polluted sea water and its probable treatment.

## **1.7 Thesis Construction**

Chapter two elaborates the literature review conducted during this research study and encompasses the background knowledge and research already conducted on this alloy. Chapter three discusses the experimentation including the material and equipment utilized for this research. Chapter 4 elaborates the data gathered before and after the experimental study was conducted and analyses based on these readings. Chapter 5 highlights the conclusion and entails recommendation based on this experimental study for research to be conducted in future.

## Chapter 2

### LITERATURE REVIEW

#### **2.1 Factors Effecting Corrosion**

Corrosion cannot take place in the absence of any of the four listed components [10].

- a. Anodes
- b. Cathodes
- c. Electrolytes
- d. Conductors

The changed potency of electrolyte has a notable impact on corrosion rate [11]. Following factors, if not well calculated can speed up the action of a corrosion cell [12].

- a. Material
- b. Corrosive Environment

##### **2.1.1 Material**

If the material being used is having any kind of impurities, the corrosion rate will be higher than that of the pure material. The reason for this phenomenon is that the impurities become infinitesimal electrochemical cell and enhances the corrosion rate [12]. The physical properties e.g grain size also has an impact on the corrosion rate. The areas of material exposed to stress conditions have higher rate of corrosion.

The formation of oxide layer and its type governs the corrosion rate that if it is steady, unsteady, permeable etc. at the same time passive materials have the natural ability to form a thin protective layer on their surface. These materials offer more resistance to corrosion than anticipated from their location in the electrochemical series e.g. Titanium, Aluminum [12].

Corrosion products are the result of corrosion phenomenon. If they are not insoluble or certain volatility is observed in their nature, the corrosion rate will increase [12].

The oxidation potentials can be observed from the galvanic series. If a material is more anodic, the faster will be the corrosion rate. The material's position in galvanic series depicts its behavior. The higher the material in the galvanic series more anodic the material is. Galvanic series for metals is shown in Fig. 2.1.

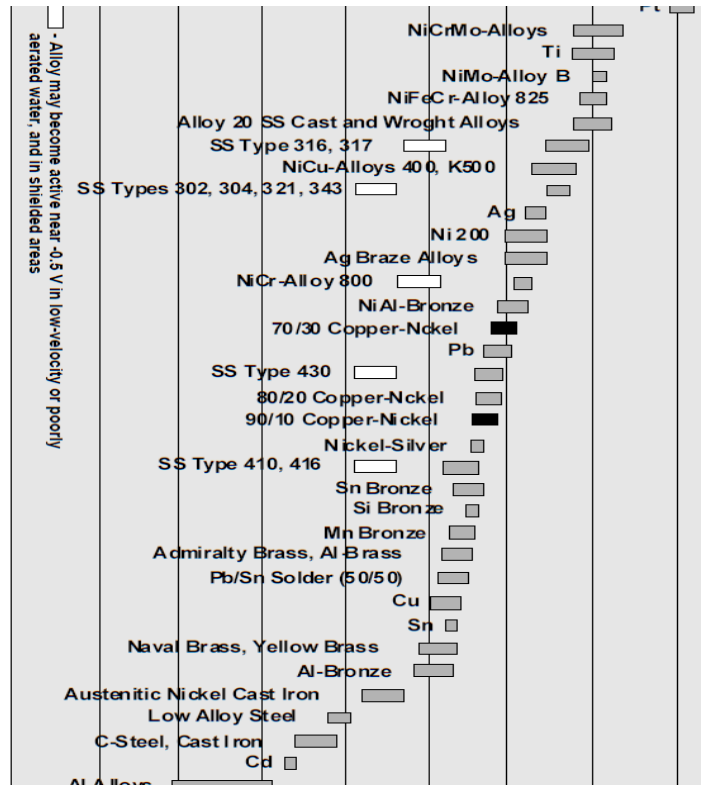


Figure 2-2-1 Galvanic Series [13]

### 2.1.2 Corrosive Environment

Following factors play a vital role on corrosiveness of environment [12];

- a. The temperature and corrosion rate are directly proportional to each other. so the corrosion rate increases with increase in temperature and decreases with temperature reduction.
- b. Oxygen content increases with increase in humidity level. And higher oxygen contents leads to higher corrosion rate. It can be stated that humidity has a direct impact on corrosion rate. Higher corrosion rate are observed in areas having industrial setups, provided with less protective environment. The corrosion rate also increases in the presence of pollutants such as acid rain, acid gases, and chlorides.
- c. The presence of chemical salts also enhances the corrosion rate. The electrolytic action increases due to the presence of these salts hence increasing the corrosion. Sodium chloride is one example

of chemical salt. At the same time, the lower pH values i.e. acidic atmosphere results in increased corrosion rate [12].

## 2.2 Corrosion Types

The corrosion type is generally dependent on the nature of corrosive atmosphere to which the material is exposed. The known types of corrosion are as follows.

### 2.2.1 Uniform Corrosion

The very commonly observed type is uniform corrosion. It is also recognized as general corrosion [14, 15]. Figures 2-2 and 2-3 depicts the uniform corrosion. Uniform corrosion typically starts from the surface and results in metal deformation because of electrochemical reaction. Materials can easily be protected against this type of corrosion.

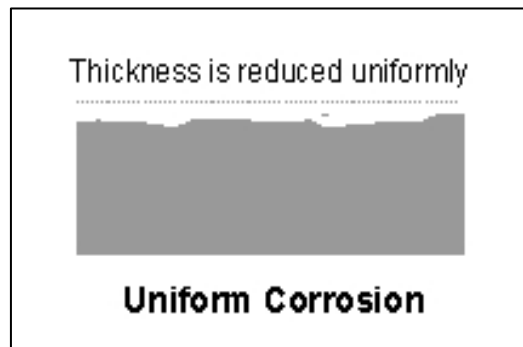


Figure 2-2; Uniform corrosion on metal surface [14]



Figure 2-3; Uniformly corroded surface [15]

### 2.2.2 Galvanic Corrosion

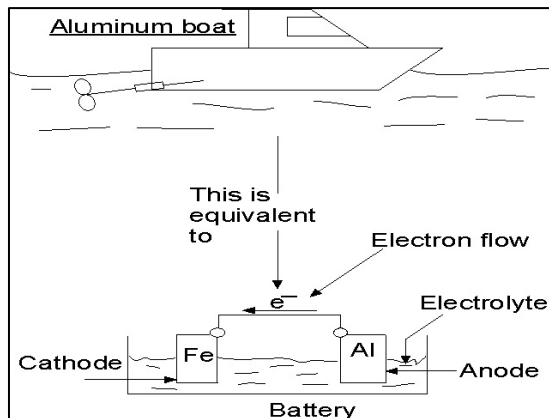
When two different metals are employed together, the type of corrosion being observed is known as galvanic corrosion. Reason for this corrosion to take place is that the materials in contact have different electrochemical charges



[16–18]. This results in conduction to occur when these materials have electrically established contact.

One of the materials becomes anode and the other acts as cathode. Initially, corrosion starts at the anode, whereas cathodes are located at the oxygen decreasing spots [19, 20]. Figures 2-4 and 2-5 depict galvanic corrosion.

This type of corrosion generally occurs in corrosive environments having high chloride contents. The common sites are related to marine atmosphere.



**Figure 2-4; Galvanic corrosion process [19]**



**Figure 2-5; Galvanized surface [19]**

### 2.2.3 Caustic Agent Corrosion

When the material is exposed to contaminated liquids, solids or gases, this type of corrosion takes place [20]. If the material is kept dry, these gases or liquids do no harm to the material but the humid atmosphere act as a catalyst

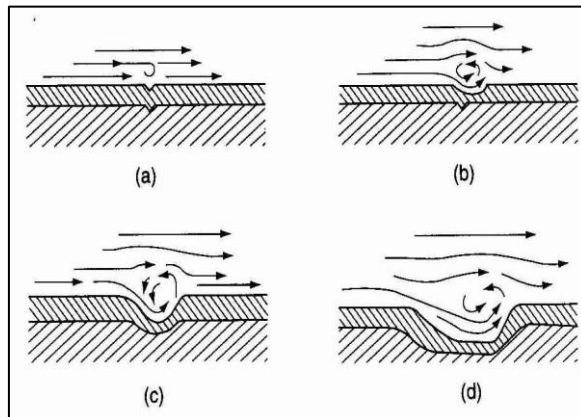
and ignites this type of corrosion. The formation of hydrogen sulfide is one of the examples of caustic agent corrosion. Figure 2-6 depicts this type of corrosion on metal surface.



**Figure 2-6; Caustic corrosion [20]**

#### **2.2.4 Erosion Corrosion**

The movement of liquid with respect to the stationary material's surface causes this type of corrosion [21–25]. This is shown in Figs. 2-7 and 2-8.



**Figure 2-7; Erosion corrosion process [24]**

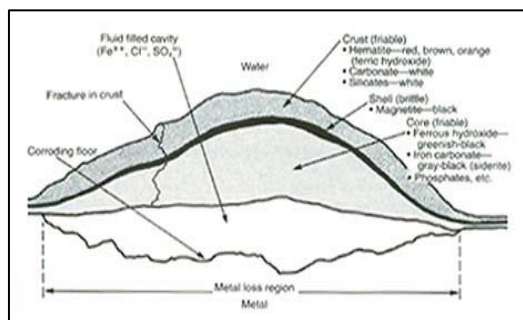


**Figure 2-8; Eroded metal surface [25]**

### 2.2.5 Microbiologically Influenced Corrosion (MIC)

There are two kinds of microbes which enhances the corrosion. These two types are Acid Producing Bacteria (APB) and Sulfate Reducing Bacteria (SRB). These microbes live in a colonial setup and are affixed to the material's surface where they assist each other in their growth [26, 27]. This type of corrosion occurs due to presence of localized pitting under the film formed by these microbes [28-37]. Ferrous material is formed inside these pits [38–40]. Figure 2-9 shows evolution of MIC process while Fig. 2.10 depicts the surface attacked by microbes.

This type of corrosion may also occur in the presence of Sulphur contents in tanks utilized for storage of crude oil [41, 44].



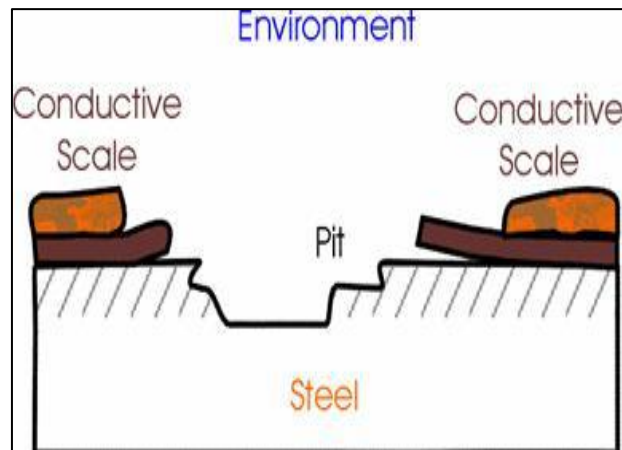
**Figure 2-9; MIC corrosion process [43]**



**Figure 2-10; MIC corrosion on heating oil tank [44]**

## 2.2.6 Pitting

In this type of corrosion, tiny holes are formed at scattered locations on the surface of material. The remainder of the surface is slightly affected or not at all. It is also known as localized corrosion [45–49]. The electrochemical process for this type of corrosion is shown in Fig. 2-11. The pictorial evidence of pitting is shown in the Fig. 2-12.

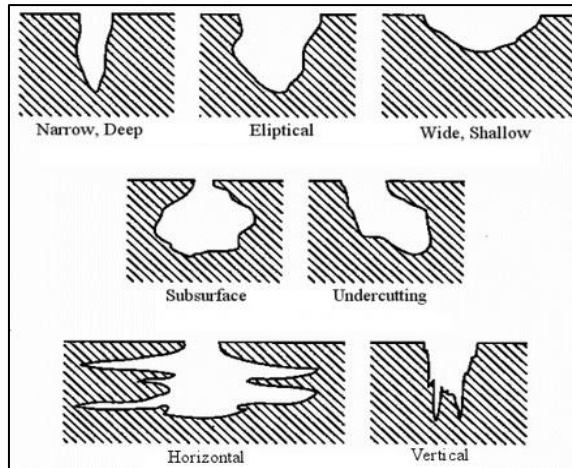


**Figure 2-11; Pitting process [48]**



**Figure 2-12; Pits on metal surface [49]**

The pits formed on any of the metal's surface are never uniform. It has been noted that these pits adopt different shapes [50]. These shapes are shown in Fig. 2.13.



**Figure 2-13; Pitting shapes [50]**

### **2.3 Marine Environment and Cupronickel 90/10**

Design engineers generally have to consider corrosion when dealing with selection of appropriate metals for marine infrastructure. It is prudent to mention that no such material weather a metal or synthetically developed products are safe from the devastating effects of corrosion [51].

Corrosiveness of any atmosphere can be appreciated by the presence of moisture content in it. Marine environments are generally corrosive for mild and low alloy steels. Due to comparatively better sustenance in sea water, the variants of Cupronickel are widely utilized in the desalination plants and in related marine engineering infrastructures [51]. Cupronickel alloys, generally contain 10 or 30% nickel and minor ratios of iron and manganese. These alloys are generally employed for heat transfer tubes and also for marine related pipework. These alloys are generally well recognized, however, they have certain restrictions while offering opposition to rapidly flowing / impinging sea water [52–54]. Despite this fact many marine industries use Cupronickel as a major element in its machineries because of high resistance against corrosion.

The oxidation rate is proportional to the oxygen content in the environment of sea water. Higher the oxygen content in marine atmosphere, higher will be the corrosion rate, which ultimately leads to faster degradation of concerned materials and alloys [50]. Alloys are significantly utilized to maintain the materials integrity against erosion in marine atmosphere. To ensure structural integrity of marine infrastructure, the understanding of corrosion resistance phenomena is considered a necessity.

### **2.4 Corrosiveness of Seawater**

Sea water entails about 70% of the surface of earth and it is presumed to be vastly corrosive in nature [55]. The sea water properties vary with one another and are dependent on geographical locations, weather conditions, and depth of the sea. It

has also been observed that the corrosiveness of sea water is dependent on mineral content of the sea water. Meanwhile, the presence of elements like chlorides, sulphates, low pH, dissolved oxygen, high conductivity, bio fouling, effects the corrosiveness of seawater [56,57].

Gardiner and Melchers [58] suggested that immersion time, salt deposition and temperature influence the corrosion rates. They established that atmospheric corrosion are directly dependent on temperature and salt deposition. When oxides are deposited on the surface, corrosion occurs on the material's surface. And when these oxides gain more potential, it results in pitting [59]. The marine environment marine is distributed in five zones. They include subsoil zone, fully submerged zone, tidal zone, atmospheric zone and splash zone. Corrosion rate for each zone will be different from one another. In submerged zones, pitting and crevice corrosion are commonly observed [60]. The salinity of sea water, sea water temperature and wind speed are major factors having an effect on corrosion rate [61]. The only possible solution to avoid corrosiveness of sea water is to eradicate the excessive salt contents which not only enhances the corrosion rate but ultimately results in complete failure of a material [62].

The composition of sea water fluctuates with its depth hence resulting in changing behavior of metals with respect to corrosion and resistance offered against corrosion at different depths. However, in case of cupronickel, the alloys demonstrates an unexpected response as the corrosion rate depends on dissolved impurities like sulphates [63].

A formula was derived by Mars G Fontana [64] to calculate corrosion rate using weight loss measurement for Cupronickel 90/10 and associated alloys which is;

$$CR_{(mmpy)} = 87.6 \times (W/DAT) \quad (2.1)$$

Where

W= Weight loss in Milligrams

D= Metal density in grams/cm<sup>2</sup>

A= Area of sample in cm<sup>2</sup>

T= Exposure Time of sample at seawater in hours

## 2.5 Corrosion Tests

The tests are conducted for corrosion are depicted in table 2.1.

<b>S No</b>	<b>Tests</b>	<b>Application Scale</b>	<b>Purpose</b>
1.	Laboratory test	Samples of corrodents	As Screening tests
2.	Pilot-plant tests	Small-scale plant	For more precision
3.	Plant tests	Operating plant	Evaluate and observe corrosion behavior of existing materials
4.	Field tests	On field tests	To obtain general corrosion information

**Table 2-1; Corrosion Tests**

Following are the important features to understand while studying corrosion;

- a. The selection of an alloy for a specific environment and its analysis.
- b. Assessing the metals / alloys compatibility to changing environments.
- c. Data gathering of metal's corrosive as well as anticorrosive nature in the environment under exposure.
- d. Study of corrosion tests, which can lead to aid other research and development processes.

## **2.6 Corrosion Protection Techniques**

Following are methods to prevent corrosion;

### **2.6.1 Active Corrosion Protection**

This protection is concerned with the reaction aiding in corrosion. It holds the chemical action so that the phenomenon of corrosion halts. Alloys having high resistance for corrosion and corrosion inhibitors are utilized in this type of protection [65].

### **2.6.2 Passive Corrosion Protection**

If the metal or alloy is separated from the surrounding atmosphere, the corrosion rate can be reduced [65]. This is primarily achieved by inserting a protective coating between the metal and the atmosphere. The problem arises when the protective layer gets deteriorated.

### **2.6.3 Permanent Corrosion Protection**

It handles the corrosiveness of the metals or alloys [65]. Plating, enameling etc. are the examples of this type of protection.

## 2.6.4 Temporary Corrosion Protection

The common temporary corrosion protection methods are application of protective coatings [65].

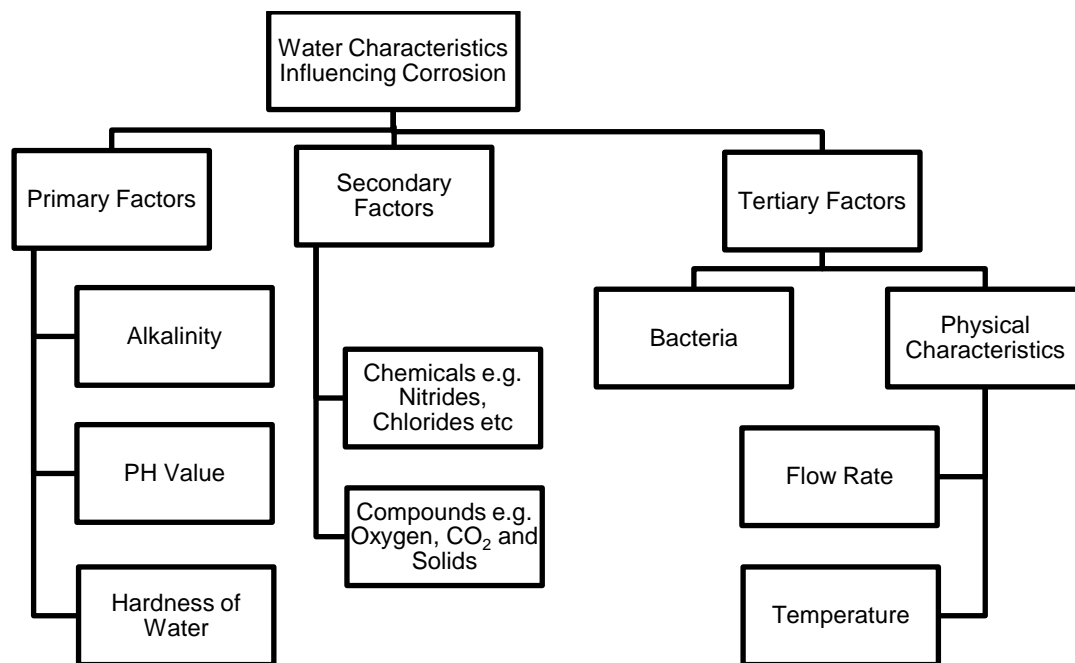
## 2.7 Sea Water Characteristics Influencing Corrosion

The characteristics of sea water do have a certain impact on corrosion rate. These factors are illustrated in the Fig. 2-15.

### 2.7.1 Primary Factors

Alkalinity, hardness of water and pH are the primary factors.

- a. Low pH value increases the corrosiveness of sea water.
- b. If sea water is soft in nature, then calcium will not penetrate and sulfates will increase the corrosiveness.



**Figure 2-14; Water characteristics influencing corrosion**

- c. Alkalinity depicts a moderating effect but for sea water having low alkalinity can easily convert to acidic in nature and increase and corrosiveness.

### 2.7.2 Secondary Factors

The impurities like CO<sub>2</sub>, O<sub>2</sub> and dissolved solids present in sea water are known as secondary factors.



- a. Oxygen increases the corrosion rate, so sea water having dissolved oxygen are more corrosive than the one with less dissolved oxygen. Carbon dioxide also increases corrosiveness of sea water. It combines with sea water and forms carbonic acid which ultimately results in lowering the pH value.
- b. Dissolved solids in sea water gives rise to electrical conductivity, it in turns, force the electrolyte to have more influence and hence increasing the corrosiveness.

### **2.7.3 Tertiary Factors**

- a. Physical characteristic of water

1. Temperature has a significant impact on corrosiveness but its impact on corrosion rate is complex. The solubility of calcium carbonate reduces with increase in temperature, hence resulting in formation of scales which ultimately causes reduction in corrosion rate. High temperature reduces the corrosion process.

2. Flow velocity also plays a complicated role in corrosion. A standard flow rate enhances formation of scale thus reducing the corrosiveness. Corrosion enhances with decrease in velocities. At high velocities, the material depicts wear and tear. In this condition, if the protective film is removed, the corrosion rate increases as the material is exposed to oxygen contents.

- b. Effect of bacteria

The presence of bacteria not only enhances corrosion rate but they actually hasten the phenomenon. Some bacteria generates  $\text{CO}_2$ , which in collaboration with water generates carbonic acid. This process increases the corrosion rate.

## **2.8 Application of Alloys in Marine Environment**

The selection of a suitable material for seawater service is a challenging assessment that has to be finalized by the design engineer prior the system's specifications are made [66]. The effect of seawater on performance of any alloy is defined by a number of variables which includes material condition, system design, manufacturing / fabrication procedure, various variables such as seawater temperature, flow patterns, biological activity and presence of oxidizing compounds. For better understanding, factors including physical and mechanical properties, accessibility, material costs, ease of fabrication / manufacturing, maintenance, projected design-

life and previous design experience are to be considered while selecting an alloy for utilization in marine systems [66].

### **2.8.1 Use of Copper as Base Metal**

Copper, a naturally occurring metal, being extracted from earth since decades, is considered essential for the growth of all forms of advancement and has been playing a pivotal role in the development of mankind [67]. Copper, is one of the oldest metals being used and its use is tracked back for more than 10,000 years.

Copper along with its alloys, either in wrought or cast forms, are well known for offering more resistance to corrosion and its effects once utilized in marine environment. Sea water is corrosive in nature for almost every metal and over the years the design engineers have developed numerous alloys with improved properties to overcome challenges being encountered. Copper alloys have offered significant contribution to design engineers while overcoming the problem being faced due corrosion in marine applications [67].

Copper as a stand-alone metal has found to be very adaptable; it has been found that this metal offers significant corrosion resistance in sea water with moderate flow velocities. This natural ability of copper against corrosion and mechanical properties were later enhanced by introduction of copper's alloys [67]. A number of variants of copper alloys including their main groups are shown in Table 2-2.

For marine application, copper-nickel and aluminum bronze are chosen often as they offer specific advantages over other alloys. Copper alloys are preferred over other metals and alloys as they have an intrinsic high resistance to biofouling, particularly macrofouling, which removes the need for antifouling coatings or water treatment [67].

Copper Development Association publication [68] describes a more detailed interruption of standards, compositions and properties. Typical applications for marine environments include heat exchangers and condensers, seawater piping, hydraulic tubing, pump and valve components, bearings, fasteners, marine fittings, propellers, shafts. The alloy groups, and alloys within each group, are described in Table 2-2.

<b>Alloy Group</b>	<b>Alloy Types</b>
Coppers	Cu
Copper-nickels	Cu-Ni 90-10
	Cu-Ni 70-30
	Cu-Ni-Cr
	Cu-Ni-Sn
	Cu-Ni-Al
Bronzes	Cu-Sn-P (phosphor bronze)
	Cu-Sn-Zn (gunmetal)
	Cu-Al (aluminum bronze/nickel aluminum bronze)
	Cu-Si (silicon bronze)
Brasses	Cu-Zn
Copper-beryllium	Cu-Be

**Table 2-2; Alloy Groups [68]**

### **2.8.2 Use of Cupronickel 90/10**

Since decades, thousands of tons of copper-nickel alloys have been mounted in several marine infrastructures for shipbuilding, offshore applications, power and desalination industries [66]. CuNi 70/30 is primarily being used in submarines as this alloy has higher strength, low magnetic permeability while having maximum allowable flow rate. However, the use of this alloy is limited due to very high material cost. As an alternate, CuNi 90/10, delivers a stable equation being cost effective and having the characteristics for its wide commercial and economical applications [66].

The copper-nickel alloy systems are simple in comparison with other alloys, as the physiognomies of copper in terms of strength and corrosion resistance are improved in addition to its natural ability to resist biofouling. Cupronickel 90/10 (C-70600) is the most frequently used copper based alloy for marine applications and the same is available in commercial and naval shipping, offshore oil and gas productions and other shore based marine applications [67].

To offer better resistance to flow conditions, abrasion due to presence of sand particles, and to have higher mechanical properties and castability, copper alloys are used with high nickel content inclusive of Tin, Aluminum and Chromium [67]. The application of copper-nickel alloys are shown in Table 2-3. These alloys are generally divided in two main groups: the general engineering grades (having 90-10 and 70-30 copper-nickel alloys) and the high strength grades (having Cr and Al in addition with Cu and Ni) [67].

<b>Alloy</b>	<b>Applications</b>
<b>General Engineering</b>	
90-10 Cu-Ni and 70-30 Cu-Ni	Seawater cooling and firewater systems, heat exchangers, condensers and piping, offshore platform leg and riser sheathing, MSF desalination units, aquaculture cages and boat hulls
Cu-Ni-Cr	Wrought condenser tubing  Cast seawater pump and valve components
<b>High Strength Copper-Nickels</b>	
Cu-Ni-Al	Shafts and bearing bushes, bolting, pump and valve trim, gears, fasteners
Cu-Ni-Sn	Bearings, drill components, subsea connectors, valve actuator stems and lifting nuts, subsea manifold and ROV lock-on devices, seawater pump components

**Table 2-3; Application of Copper-Nickel Alloys [67]**

Table 2-4 shows the composition of Copper-Nickel alloys while Table 2-5 shows the mechanical properties of the same.

<b>Alloy</b>	<b>EN No or Other Identification</b>	<b>UNS No</b>	<b>Cu</b>	<b>Ni</b>	<b>Fe</b>	<b>Mn</b>	<b>Al</b>	<b>Sn</b>	<b>Other</b>
Cu-Ni	CW352H	C70600	Rem	10	1.5	1	-	-	-
	CW353H	C71640	Rem	30	2	2	-	-	-
	CW354H	C71500	Rem	30	0.7	0.7	-	-	-
Cu-Ni-Cr	Def Stan 02-824 Part 1	-	Rem	30	0.8	0.8	-	-	1.8Cr
	-	C72200	Rem	16	0.7	0.7	-	-	0.5Cr
Cu-Ni-Al	Nibron Special™	-	Rem	14.5	1.5	0.3	3	-	-
	Def Stan 02-835	C72420	Rem	15	1.0	5	1.5	-	0.4Cr
Cu-Ni-Sn	-	C72900	Rem	15	-	-	-	8	-

**Table 2-4; Composition of Copper-Nickel Alloys [67]**

Alloy	EN No or Other Identification	UNS No	0.2% Proof Strength N/mm <sup>2</sup>	Tensile Strength N/mm <sup>2</sup>	Elongation %	Hardness HV
Cu-Ni	CW352H	C70600	100-350	290-420	12-40	80-160
	CW353H (tube only)	C71640	150 min	420 min	30 min	110
	CW354H	C71500	130-450	350-520	12-35	90-190
Cu-Ni-Cr	Def Stan 02-824 Part 1	-	300 min	480 min	18 min	-
	-	C72200	110 min	310 min	-	-
Cu-Ni-Al	Nibron Special™	-	555-630	770-850	12 min	229-240
	Def Stan 02-835	C72420	400 min	710 min	18 min	170
Cu-Ni-Sn	-	C72900	620-1030	825-1100	2-15	272-354

**Table 2-5; Mechanical Properties Copper Nickel Alloys [67]**

### 2.8.3 General Corrosion on Cupronickel 90/10

As Cupronickel 90/10 acts as cathodic to the hydrogen electrode so its behavior for corrosion primarily depends on the oxygen content including other oxides in seawater. Once this alloy is exposed to sea water, a film of cuprous oxide is formed on its surface which offers significant protection to the alloy against corrosion. Due to the presence of multiple oxide layers, the corrosion rate decreases instantly [67]. In addition, Saleh A et al. [68] stated that cupronickel 90/10 is prone to higher corrosion rate in seawater while fully submerged.

In the longer run, CuNi 90/10 has shown continuous decrease in corrosion rate with increase in exposure time to seawater. It has been observed that the corrosion rate for this alloy has been below 2.5  $\mu\text{m}/\text{yr}$  [66]. For seawater having temperature ranges from 15-17°C, the oxide layer generally takes 27-35 months to mature. However, for temperature ranges above 27°C (Middle East and Arabian Gulf), this protective films matures within hours starting from time to exposure [66].

### 2.8.4 Effect of Polluted Seawater on Cupronickel 90/10

CuNi 90/10 is believed to have higher corrosion rates and premature failures in presence of hydrogen sulfides which initiates the Sulfate Reducing Bacteria (SRB). B.C Syrett et al. [69] demonstrated that hydrogen progression is primarily responsible for corrosion free CuNi 90/10 in sulfide free seawater. In

contrary, seawater having sulfide content, a non-protective cuprous sulfide film is formed on the alloy making it susceptible for erosion attack.

## **Chapter 3**

### **EXPERIMENTATION**

The conducted experiment for this research is briefly elaborated in this chapter.

#### **3.1 Design of Experiment (DOE)**

At present, Design of Experiment (DOE) is highly recognized as a significant tool for the validation process [70]. The defining of statistical methods, designing the experiment and to perform the analysis, "Design of Experiment" is utilized. DOE is used to demonstrate the effect of variables which may be one or more on the organized outcome of the experiment being conducted. The DOE has following types [71, 72]:

a. Single Factor:

It is used to establish the reaction of only single factor. The factor might be either qualitative or quantitative in nature.

b. Two Level Trial:

It is also recognized as screening trial. It is used to establish the critical factors for enhanced research.

c. Factorial Design:

It is used to enhance the efficient experimentation. This is being achieved by investigating multiple factors at one time.

d. Taguchi Method:

It is utilized to design robust procedures by minimizing the variation in product [73].

e. Mixture Method:

It is utilized to determine product formulation techniques.

f. Response Surface Model:

It is utilized to determine impact of varying factors which may be two or more across a range of different values.

Following are the benefits obtained by adopting DOE [74]:

- a. Effective utilization of resources including time, machine, material, etc.
- b. In depth analysis.
- c. Provide statistics pertaining to errors
- d. Forecast systems proficiency.

### **3.2 Experimental Setup**

The material under consideration is Cupronickel 90/10 (UNS No C-70600). Eight samples of the acquired material were cut to obtain the approximate measurements of 30mm x 30mm x 2mm. Four samples, later referred as coupons were dipped at two main ports of Karachi and Ormara each. It is important to note that these coupons were fully submerged and were exposed to real time scenarios in sea water at these two ports.

Once the coupons were ready, the weight was noted of each by using analytical weighing scale having ability to measure the weight in micrograms. Four coupons were dipped simultaneously at Karachi and four at Ormara. The exposure time for first coupon on each site was fifteen days. Similarly, the remaining coupons on each site were recovered with a gap of fifteen days after the removal of previous sample.

Upon recovery of these coupons from sea water, they were cleaned in accordance with the ASTM standards to remove the corrosion products for measurement of exact weight loss. For this chemical cleaning, ASTM Standard "G1 – 03 Reapproved 2011" (Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens) [75] was used. Once the samples were chemically cleaned, the weight of each coupon was noted using the analytical balance. This resulted in obtaining the weight loss of each coupon. This weight loss was ultimately utilized to determine the corrosion rate of Cu-Ni 90/10.

### **3.3 Utilized Equipment**

The equipment utilized for this research is as follows;

- a. Optical microscope
- b. Infinity software
- c. Analytical balance
- d. Cupronickel 90/10 (UNS-C70600)
- e. Abrasive cutter



- f. Digital Vernier caliper
- g. Sea water (Karachi and Ormara)

### **3.4 Assumptions**

During the course of experimentation, assumptions made are as follows;

- a. Constant temperature and Pressure was assumed throughout the exposure time.
- b. The sea water temperature at both sites is similar.
- c. The corrosion impact on area under consideration is similar to that of the whole area of the coupon i.e. area of inspection is homogeneous.
- d. The effect of sea water on Cupronickel 90/10 is considered similar at Ormara and Gawadar as they have similar sea water compositions.
- e. The sea water compositions remained similar at each site during period under review.

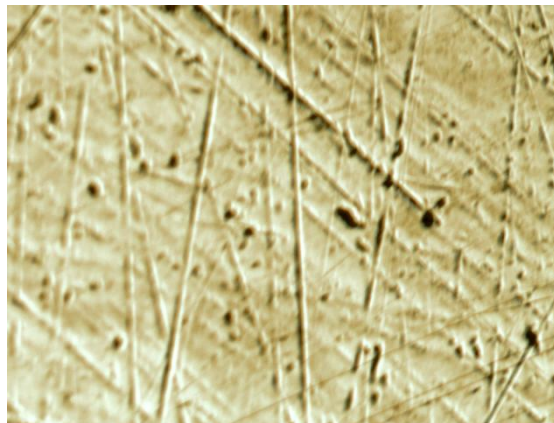
## Chapter 4

### DATA COLLECTION AND ANALYSIS

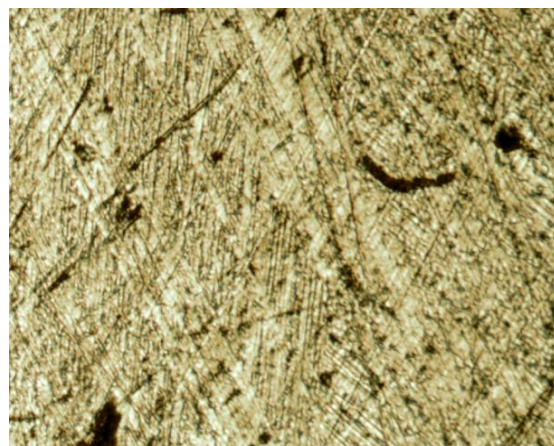
This chapter entails the method adopted for collection of data and analyses conducted during the course of study.

#### **4.1 Data Collected Before Experiment**

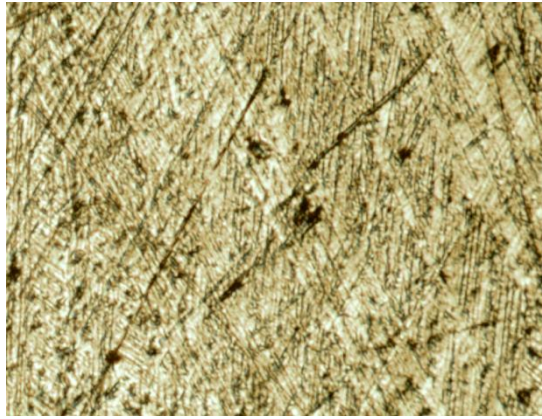
Once the coupons were cut into required size with help of abrasive cutter, images of all the eight coupons i.e. four for Karachi (Site 1) and four for Ormara (Site 2) were taken from optical microscope with help of infinity software. Figures 4-1 to 4-4 are the images of coupons 1 to 4 dipped at Karachi harbor.



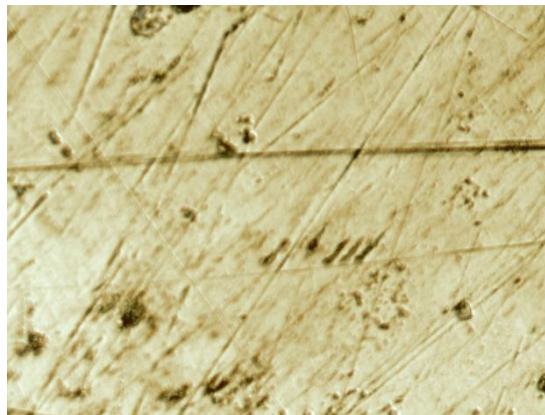
**Figure 4-1; Microscopic view of Coupon 1 for Site 1**



**Figure 4-2; Microscopic view of Coupon 2 for Site 1**

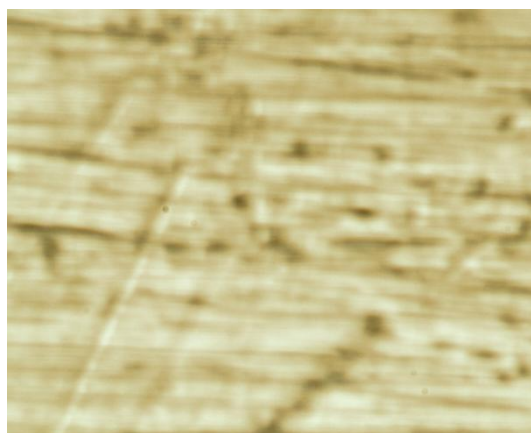


**Figure 4-3; Microscopic view of Coupon 3 for Site 1**

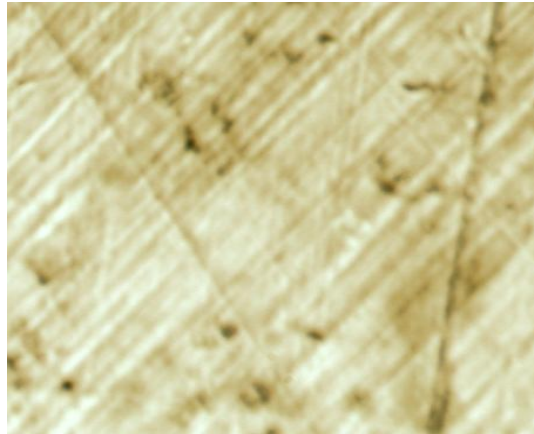


**Figure 4-4; Microscopic view of Coupon 4 for Site 1**

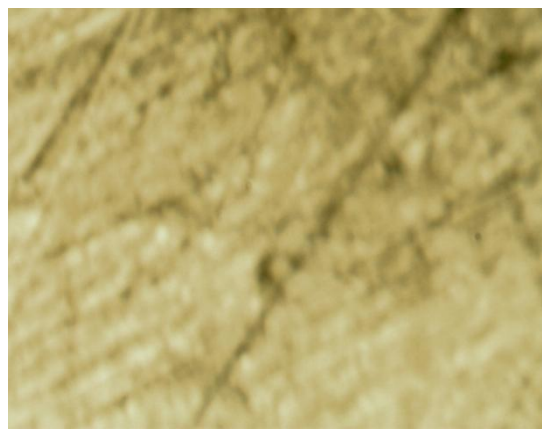
Figures 4-5 to 4-8 are the images depicting the microscopic view of coupons 5 to 8 dipped at Ormara.



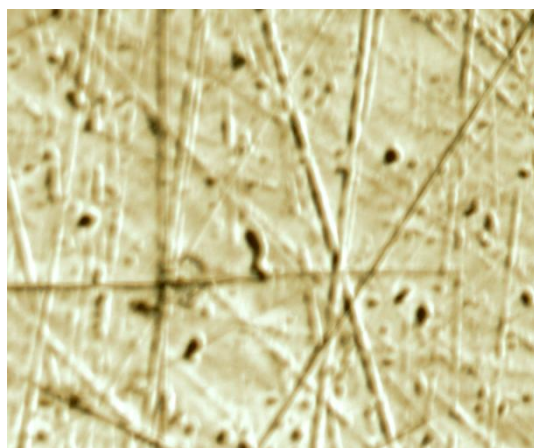
**Figure 4-5; Microscopic view of Coupon 5 for Site 2**



**Figure 4-6; Microscopic view of Coupon 6 for Site 2**



**Figure 4-7; Microscopic view of Coupon 7 for Site 2**



**Figure 4-8; Microscopic view of Coupon 8 for Site 2**

The sea water from the two sites of Karachi and Ormara was obtained and laboratory test was conducted to obtain the exact sea water chemistries of the same. Table 4-1 depicts the results of the same.

S. no	Composition	Sea water Karachi	Sea water Ormara
1	pH	6.20	7.00
2	Chloride (ppm)	20900	18000
3	Sulfate (ppm)	2922	1900
4	Oil traces	Nil	Nil

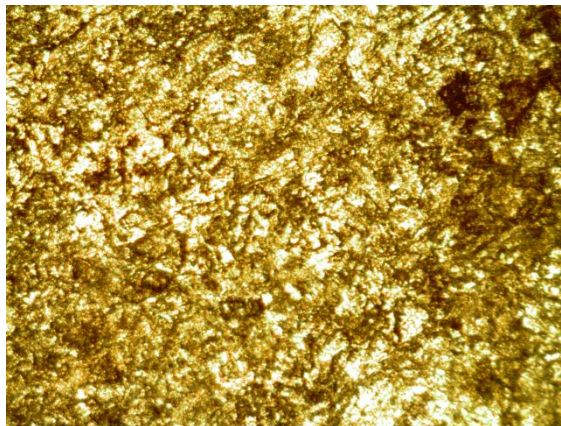
**Table 4-1: Sea water Chemistry of Karachi (Site 1) and Ormara (Site 2)**

The coupons were dipped simultaneously at Karachi and Ormara harbor. It was ensured that the coupons remain fully submerged during high water and low water timings. The same was done as to provide a similar exposure to the coupons at these two sites.

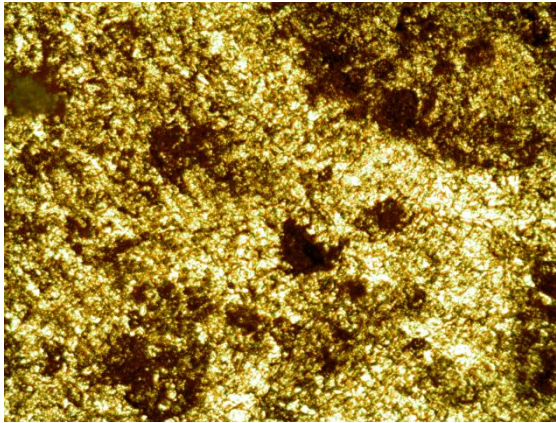
## 4.2 Data Collected After Experiment

### 4.2.1 Microscopic view of Coupons

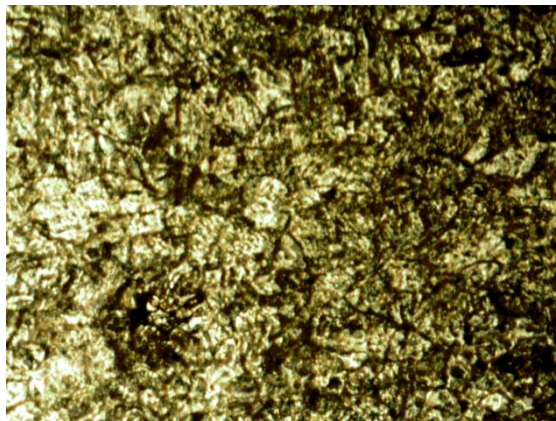
Once the coupons were extracted from the two sites, they were chemically cleaned to remove the corrosion products as per the guidelines promulgated through ASTM standards as already mentioned. The images of the coupons extracted from harbors of Karachi and Ormara are appended below.



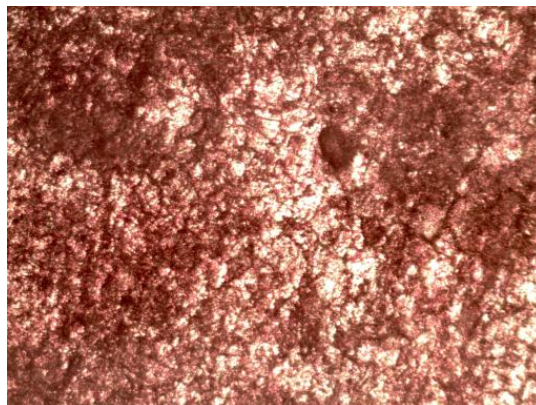
**Figure 4-9; Microscopic view of coupon 1 after exposure at Site 1**



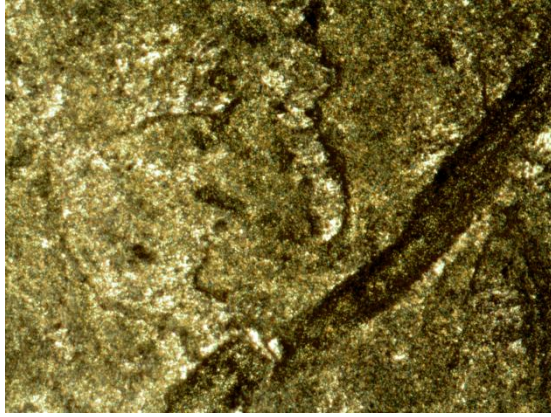
**Figure 4-10; Microscopic view of coupon 2 after exposure at Site 1**



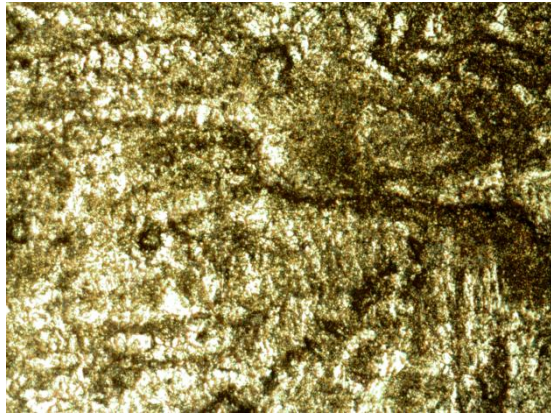
**Figure 4-11; Microscopic view of Coupon 3 after exposure at Site 1**



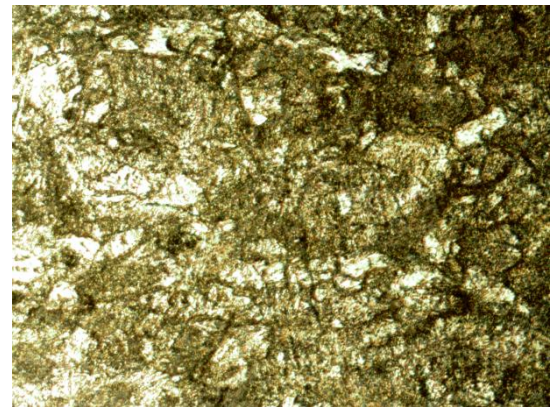
**Figure 4-12; Microscopic view of Coupon 4 after exposure at Site 1**



**Figure 4-13; Microscopic view of Coupon 5 after exposure at Site 2**



**Figure 4-14; Microscopic view of Coupon 6 after exposure at Site 2**



**Figure 4-15; Microscopic view of Coupon 7 after exposure at Site 2**



**Figure 4-16; Microscopic view of Coupon 8 after exposure at Site 2**

#### **4.2.1 Weight Comparison of Coupons**

The weight of the coupons was carefully measured by analytical balance before and after providing exposure to real time sea conditions. The same is appended below in table 4-2.

<b>Coupon No.</b>	<b>Site</b>	<b>Weight Before Dipping (g)</b>	<b>Weight After dipping (g)</b>	<b>Weight Difference (g)</b>
1	Site 1	17.18558	17.0518	0.13378
2		17.39459	17.1921	0.20249
3		16.14494	15.8017	0.34324
4		17.29974	16.8783	0.42144
5	Site 2	18.45255	18.4205	0.03205
6		18.32803	18.2876	0.04043
7		18.39107	18.3362	0.05487
8		19.04827	18.9727	0.07557

**Table 4-2; Weight Comparison of Coupons**

### **4.3 Analysis**

Following analysis are being deduced from the data gathered during the study.

#### **4.3.1 Comparison of Percentage Weight Loss**

The percentage weight loss was determined with help of the above mentioned data. The percentage weight loss of the all the coupons is appended below in Table 4-3.

It is evident from the listed figures that the percentage weight loss of Cupronickel 90/10 is much higher than that of coupons dipped at Ormara. It is

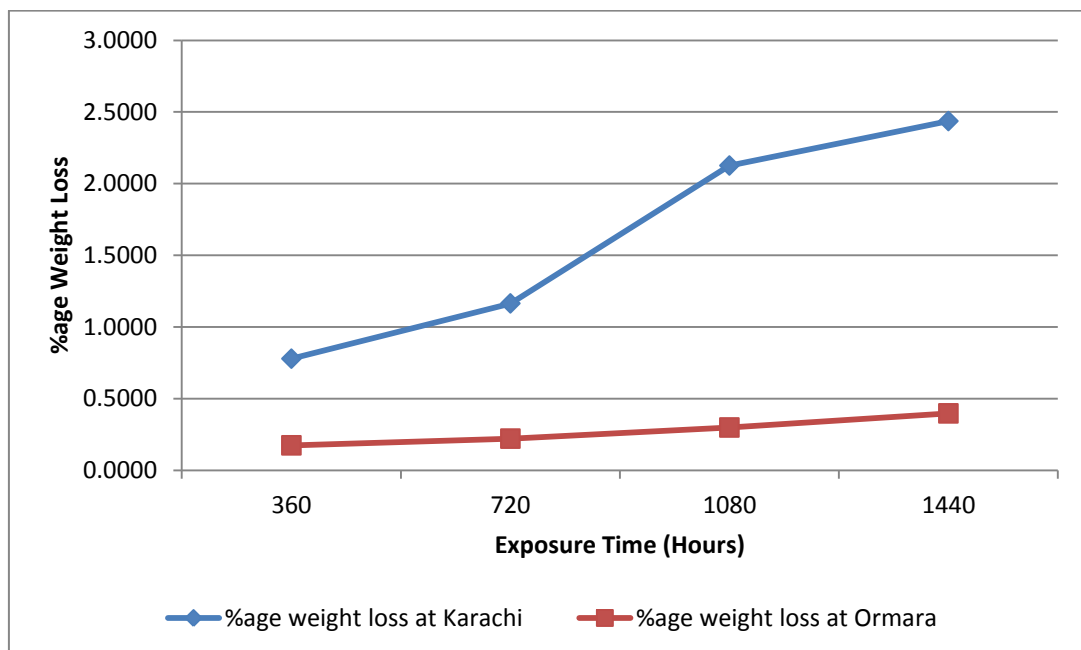


also evident that the percentage increase at Karachi has drastically increased with respect to time in comparison to that of Ormara which is gradually increasing.

Coupon No	Site	Weight Before Dipping (g)	Weight After dipping (g)	Weight Difference (g)	Percentage weight Loss
1	Site 1	17.18558	17.0518	0.13378	0.7784
2		17.39459	17.1921	0.20249	1.1641
3		16.14494	15.8017	0.34324	2.1260
4		17.29974	16.8783	0.42144	2.4361
5	Site 2	18.45255	18.4205	0.03205	0.1737
6		18.32803	18.2876	0.04043	0.2206
7		18.39107	18.3362	0.05487	0.2984
8		19.04827	18.9727	0.07557	0.3967

**Table 4-3; Percentage Weight Loss Comparison of Coupons at Both Sites**

The graphical representation of the comparison of above mentioned data is shown in Graph 4-1. It clearly shows that percentage weight loss of Karachi is significantly higher than that of Ormara.



**Graph 4-1; Comparison of Percentage Weight Loss at Both Sites**

## 4.4 Results and Discussions

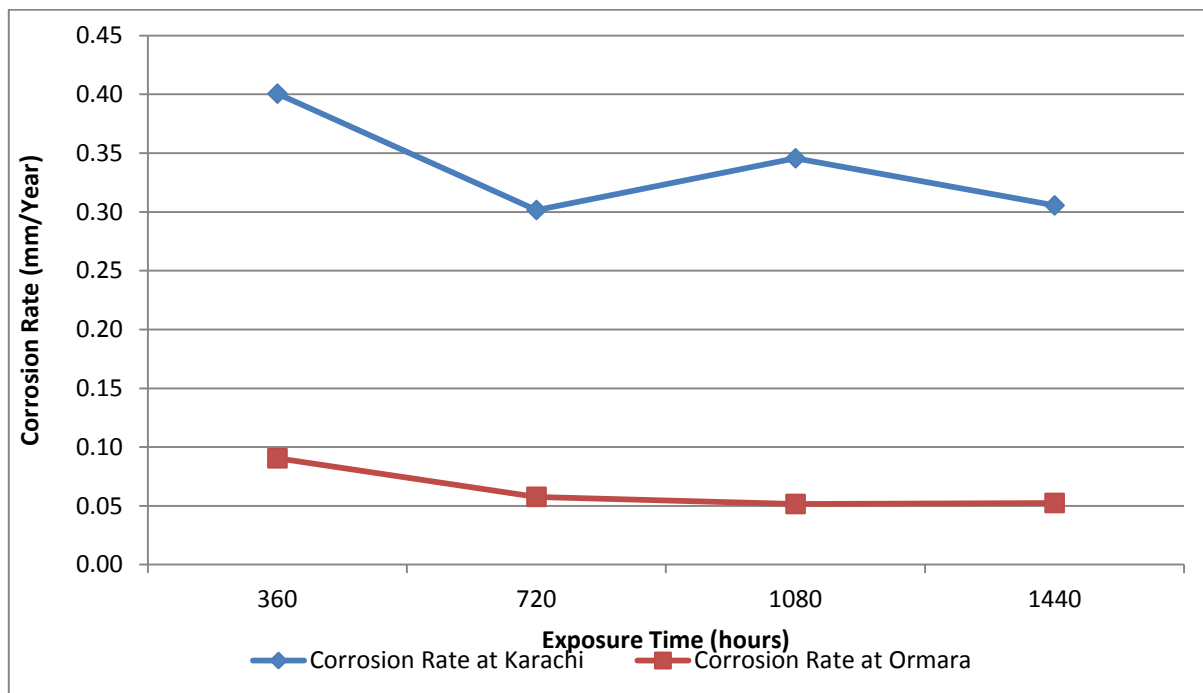
### 4.4.1 Corrosion Rate

To determine the outcome of the experimental set up, the corrosion rate is calculated with help of Equation 2-1. The results are tabulated in Table 4-4.

Coupon No	Site	Weight Before Dipping (g)	Weight After dipping (g)	Weight Difference (g)	D (g/cc)	A (cm <sup>2</sup> )	T (hrs)	CR (mm/y)
1	Site 1	17.18558	17.0518	0.13378	8.91	9.1215	360	0.40
2		17.39459	17.1921	0.20249	8.91	9.1675	720	0.30
3		16.14494	15.8017	0.34324	8.91	9.0415	1080	0.35
4		17.29974	16.8783	0.42144	8.91	9.4185	1440	0.31
5	Site 2	18.45255	18.4205	0.03205	8.91	9.6783	360	0.09
6		18.32803	18.2876	0.04043	8.91	9.5759	720	0.06
7		18.39107	18.3362	0.05487	8.91	9.6832	1080	0.05
8		19.04827	18.9727	0.07557	8.91	9.8408	1440	0.05

**Table 4-4; Corrosion Rate of Karachi and Ormara**

The graphical representation for the comparison of calculated corrosion rate for both sites i.e. Karachi (Site 1) and Ormara (Site 2) are depicted below in Graph 4-2.



**Graph 4-2; Comparison of Corrosion Rate at Ormara and Karachi**

The comparison of corrosion rate for both sites depicts that the same for Karachi is observed to be on much more higher side as compared to the calculated corrosion rate of Ormara. It is also to be noted that the calculated corrosion rate for Karachi is more than the noted average corrosion rate of Cupronickel 90/10 in normal sea water condition. It is also evident that the calculated corrosion rate of Cupronickel 90/10 at Ormara is within safe limits as compared to that of Karachi.

#### **4.4.2 Equation Development for Predicting Corrosion Rate and Weight Loss at Both Sites**

Statistical and probabilistic methods are broadly utilized to quantify unpredictability and complicated problem of corrosion / erosion advancement which can help to assess the marine related infrastructure. Mathematical models are made to have a better understanding of any natural and physical phenomena taking place. Later, these mathematical modes need to be validated with help of certain measurements. At this instant, errors may jeopardize the efforts. To take into account these errors and uncertainty, statistical models are made in form of an equation or set of equations.

These models can also be described as a formal expression of theory or an experimental setup which resulted in generating the observed data [76]. Hence, modeling can be referred as developing a mathematical expression that explains the response of a concerned random variable. The random variables are also known as dependent variables and the variables wither real and dummy are known as independent variables. These independent variables are to elaborate the behavior of the dependent variables being used in the mathematical models.

$R^2$  is a value which as a fraction is supposed to be ranging from 0.0 to 1.0. If the value of  $R^2$  is 0.0, it suggests that the relationship between the independent and independent variable does not exist and the independent variable cannot be utilized to predict the value of dependent variable. However, if the value of  $R^2$  is 1.0, it means that the relationship of independent and dependent variables is too strong and in this case the independent variable can be utilized to determine the exact value of dependent variable. So it can be easily said that the value of  $R^2$  being close to 1, the relationship between the dependent and independent variables is considered strong [76].

In this study, linear and non-linear approaches were used to quantify corrosion rate and weight loss of Cupronickel 90/10 which was exposed to the sea water environment with respect to Karachi and Ormara harbor. Equations

estimated by the data collected and calculated for Cupronickel 90/10 by utilizing above mentioned techniques are as follows;

Equation 4-1 can be utilized to predict Weight Loss of Cupronickel 90/10 at Karachi Port.

*Weight Loss (WLK) Model at Karachi Harbor*

$$WLK_t = 0.142 + .0016 T_t + \epsilon_t \quad (4-1)$$

t - stat        (.593)     (6.771)

Prob. Value (0.02)     (0.06)

$$R^2 = 0.95$$

Equation 4-2 can be utilized to predict Corrosion Rate of Cupronickel 90/10 at Karachi Port.

*Corrosion Rate (CRK) Model at Karachi Harbor*

$$CRK_t = -0.115 + 0.059 \text{LOG}(T_t) + \frac{1234.18}{T_t^2} + \epsilon_t \quad (4-2)$$

t – stat        (-0.129)     (0.477)     (0.957)

Prob. Value (0.07)     (0.03)     (0.05)

$$R^2 = 0.74$$

Equation 4-3 can be utilized to predict Weight Loss of Cupronickel 90/10 at Port of Ormara.

*Weight Loss Model at Ormara (WLO) Harbor*

$$WLO_t = 0.161 + 7.4 e^{-09} T_t^{2.5} - 1.16 e^{-10} T_t^3 + \epsilon_t \quad (4-3)$$

t – stat        (2006)     (408)     (-250)

Prob. Value (0.0003)     (0.0016)     (0.0025)

$$R^2 = 0.98$$

Equation 4-4 can be utilized to predict Corrosion Rate of Cupronickel 90/10 at Port of Ormara.

### Corrosion Rate Model at Ormara (CRO) Harbor

$$\text{CRO}_t = 0.251 + \frac{0,0016 Tt}{\text{Log } Tt} - 0.014 T_t^{0.5} + \varepsilon_t \quad (4-4)$$

t - stat            (3321)    (1698)    (-2011)

Prob. Value (0.0002) (0.0004) (0.0003)

$$R^2 = 0.99$$

#### 4.4.3 Model Validation

Model validation is the most significant part for the model construction process. There are many techniques to check the validity of the constructed model. Here, analysis of residual are carried out to check the statistical assumptions of constant variance, independence of variables and normality of the distribution among error terms for the validation of estimation under equation 4-1 to 4-4.

- a. The test statistics (t-test) with corresponding probabilities values given in parenthesis under equations 4-1 to 4-4 for each parameter of predicted model confirms the significant of approximation.
- b. Coefficients of determination mention against each computed model indicates that variation in weight loss (WLK & WLO) as well as corrosion rate (CRK & CRO) can be explained by the time t (in Hours) evocatively.
- c. The consistency in residual for the each model is observed by the variance in the error terms for these models. For this purpose Breush Pegan Gogfrey test has been used which is based on following Hypothesis

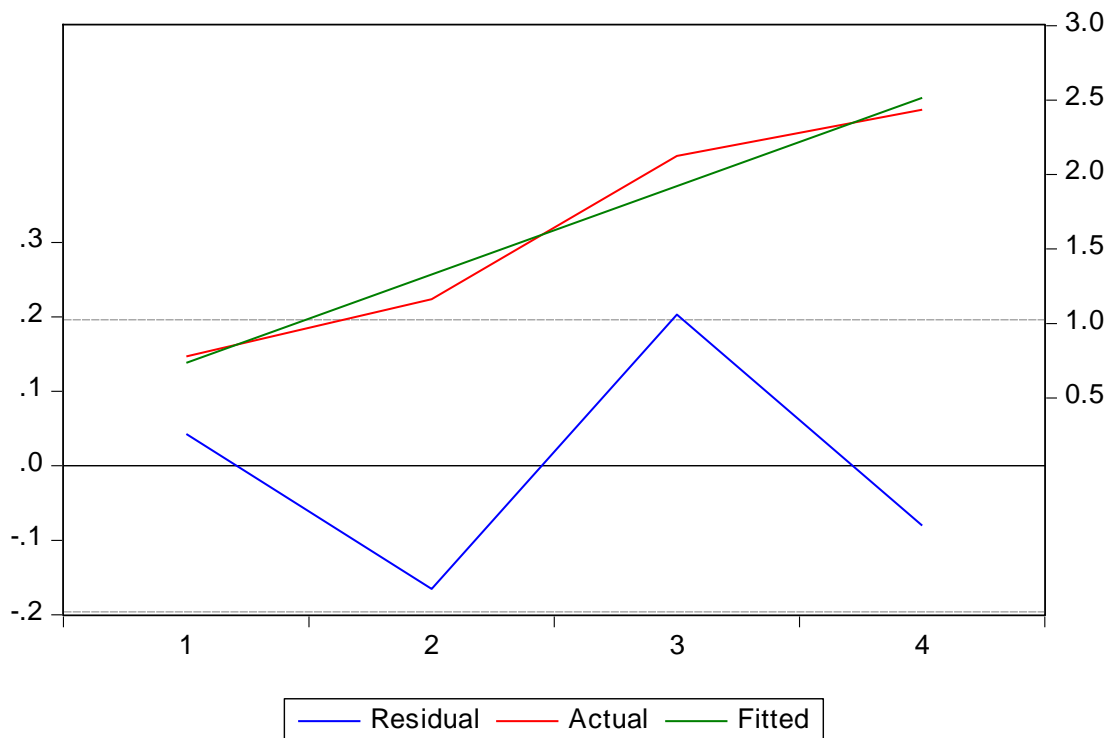
$H_0$  : Residuals are having constant Variance

$H_1$  : Residuals are not having Constant Variance

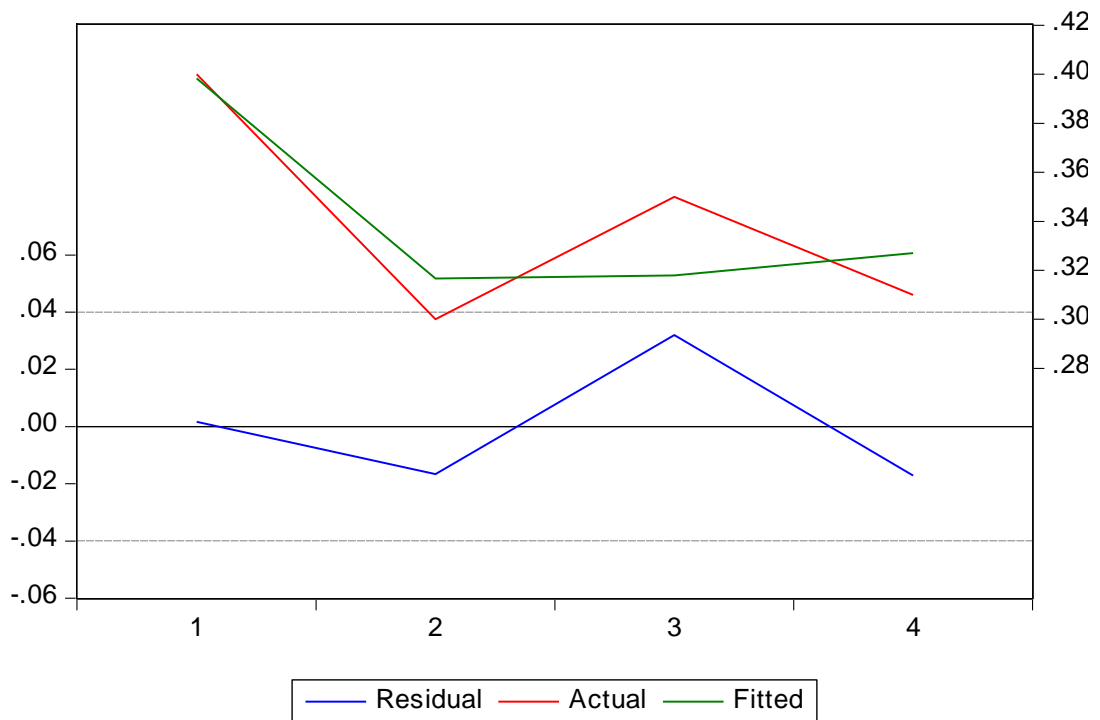
Model	Obs x R-squared Value	Prob. Chi-Square
$WLK_t = 0.142 + .0016 T_t + \varepsilon_t$	0.1522	0.69
$CRK_t = -0.115 + 0.059 \text{LOG}(T_t) + \frac{1234.18}{T_t^2} + \varepsilon_t$	1.641	0.44
$WLO_t = 0.161 + 7.4 e^{-09} T_t^{2.5} - 1.16 e^{-10} T_t^3 + \varepsilon_t$	2.522	0.23
$CRO_t = 0.251 + \frac{0,0016 T_t}{\text{Log } T_t} - 0.014 T_t^{0.5} + \varepsilon_t$	3.304	0.19

**Table 4-5; Probabilities values of each observation x R<sup>2</sup>-value endorsed consistency of the model**

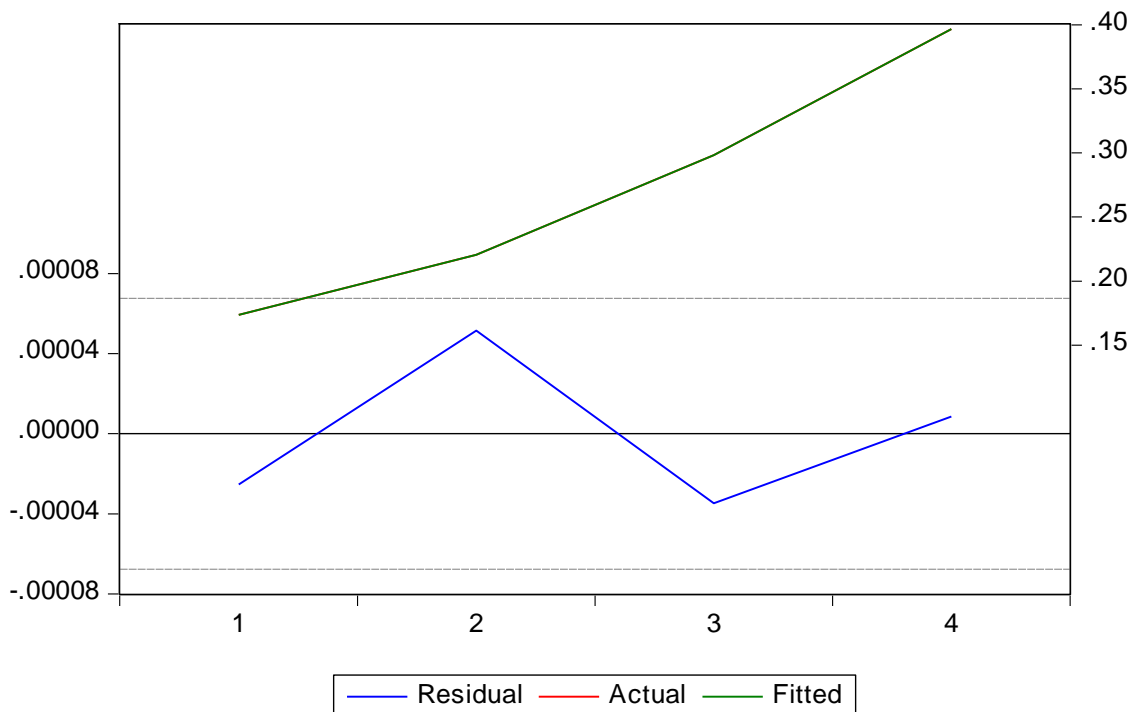
d. Actual and simulated graph depicted below shows that simulated data follows the actual pattern which is desired for the acceptance of the constructed models. In the following graphs, the residual is also kept so as to analyze the degree of error in the actual and simulated graph. The same is considered to fall within the minimum required rate.



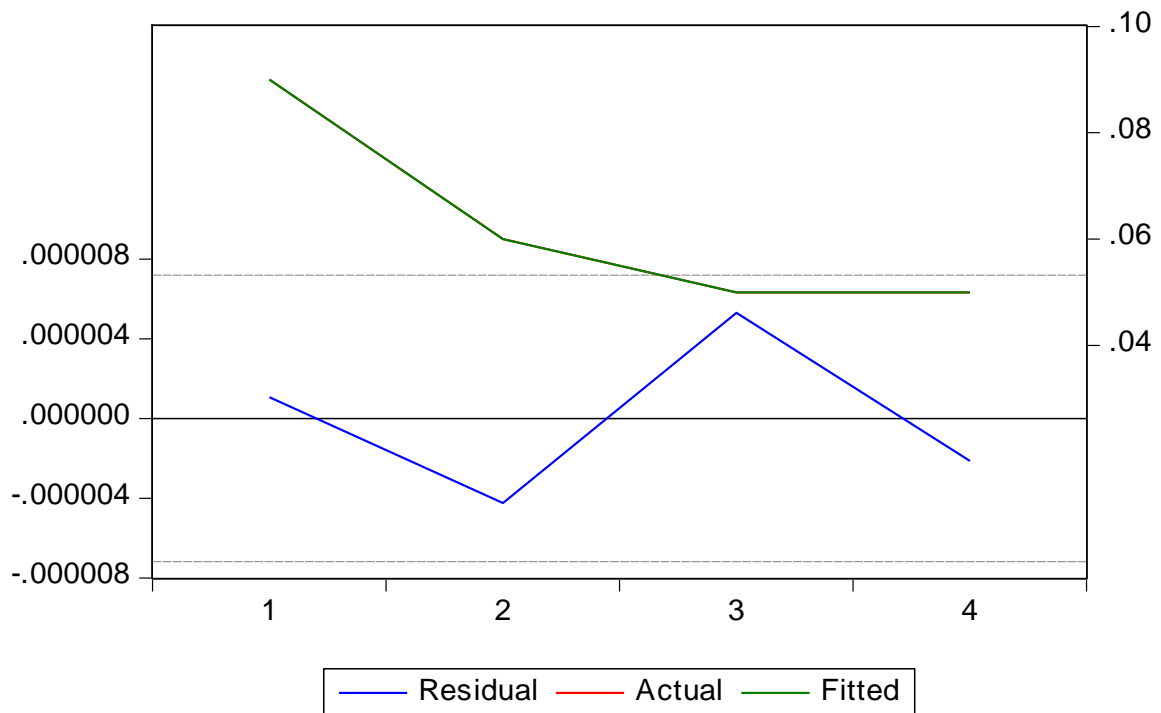
**Graph 4-3; Actual, simulated and residual plot of Weight Loss (WLK) at Site 1**



**Graph 4-4; Actual, simulated and residual plot of Corrosion Rate (CRK) at Site 1**



**Graph 4-5; Actual, simulated and residual plot of Weight Loss (WLO) at Site 2**



**Graph 4-6; Actual, simulated and residual plot of Corrosion Rate (CRO) at Site 2**

All the diagnostic checks including graphs 4-2 to 4-6 confirm the adequacy of the constructed model for quantification of corrosion weight loss and rate of erosion growth for under study material at Karachi and Ormara marine environment.



## Chapter 5

### CONCLUSION AND RECOMMENDATIONS

#### 5.1 Conclusion

On the basis of derived results from the data collected during the study, following is concluded:

- a. The results of the study are in line with the available literature and previously conducted studies.
- b. The water chemistry of Karachi's sea water is having adverse effect on the protective film formed on Cupronickel 90/10 in comparison with that of Ormara's sea water.
- c. The percentage weight loss noted for coupons dipped at Karachi was much higher than that of coupons dipped at Ormara.
- d. Karachi sea water has higher concentration of chloride, sulphates and, lesser pH values as compared to Ormara's sea water. The surface morphology of Cupronickel 90/10 is adversely affected by higher chloride, sulphate and lesser pH values.
- e. Microscopic images of coupons revealed that the chemical composition of Karachi's sea water has significantly greater effect on Cupronickel 90/10 in comparison to that of Ormara.
- f. The protective film is generally formed on surface within hours of exposure. The corrosion rate of Cu-Ni 90/10 is generally below 2.5  $\mu\text{m}/\text{yr}$ . However, in this case, the corrosion rate at Karachi was much higher than this limit and that of Ormara was well within this limit.
- g. Appropriate formation of the protecting film is to be ensured as it is also opined that the protective film during its formation is being damaged / eroded because of the presence of sulphates and chlorides.
- h. As Cupronickel 90/10 is being widely used in marine applications in conjunction with other alloys / metals, the chances of galvanic corrosion increases. This can also be a major cause of reported failures of this alloy at Karachi's harbor.

## 5.2 Recommendations

At the end of conducted study, following is recommended.

- a. In depth analysis to study the impact on surface morphology can also be conducted with help of AFM while calculating the depth and diameter of pits.
- b. This research can further be refined by elongating the exposure time of alloy at sea side.
- c. Concerned departments are to be approached by relevant authorities for enhancing the measures to safeguard the sea water against the industrial waste / pollution being disposed-off at sea side.
- d. Two stage strainers can be used instead of single stage strainer as it will offer more resistance to the foreign objects e.g. dirt, lubricants, debris etc entering the ship bound sea water systems during suction.
- e. Where possible, non-metallic materials are to be explored for inclusion in sea water service instead of traditionally used alloys / metals.
- f. Prolonged exposure of ship bound running machinery to polluted sea waters is to be avoided.
- g. Ensure the cleaning of ship bound machinery / systems with fresh water or clean sea water to remove deposits on periodic basis.
- h. Once a marine system is being commissioned or re-tubing is done, it is to be ensured that the system runs on neutral / clean sea water for at-least three months so the protective film has completely formed on the alloy.
- j. For the ships stationed at Karachi harbor, it is recommended that ship bound machinery may be used only for emergency purposes and shore electric supply / air conditioning plants be utilized to avoid the damages / expected failures due to polluted sea water.
- k. If in any case, the ship bound machinery is to be operated, an alternate arrangement to utilize the water in ballast tanks or fresh water tanks for safe operations.
- l. Ships stationed at harbor in Gawadar / Ormara may continue operating ship bound machinery as the sea water is considered safe to operate.

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