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 Mohamed El Mubarak Yousif  
 Osama Mohammed Elmardi Suleiman Khayal

# Ships' Hull Corrosion Prevention Using ICCP System

Impressed Current Cathodic Protection Approach

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Ali, Yousif, Khayal



**Surag Mohammed Saeed Ali  
Mohamed El Mubarak Yousif  
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Osama Mohammed Elmardi Suleiman Khayal

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# **Ships' Hull Corrosion Prevention Using ICCP System**

**Impressed Current Cathodic Protection Approach  
(A Case Study of Sudan Navy Ships, Portsudan  
2017/2019)**

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**April 2019**

## **Dedication**

In the name of Allah, the merciful, the compassionate

All praise is due to Allah and blessings and peace is upon his messenger and servant, Mohammed, and upon his family and companions and whoever follows his guidance until the day of resurrection.

This research study is dedicated mainly to undergraduate engineering students, especially mechanical, and production engineering students where most of the applications presented are focused on the necessity and importance of studying of corrosion. This study aims to at increase ships' power and performance by protecting its hull from corrosion and bio-fouling which cause reduction of the vessels power.

This work is dedicated to the soul of my mother

To my father

To my brothers and colleagues

To my family and friends

To my beloved country Sudan

Hoping to contribute in its development and superiority

Last but not least, may Allah accepts this humble work and i hope that it will be beneficial to its readers.

## **Acknowledgements**

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## Abstract

This study aimed at increasing ships' power and performance by protecting its hull from corrosion and bio-fouling which cause reduction of the vessels power. The study is based on four assumptions. First, the vessels hulls should be protected from corrosion to increase their power and performance. Second, vessels hulls corrosion can instantly be controlled using Impressed Current Cathodic Protection 'ICCP'. Third, coating has a great effect on protecting vessels hulls and increasing their performance. Finally, there are many factors that contribute on ships' hull corrosion. The data were gathered through experimental approach. The researcher used multi physic software program (Comsol 5.3a) to build a model of 'ICCP'. The experiment included two cases to protect ships' hulls from corrosion effectively and efficiently. The first case is hull with coated propeller and the second one a non-coated propeller. The researcher runs the corrosion model on 'Comsol 5.3a', the results were set in the form of graph and chart that shows the value of the current density for corrosion prevention for coated and non-coated case. The results have shown a significant difference. For the coated propeller the demanded current for protection is 4 A. In this case the potential distribution across the ship hull surface is quite uniform (greenish color), except in the region close to the anode surface and the propeller and shaft surfaces. For the uncoated case, the value of the total current density over the shaft and propeller surfaces is 9A. The potential distribution across the ship hull surface is less uniform (reddish color) compared to the coated propeller case. There is high ionic current flow from the anode surface to the shaft and propeller surfaces which lead to oxidization of the anode more than the coated case. The total current demand is found to be higher in case of the

uncoated propeller compared to the coated propeller case which leads to the higher consumption of the anode material than in the coated case. The study concluded with some recommendations: Impressed Current Cathodic Protection (ICCP) should be used in corrosion protection of the ship hull to increase the ship performance and to prolong the vessel structure to its maximum allocated lifetime. The anode material is consumed based on the current density, i.e. the higher current the more consuming anodes. Therefore, the research recommend for coated cases to reduce the amount of the protection current, this leads to less consuming of anodes. It is important to set a periodic time to check the serviceability of the anodes to ensure the structure protection from corrosion. The protection current density should be checked periodically to its limit to ensure vessels' hull protection from corrosion.

## مستخلص

تهدف هذه الدراسة إلى زيادة طاقة السفن وكفاءتها بواسطة حماية هياكلها من التآكل والعوالق الحيوية التي تسبب الحد من طاقتها. تستند الدراسة إلى أربعة افتراضات. أولاً ، يجب حماية هياكل السفن لزيادة طاقتها وأدائها. ثانياً ، يمكن التحكم في صدأ هياكل السفن فوراً بتطبيق التيار القسري لحماية الهيكل (ICCP). ثالثاً ، للطلاء تأثير كبير على حماية هياكل السفن وزيادة أدائها. أخيراً ، هناك العديد من العوامل التي تساهم في تآكل بدن السفن يستوجب التحكم فيها. تم جمع البيانات من خلال النهج التجريبي. استخدم الباحث برنامج الفيزياء المتعدد (Comsol 5.3a) لبناء نموذج التيار القسري لحماية الهيكل "ICCP". شملت التجربة حالتين لحماية أجسام السفن من التآكل بفعالية وكفاءة. الحالة الأولى هي اعتبار مروحة الدفع بطلاء والثانية اعتبار المروحة دون طلاء. قام الباحث بتشغيل نموذج الصدأ على برنامج "Comsol 5.3a". تم توضيح النتيجة في شكل مخطط ورسوم بيانية توضح قيمة كثافة التيار لمنع الصدأ للحالتين ودرجة الحماية موضحة بالألوان. أظهرت النتائج اختلافاً معتبراً بين الحالتين. بالنسبة للمروحة المطلية ، يكون التيار المطلوب للحماية من الصدأ هو 4 أمبير. وفي هذه الحالة نجد توزيع الجهد عبر سطح هيكل السفينة منتظماً تماماً (اللون اخضر) لتشكيل الحماية اللازمة إلا في المنطقة القريبة من سطح الأنود و سطح المروحة والعمود وهي اقل حماية من الهيكل. اما بالنسبة لحالة المروحة الغير مطلية ، تبلغ قيمة كثافة التيار الكافية على أسطح العمود والمروحة 9 أمبير وهي اعلى بكثير من

الحالة السابقة. في هذه الحالة نجد توزيع الجهد عبر سطح هيكل السفينة أقل اتساقاً (اللون الأحمر متباين من مكان لآخر) مقارنة بحالة المروحة المطلية ذات اللون الاخضر المتسق. يوجد تدفق أيوني لارتفاع التيار من سطح الأنود إلى أسطح العمود والمروحة والذي يؤدي إلى أكسدة الأنود. اختتمت الدراسة ببعض التوصيات والاقتراحات لمزيد من الدراسات. يجب استخدام نظام التيار القسري للحماية من الصدأ (ICCP) في السفينة لزيادة أداءها وإطالة العمر الفني المخصص لها. يتم استهلاك مادة الأنود (anode) بناء على كثافة تيار الحماية القسري فكلما كان التيار القسري عالي كان استهلاك الأنودات (anodes) اكثر. لذلك ، يوصي البحث في حالة المروحة المطلية بتقليل مقدار التيار القسري للحماية لتقليل استهلاك الانود وتوفير حماية اكبر. من المهم أن يحدد وقتاً دورياً للتحقق من صلاحية الأنودات لضمان حماية هيكل السفن من التآكل. وايضا يجب فحص حدود كثافة تيار الحماية بصورة دورية من أجل توفير الحماية اللازمة.



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## List of Abbreviations

| No. | Abbreviations | Word/s                                |
|-----|---------------|---------------------------------------|
| 1   | <b>ICCP</b>   | Impressed Current Cathodic Protection |
| 2   | <b>SCC</b>    | Stress corrosion cracking             |
| 3   | <b>SACP</b>   | Sacrificial Anode Cathodic Protection |
| 4   | <b>IMO</b>    | International Marine Organization     |
| 5   | <b>MIC</b>    | Microbial Induced Corrosion           |
| 6   | <b>SRB</b>    | Sulphur-reducing Bacteria             |
| 7   | <b>EPS</b>    | Extracellular Polymeric Substances    |
| 8   | <b>HMS</b>    | His Majesty's Ship                    |



## Definitions of Terms

| <b>Term</b>                      | <b>Definition</b>   |
|----------------------------------|---|
| Corrosion                        | The degradation of a material's properties or mass over time due to environmental effects.                            |
| Seawater                         | A biologically active medium that contains a large number microscopic and macroscopic organisms                       |
| The standard electrode potential | The tendency of each metal to be oxidized and is expressed in volts   |
| Cathodic Protection              | An established corrosion control method for protection of underground and undersea metallic structures i.e. Ship Hull |
| Bio fouling                      | A complex process involves the growth of a community of organisms on a surface in contact with an aqueous medium.     |
| Coating System                   | The use of an anticorrosive paint and an antifouling paint.   |

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# Chapter One

## Introduction

### 1.1 An Overview

Nowadays, ships have been very significant worldwide as sea transportation mean and it is considered safe, economic and cheap. However, there are some challenges that face operation and maintenance of sea vessels.

Ships sail on different water surfaces such as oceans, seas, lakes and rivers. Oceans, seas and lakes are considered as the most corrosive environment that ships could encounter. Therefore, it important to find suitable maintenance measures and protection system to resist tough atmosphere and to increase the performance of sea vessels.

There are many factors in marine environment such as salinity, pH, and temperature, velocity which cause corrosion and also, aquatic organism bio-film which covers the vessels hull, This phenomenon is called fouling and it results in increasing hydrodynamic drags, lower the maneuverability of the vessels and increase the fuel consumption. All these factors lead to the deficiency of ships performance. There are many methods that can be used to prevent vessels from the results of fouling and corrosion, among these methods coating i.e. Using a highly corrosion resistant material on the ship hull and cathodic method i.e. using zinc for electro mechanic interaction could be effective if implemented properly.

Ships maintenance has paramount role in ensuring ship's high performance operation and makes it free from corrosion. However, lack of maintenance principles may cause corrosion accumulation to the ship's hull and deficiency of vessels performance. The researcher, therefore, is intended to find a suitable way to increase ships performance by controlling the factors the

affects ship's hull to corrode using Impressed Current Cathodic Protection System 'ICCPS' to instantly monitor these factors and react against; besides setting an effective maintenance measures.

Maintenance does not only keep any mechanical equipment or machinery going but also can help with prolonged life and a favorable outcome and increase its performance. For a ship, maintenance is the one thing that keeps machinery in smooth running condition and it has a paramount feature of the national economy. Each year, large amounts of money are located for maintenance purpose. Poor or failed maintenance planning can result in serious incidents and high penalty costs arising from operation downtime (Dekker 1996).

## **1.2 Statement of the Problem**

From his 8 years of experience in the field of marine, the researcher observed that the ships aren't enrolled effectively in service due to many circumstances. First, the regulations of ship maintenance are not followed effectively. Second, the corrosive environment in seas and oceans extremely damages the ship's hull. The researcher, therefore, is intended to conduct an experiment to minimize or eliminate hulls' corrosion through continuous observation of the factors that cause corrosion using 'ICCPS'. Besides, setting suitable maintenance measures that serve in protection of vessels hull from corrosion.

## **1.3 Objectives of the Study**

The researcher intends to monitor vessels maintenance and hull protection using 'ICCPS' to increase ships power and performance. The sub objectives are to:

1. To maintain the vessel hull from corrosion so as to increase its power and performance.

2. To detect the factors that affects the corrosion of ships' hull.
3. To instantly control the process of hull corrosion using 'ICCPS'.
4. To determine the effect of coating on vessel performances.

#### **1.4 Questions of the Study**

The researcher is going to answer the following research questions:

1. How can we maintain vessels' hull from corrosion to increase their power and performance?
2. What are the factors that causes corrosion of ships' hull?
3. How does the corrosion of ship hull be controlled using 'ICCPS'?
4. How does coating affect vessel performance?

#### **1.5 Research Hypotheses**

In order to answer the research questions, the researcher set the following hypotheses:

1. The vessels hulls should be protected from corrosion to increase their power and performance.
2. There are many factors that contribute on ships' hull corrosion.
3. Vessels hulls corrosion can instantly be controlled using 'ICCPS'.
4. Coating has a great effect on protecting vessels hulls and increasing their performances.

#### **1.6 Significance of the Study**

This study is hoped to develop the ship maintenance in Sudanese marine. It increases ships' power and performance, and extends their lifetime by setting standard maintenance measures. The study is also expected to reduce the maintenance costs by good maintenance planning and scheduling. Moreover, the study will decrease the risk and incident factors which is caused by poor maintenance.

## **1.7 Methodology**

The study is experimental through which an 'ICCP' modeling simulation will be carried out using 'software applications' i.e. "comsol 5.3a" to detect the important parameters and produce a suitable 'impressed current' for protection. In the experiment, ship's hull structure represent cathode, the sea water represent the surrounding atmosphere, and anode boundaries i.e. a metal which is higher in potential than the cathode (Hull) are used. The second method is coating, the researcher has created the program to show the effect of ICCP system for coated and non-coated structure.

## **1.8 Limits of the Study**

This study is confined to Sudan Navy Ships-Zamzam and Almaz. It investigates the hull protection from corrosive environment and ship maintenance using coating system and Impressed Current Cathodic Protection System. The use of ICCP needs high technology, therefore the research will implement the ICCP system on modeling simulation software program 'Comsol 5.3a'. The study will be conducted in Sudan, Port Sudan during the period 2017/2019.



# Chapter Two

## Literature Review

### 2.1 Introduction

The ship's hull protection to resist the rough surrounding environment requires knowledge about the different factors that affect vessels frame and how to protect it from the damage due to accumulation of corrosion and fouling. The researcher, therefore should give an overview about the phenomena of corrosion, bio-fouling, factors that affect hull structure and various hull protection methods.

### 2.2 Corrosion

There are three main reasons concerning the study of corrosion. These reasons are safety, economics, and conservation. Early failure of vessels hull due to corrosion can result in human injury or even loss of life. Failure of operating equipment can have the same disastrous results. Corrosion is defined as the degradation of a material's properties or mass over time due to environmental effects. It is the normal inclination of a material's compositional elements to return to their most thermodynamically stable state. For most metallic materials, this means the formation of oxides or sulfides, or other basic metallic compounds generally considered to be ores. Luckily, the accumulation rate of these processes is low enough to enable the making of useful building materials. Only inert environments and vacuum can be considered free of corrosion for most metallic materials. Under usual circumstances, iron and steel corrode in the presence of both oxygen and water. If either of these materials is not present, corrosion usually will not take place. High corrosion rates may take place in water, in which the rate is increased by the acidity or velocity of the water, due to the movement of the metal, and the increase in the temperature or it may take place in aeration, due to the presence of microorganisms, or takes place due to other less

common factors. On the other hand, corrosion is generally stopped by films (or protective layers) consisting of corrosion products or adsorbed oxygen; high alkalinity of the water also reduces the rate of corrosion on steel surfaces. The amount of corrosion is controlled by either water or oxygen, which are necessary for the process to take place. For example, steel will not corrode in dry air and corrosion is insignificant when the relative humidity of the air is below 30% at normal or reduced temperatures (Wells, 1948). Protection from corrosion by dehumidification is based on this fact. All structural metals corrode to some degree in natural environments. These corrosion processes follow the basic laws of thermodynamics. Corrosion is an electrochemical process and as such, under controlled conditions, it can be measured, repeated, and predicted. Since it is governed by reactions on an atomic level, corrosion processes can act on isolated regions, uniform surface areas, or result in subsurface microscopic damage. These forms of corrosion are complicated with further subdivisions. Just consider adding basic environmental variables such as pH, temperature, and stress, and the predictability of corrosion begins to be more difficult.

## **2.3 Environmental Factors of Corrosion**

Seawater is a biologically active medium that contains a large number of microscopic and macroscopic organisms. Many of these organisms are commonly observed in association with solid surfaces in seawater, where they form bio-fouling films. These bio-films play a vital role in aggravating corrosion on vessels' hulls. Immersion of any solid surface in seawater initiates a continuous and dynamic process, beginning with absorption of nonliving, dissolved organic material and continuing through the formation of bacterial and algae slime films and the settlement and growth of various macroscopic plants and animals. This process by which the surface of all

structural materials immersed in seawater become colonialized, adds to the variability of ocean environment in which corrosion occurs (Rodgers, 1968)

The amount of oxygen and other gases dissolved in seawater depends on the temperature and salinity of the seawater and the depth of water. In some sea water compositions, hydrogen sulfide is also present. Hydrogen sulfide is formed in sea water by the action of sulfate-reducing bacteria (SRB), usually under deposit where oxygen is depleted or when the sea water is stagnant or polluted and becomes anaerobic, even in large volumes. Silt deposit in estuarial waters are also contributory. Mineral and organic materials are also carried in suspension by the sea water, particularly near the mouth of the river (Craig & Anderson, 1995).

Since sea water is a complex environment, delicately balanced solutions of many salts containing living matter, suspended silt, dissolved gases and decaying organic materials, the individual effect of each of the factors affecting the corrosion behavior is not readily separated. Because of the interrelation between many of the variables in the sea water environment, an alteration of one variable may affect the relative magnitude of the other variables. In the following subsections, the roles of oxygen, biological activity, temperature, velocity, salinity, and Ph are presented (Fink, 1993).

### **2.3.1 Oxygen**

The dissolved oxygen content is a major factor affecting the corrosively seawater. The oxygen level in seawater is of different range up to 12 ppm. Photosynthesis of green plants, wave action etc., tends to increase the oxygen level, whereas the biological oxygen demand of decomposing of dead organisms will reduce it. For a given location, seasonal variation in oxygen level will influence corrosion behavior. For metals like copper and iron, complete elimination of oxygen will reduce the corrosion to negligible

amounts. However, metals that depend on formation of a passive film for corrosion protection, i.e. stainless steel, often corrodes rapidly where the oxygen supply to the metal surface is restricted.

### **2.3.2 Biological Activity**

When a metal or other surface is first immersed in seawater, a biological slime tends to develop in a matter of hours. During an active season, a great variety of organisms are found in an immersed surface. From a corrosion point of view, the sessile organisms are of most concern. They arrive at slime-covered surface in minute emergent form and become firmly attached. Once attached, they rapidly transform to the mature form and become immobile. Organisms, which build hard shells, are: annelids, barnacles, encrusting, bryozoans, mollusks, and corals. Organisms without hard shell are: marine algae, filamentous bryozoans, coelenterates, or hydroids, tunicates, calcareous, and siliceous sponges.

### **2.3.3 Temperature**

An increase in temperature is normally expected to speed up a chemical reaction according to thermodynamic considerations. This also would be the case for the corrosion reaction in seawater where it is possible to hold all other variables fixed. Since it is not normally possible to do this, the effect of temperature has to be established indirectly. Oxygen solubility decreases with increase in temperature, biological activity increases as the water temperature increases, and the chemical equilibrium involved in the precipitation (production) of calcium carbonate and magnesium hydroxide is altered (replaced) so that calcareous scale is more likely to deposit on the metal as the temperature is increased. For temperature variations of seasonal (cyclic) nature, iron, copper, and many of their alloys show a high rate of attack during the warm months.

### **2.3.4 Velocity**

Many metals are sensitive to velocity effects in sea water. For metals like iron or copper, there is a critical velocity beyond which corrosion becomes excessive. Stainless steel and certain nickel-chrome-molybdenum alloys tend to be more resistant in high-velocity seawater. Special forms of corrosion are associated with seawater velocity, i.e. (erosion-corrosion caused by high-velocity silt-bearing seawater, impingement attack, where air bubbles are present, and cavitation, where collapsing vapor bubbles cause mechanical damage and often corrosion damage as well.

### **2.3.5 Salinity**

The major oceans of the world are completely connected and mixing is continuous. The average salt content of the sea is 3.5 wt % with the composition comprised mainly of the following ions: sodium, magnesium, calcium, potassium, chloride, bromide, carbonate, and sulfate. In addition, seawater contains measurable quantities of iodide, fluoride, phosphate, gold, silver, arsenic, rubidium, copper, barium, manganese, lithium, lead, iron, strontium, and zinc ions. Ammonia is also present, with free oxygen, nitrogen, and other gases. Variations in salinity in open-ocean surface water typically range from 3.25 – 3.75 wt %.



### **2.3.6 PH**

PH is a number range from 0 to 14 which shows how strongly acid or alkaline a substance is. The number below PH 6.5 is acid and above PH 7.5 is alkaline.

In a case of marine environment, the PH of seawater may vary slightly depending on the photosynthetic activity. Plant matters consumes carbon dioxide and affects the PH during the daylight hours. The carbon dioxide in

seawater, close to the surface is influenced by the exchange with carbon dioxide in the atmosphere. The slight daily shift in PH has little direct effect on the corrosion behavior, however it can be a factor in calcareous-scale deposition, which affects the corrosivity. As pressure is increased, PH is reduced according to thermodynamic considerations. Thus, at great depths, there is some evidence of fewer tendencies for protective carbonate-type scale formation. Table (2.1) below shows the value of PH and corrosion rate.

**Table (2.1) the Value of PH and Corrosion Rate**

| Acidity and Alkalinity of Surroundings | PH values   | Corrosion Rate   |
|--|-------------|--|
| Extremely acid                         | Below 4.5   | Highest corrosion  |
| Very strongly acid                     | 4.5-5.0     |   |
| Strongly acid                          | 5.1-5.5     |  |
| Medium acid                            | 5.6-6.0     |  |
| Slightly acid                          | 6.1-6.5     |  |
| Neutral                                | 6.6-7.3     |  |
| Mildly alkaline                        | 7.4-7.8     |  |
| Moderately alkaline                    | 7.9-8.4     |  |
| Strongly alkaline                      | 8.5-9.0     |  |
| Very strongly alkaline                 | 9.1- higher |  |

## 2.4 Corrodibility of Various Metals

The luster, ability to conduct heat and electricity, malleability of some and ductility of others are only some of the main characteristics, which define metals. However, it is the varying ability of a metal to lose its electrons and form a positive ion that is essential in understanding the range of metals that are capable of corroding. It is this understanding which is used widely in industry as the first measure for corrosion control (i.e. choosing a metal that

will not corrode easily by giving up its electrons). The electrochemical field has developed a list, which details the range of most metals relative tendency to be oxidized, called an electromotive series. The list provide nearly all the information required to determine which metals are most subjective to corrosion. The series tells us which species behaves best as the anode undergoing oxidation and the cathode undergoing reduction. The list begins with metals most easily oxidized, end with the metals least capable of oxidation, or with the greatest capability of reduction. In other words, the list begins with metals, which are most easily corrode (i.e. behave as anode in the corrosion reaction), and ends with metal, which can best behave as cathode in the corrosion reaction. The tendency of each metal to be oxidized is given in terms of 'the standard electrode potential' or 'oxidization potential' and is expressed in volts, which is measured relative to the standard oxidization of hydrogen gas, which is assigned as an arbitrary potential of (0 volts). Table (2.2) below provides an electromotive series as a list of major industrial metals. As you can see from the list, metals such as magnesium, zinc and iron will oxidize easier and therefore corrode easier than platinum or gold. This list should provide the sufficient background needed to predict which metal during the experiment should corrode more easily. Furthermore, the electromotive series has a large influence on a particular type of corrosion, known as galvanic corrosion. Table (2.2) below shows electromotive potential series.

**Table (2.2) Electromotive Potential Series**

| Element  | Reaction                                  | Electrode Potential |
|----------|---|---------------------|
| Gold     | $\text{Au}^+ + \text{e}^- = \text{Au}$    | 1.692               |
| Platinum | $\text{Pt}^{2+} + \text{e}^- = \text{Pt}$ | 1.18                |
| Silver   | $\text{Ag}^+ + \text{e}^- = \text{Ag}$    | 0.7996              |

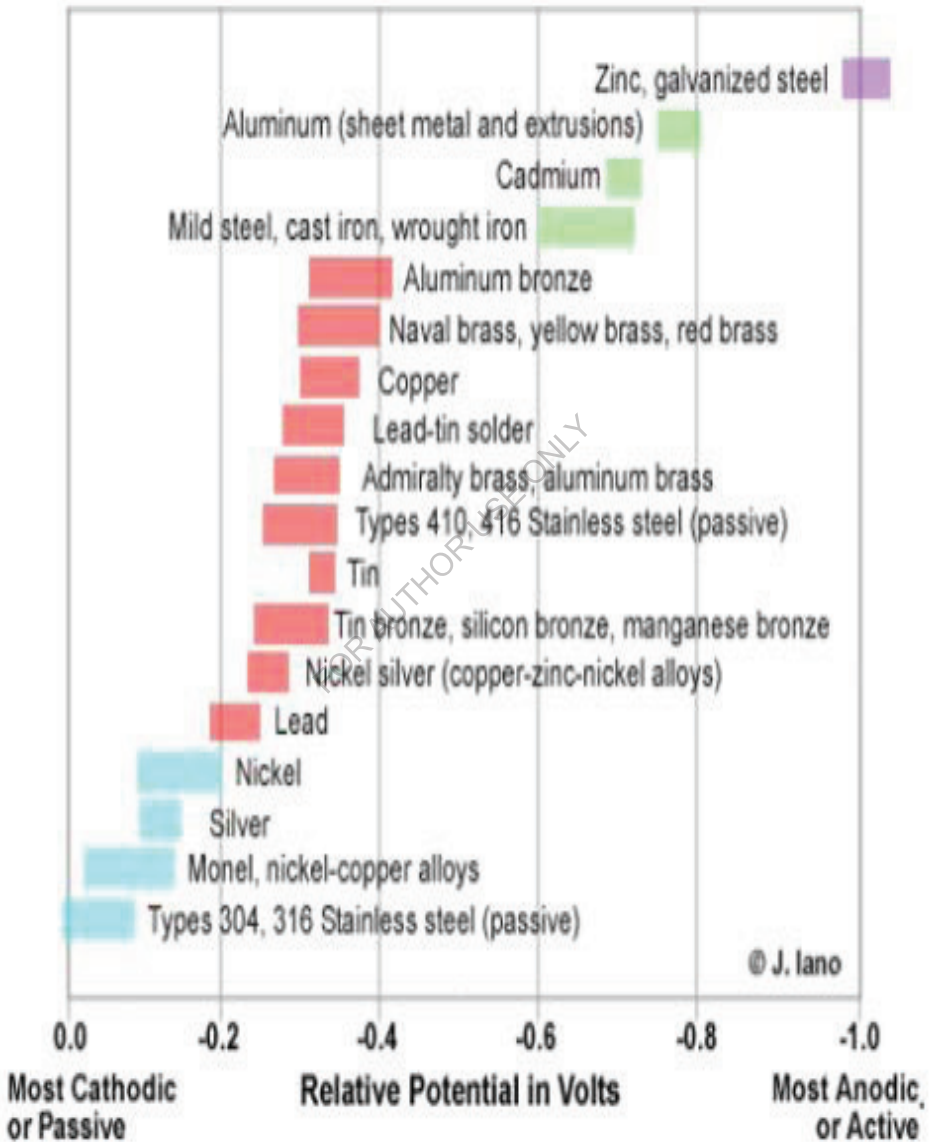
|                 |  |          |
|-----------------|--|----------|
| Copper          | $\text{Cu}^+ + \text{e}^- = \text{Cu}$     | 0.521    |
| Copper          | $\text{Cu}^{2+} + 2\text{e}^- = \text{Cu}$ | 0.3419   |
| Hydrogen (Acid) | $2\text{H}^+ + 2\text{e}^- = \text{H}_2$   | 0        |
| Iron            | $\text{Fe}^{3+} + 3\text{e}^- = \text{Fe}$ | - 0.037  |
| Lead            | $\text{Pb}^{2+} + 2\text{e}^- = \text{Pb}$ | - 0.1262 |
| Tin             | $\text{Sn}^{2+} + 2\text{e}^- = \text{Sn}$ | - 0.1375 |
| Iron            | $\text{Fe}^{2+} + 2\text{e}^- = \text{Fe}$ | - 0.447  |
| Chromium        | $\text{Cr}^{2+} + 2\text{e}^- = \text{Cr}$ | -0.913   |
| Titanium        | $\text{Ti}^{2+} + 2\text{e}^- = \text{Ti}$ | -1.63    |
| Aluminum        | $\text{Al}^3 + 3\text{e}^- = \text{Al}$    | -1.662   |
| Magnesium       | $\text{Mg}^+ + \text{e}^- = \text{Mg}$     | -2.7     |
| Sodium          | $\text{Na}^+ + \text{e}^- = \text{Na}$     | -2.71    |
| Calcium         | $\text{Ca}^{2+} + 2\text{e}^- = \text{Ca}$ | -2.868   |
| Potassium       | $\text{K}^+ + \text{e}^- = \text{K}$       | -2.931   |
| Lithium         | $\text{Li}^{3+} + \text{e}^- = \text{Li}$  | -3.0401  |
| Calcium         | $\text{Ca}^+ + \text{e}^- = \text{Ca}$     | -3.8     |

The electromotive series serve as a corrosion map for metals in particular concentrations of their own salts. It fails in describing the behavior of such metals in various corrosive environment based on varying temperature, humidity, salinity, etc. Therefore, a more general table developed by electrochemists, called galvanic series is used in practical application, (Efrid & Lee, 1997). The following Table (2.3) shows galvanic series scale.



Table (2.3) Galvanic Series

### Galvanic Series of Architectural Metals



## 2.5 Corrosion Mechanism

Common structural metals are obtained from their ores or naturally-occurring compounds by the expenditure of large amounts of energy. These metals can therefore be regarded as being in a metastable state and will tend to lose their energy by reverting to compounds more or less similar to their original states. Since most metallic compounds, and especially corrosion products, have little mechanical strength a severely corroded piece of metal is quite useless for its original purpose.

Virtually all corrosion reactions are electrochemical in nature. At anodic sites on the surface the iron goes into solution as ferrous ions, this constituting the anodic reaction. As iron atoms undergo oxidation to ions they release electrons whose negative charge would quickly build up in the metal and prevent further anodic reaction, or corrosion. Thus this dissolution will only continue if the electrons released can pass to a site on the metal surface where a cathodic reaction is possible. At a cathodic site the electrons react with some reducible component of the electrolyte and are themselves removed from the metal. The rates of the anodic and cathodic reactions must be equivalent according to Faraday's Laws, being determined by the total flow of electrons from anodes to cathodes which is called the "corrosion current". Since the corrosion current must also flow through the electrolyte by ionic conduction, the conductivity of the electrolyte will influence the way in which corrosion cells operate. The corroding piece of metal is described as a "mixed electrode" since simultaneous anodic and cathodic reactions are proceeding on its surface. The mixed electrode is a complete electrochemical cell on one metal surface.

The most common and important electrochemical reactions in the corrosion of iron are as follows:

Anodic reaction (corrosion)



Cathodic reactions (Simplified)



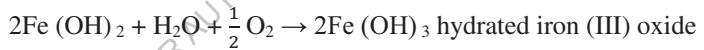
Or



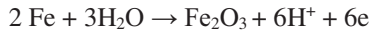
Reaction in (2a) is most common in acids and in the pH range 6.5 – 8.5. The most important reaction is oxygen reduction in (2b). In this latter case corrosion is usually accompanied by the formation of solid corrosion debris from the reaction between the anodic and cathodic products.



Pure iron (II) hydroxide is white but the material initially produced by corrosion is normally a greenish color due to partial oxidation in air.



Further hydration and oxidation reactions can occur and the reddish rust that eventually forms is a complex mixture whose exact constitution will depend on other trace elements which are present. Because the rust is precipitated as a result of secondary reactions it is porous and absorbent and tends to act as a sort of harmful poultice which encourages further corrosion. For other metals or different environments different types of anodic and cathodic reactions may occur. If solid corrosion products are produced directly on the surface as the first result of anodic oxidation these may provide a highly protective surface film which retards further corrosion, the surface is then said to be “passive”. An example of such a process would be the production of an oxide film on iron in water, a reaction which is encouraged by oxidizing conditions or elevated temperatures.



## 2.6 Types of Corrosion

There are several forms of corrosion that can occur. Each form of oxidation has specific arrangement of anodes and cathodes and the corrosion which occurs has specific location and pattern. Each form of corrosion can be effectively controlled during design if it is anticipated. By understanding the various forms of corrosion, the conditions under which they occur, and how they are quantified, then they can be addressed and controlled. The most common types of corrosion are: (Khayal, O.M.E.S., 1993).

### 2.6.1 Uniform Corrosion

Uniform corrosion results from the sites, is not necessarily fixed in location, and is distributed over a metal surface where the anode and cathode reactions happen. Uniform corrosion damage, something called wastage (wear), is usually manifested in the progressive thinning of a metal part until it virtually dissolves away (melts). (Khayal, O.M.E.S., 1993).

### 2.6.2 Pitting (hole) Corrosion

The initiation of a pit (hole/cavity) occurs when electrochemical or chemical breakdown exposes a small local site or a metal surface to damaging species such as chloride ions. The sites where pits (dents) initiate are not completely understood, but possibly could be found at scratches, surface composing heterogeneous inclusions, or place where environmental variations exist. The pit grows if the high current density and the area of breakdown initiation are exceedingly small. If the rate of repassivation is not sufficient to choke off (block) the pit growth, two new conditions develop. First, the metal ions produced by the breakdown process are precipitated as solid corrosion products (such as  $\text{Fe}(\text{OH})_2$ ) which usually cover the mouth

of the pit. This covering traps the solution in the pit and allows the building of positive hydrogen ions through a hydrolysis reaction. Then, chloride or another damaging negative ion diffuses into the pit to maintain charge neutrality. Consequently, the re-passivation becomes considerably difficult because the solution in the pit is highly acidic, contains a large concentration of damaging ions and metallic ions, and contains a low oxygen concentration. Thereby, the rate of pit growth accelerates.

The pit is the anode of an electrochemical corrosion cell, and the cathode of the cell is the non-pitted surface. Since the surface area of the pit is a very small fraction of the cathodic surface area, all of the anode corrosion current flows to the extremely small surface area of the breakdown initiation site. Thus, the anodic current density becomes very high and pitting can be rapid. (Khayal, O.M.E.S.).

### **2.6.3 Crevice (Crack) Corrosion**

Crevice corrosion results when a portion of a metal surface is shielded in such a way that the shielded portion has limited access to the surrounding environment. Such surrounding environments contain damaging corrosion species, usually chloride ions. A typical example of crevice corrosion is the crevice formed at the area between two metal surfaces in close contact with a gasket and another metal surface. The environment that eventually forms in the crevice is similar to that formed under the precipitated corrosion product that covers a pit. Similarly, an electrochemical corrosion cell is formed from the couple between the unshielded surface and the crevice interior exposed to an environment with a lower oxygen concentration compared with the surrounding medium. The combination of being the anode of corrosion cell and existing in an acidic, high chloride environment where re-passivation is difficult to make the crevice interior to corrosive attack. Figure (2.1) shows the chemical mechanism of crevice corrosion.

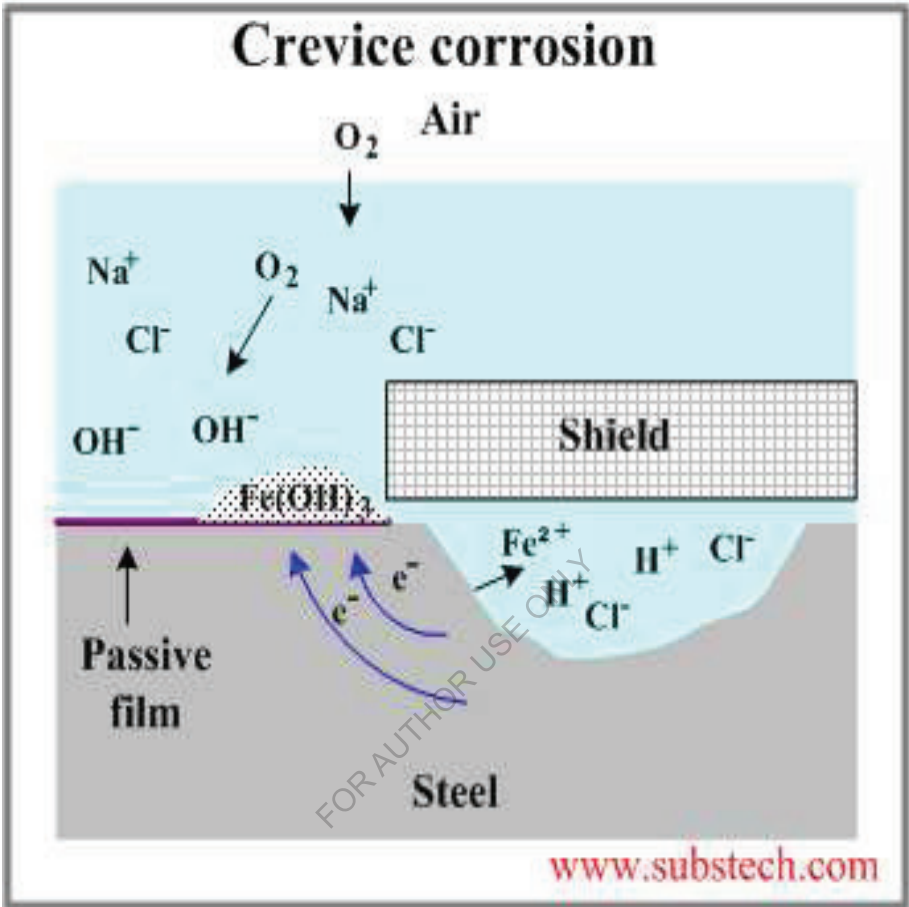


Figure (2.1) Crevice Corrosion

### 2.6.4 Galvanic (and thermo galvanic) Corrosion

Two metals having different potentials in a conducting electrolyte result in the more anodic metal usually being attacked by galvanic corrosion. Because of electrical contact between the two different metals, galvanic corrosion differs from the other forms of corrosion described previously in that anode and cathode sites of the corrosion cell reside (stay) separately on the two coupled different metals comprising the corrosive cell, while for the other

forms of corrosion, the cathodes and anodes exist on the surface of the same metal.

The value for the difference in potential between two dissimilar metals is usually obtained from a listing of the standard equilibrium potentials for the various metals.

Another factor besides the coupling of two different metals that can lead to galvanic corrosion is a difference in temperature at separate sites on the same metal surface. Such a situation leads to thermo galvanic corrosion. This type of corrosion can be found in heat exchanger systems where temperature differences are common. (Khayal, O.M.E.S., 2018).

### **2.6.5 Selective Leaching (leak)**

This kind of corrosion occurs when the components of an alloy is removed selectively by corrosion because of differences in potential between different constituents of an alloy i.e. a situation analogous to that of the galvanic corrosion of couple dissimilar metals. This results in an increase in the concentration of the remaining components and selective leaching occurs. This type of corrosion is also called parting. The most common example is selective leaching out of 'zinc' from 'brass' (dezincification).

### **2.6.6 Erosion Corrosion**

Erosion corrosion is caused by the disruption of protective passive films by erosive (wearing) or abrasive (scratch) processes. Once the protective or passive film is removed in an aqueous electrolyte, the electrochemical processes for the types of corrosion described above take place.

### **2.6.7 Stress Corrosion Cracking, Hydrogen Damage and Corrosion Fatigue**

Stress corrosion cracking (SCC) is a form of localized corrosion, which produces cracks in metals by the simultaneous action of a corroding and tensile stress. The electrochemical cell between the exterior and the interior environment of a crack is similar to that described above in section (2.6.3) for a crevice. Because of the necessity for the application of the stress, the breakdown of the passive layer on a metal service surface in SCC is generally attributed to mechanical causes but many suggest that electrochemistry is significant factor because it controls the rate of repair of the passive layer cracked by mechanical stress.

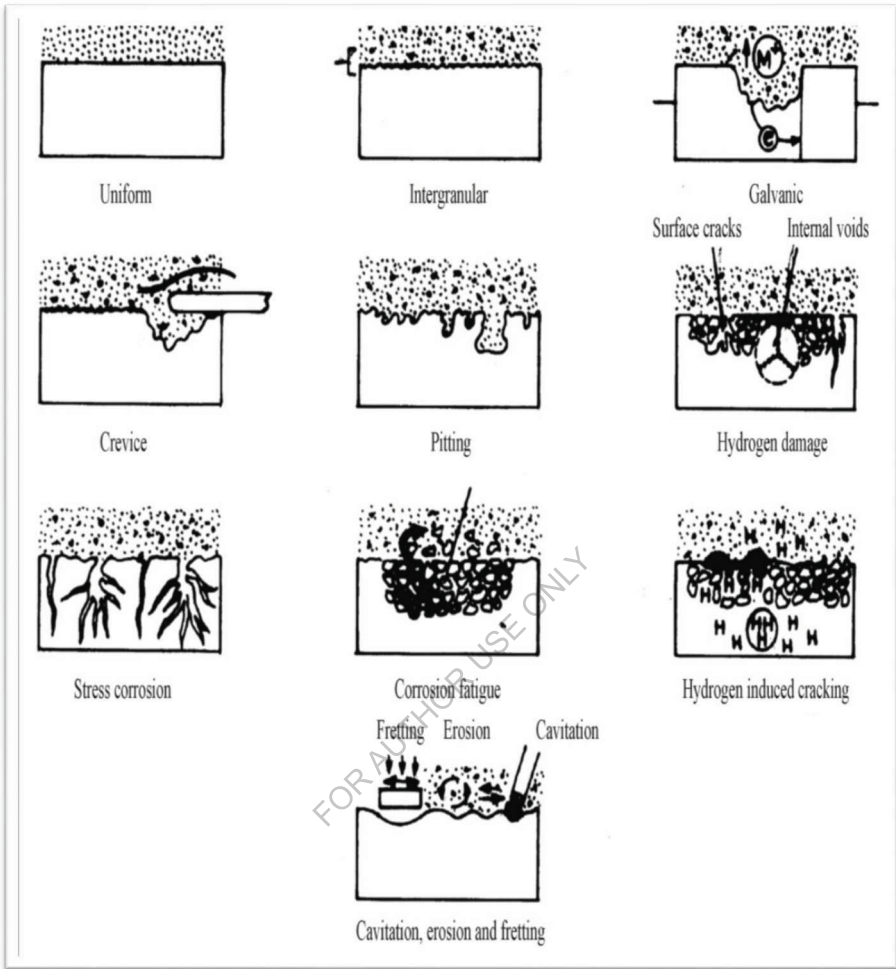
Corrosive fatigue has a somewhat similar mode of failure to SCC. It mainly differs from SCC in that it involves situation where the stress is applied cyclically rather than as a static sustained tensile stress. With both corrosion fatigue and SCC, the issues of film mechanical breakdown, repassivation, and adsorption of damaging species, hydrogen embrittlement and electrochemical dissolution are to greater or lesser extents involved in determining weakness. (Khayal, O.M.E.S., 1993).

### **2.6.8 Inter - granular Corrosion**

Figure (2.2) below shows the different types of corrosion that is found in metallic structures.

With the exception of metallic glasses, the metals used in practical devices are made up of small crystals (grains) whose surface join the surfaces of other grains to form grains boundaries. Such boundaries or the small regions neighboring to these boundaries can under certain conditions be considerably more reactive (by being more anodic) than the interior of the grains. The resulting corrosion is called inter - granular corrosion. It can result in a loss of strength of metal part or the production of debris (grains that have fallen out). (Khayal, O.M.E.S., 1993).





**Figure (2.2) Types of Corrosion**

### 2.7 Corrosion Control Methods

In marine technology, the application of organic coating is an old method used to stop corrosion but this method has a limited time then the hull starts to corrode again. However, by selecting a suitable coating the ship hull could be protected for the lifetime span of the ship. Barrier (coating), cathodic (electrochemical) and inhibitive (oxygen deprivation) are the main three methods of controlling the corrosion. (Khayal, O.M.E.S., 1993).

### **2.7.1 Water-Resistant Coatings**

The most commonly used method of preventing corrosion is to place a water resistant barrier between the sheet metal and the electrolyte (sea water). The type of anti-corrosive coating required is dependent on two main factors: the type of antifouling to be used and the location of application on the ship. Obviously the antifouling and the anti-corrosive must be compatible, there must be good adhesion between them and also no reaction to impair the properties of either coating. Different areas of the ship require specific anti-corrosives; for example, around the steering gear, the hull and the splash zone where the environmental situations are very different.

Although it is not ideal, in practice only one anticorrosive coating is used and this is based either on a chlorinated rubber resin or a pitch base, the system being chosen to be compatible with the antifouling to be used.

Inevitably the coatings will not be continuous and pinhole free, and in service are likely to be damaged. There are also areas of the ship, such as steering gear, propulsion units and anchorage points which cannot be permanently coated, consequently other techniques to combat corrosion have been developed.

### **2.7.2 Cathodic Protections**

Cathodic protection is an established corrosion control method for protection of underground and undersea metallic structures, such as ships' hull, oil and gas pipelines, cables, utility lines and structural foundations. Cathodic protection is generally useful in the protection of ships' hull platforms, dockyards, jetties, submarines, condenser tubes in heat exchangers, bridges and decks, civil and military aircraft and ground transportation systems. The designing of cathodic protection systems is rather complex. However, it is based on simple electrochemical principles. Corrosion current flows between

anodes and cathodes due to the existence of a potential difference between the two elements. (Khayal, O.M.E.S., 2018).

As can be seen in Figure (2.3) below which shows cathodic protection, electrons released in an anodic reaction are consumed in the cathodic reaction. If we supply additional electrons to a metallic structure, more electrons would be available for a cathodic reaction which would cause the rate of cathodic reaction to increase and that of anodic reaction to decrease. This action would finally minimize or eliminate corrosion. This is basically the purpose of cathodic protection. The additional electrons are supplied by direct electric current. If enough direct current is applied, the potential difference between the anode and cathode is eliminated and corrosion would finally stop.

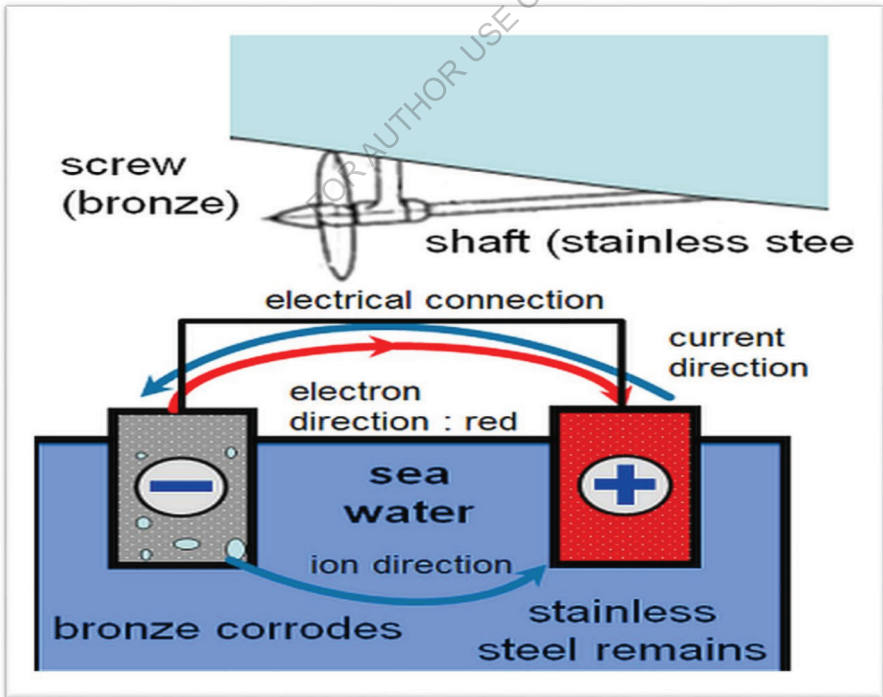


Figure (2.3) Cathodic Protection

Figure (2.4) and Figure (2.5) below demonstrate how cathodic protection works in terms of E-pH diagram. Cathodic protection brings down the potential of a metal that has a free corrosion potential at the active potential and pH to a lower potential that is defined as an “immune” area. Figure (2.5) below demonstrates

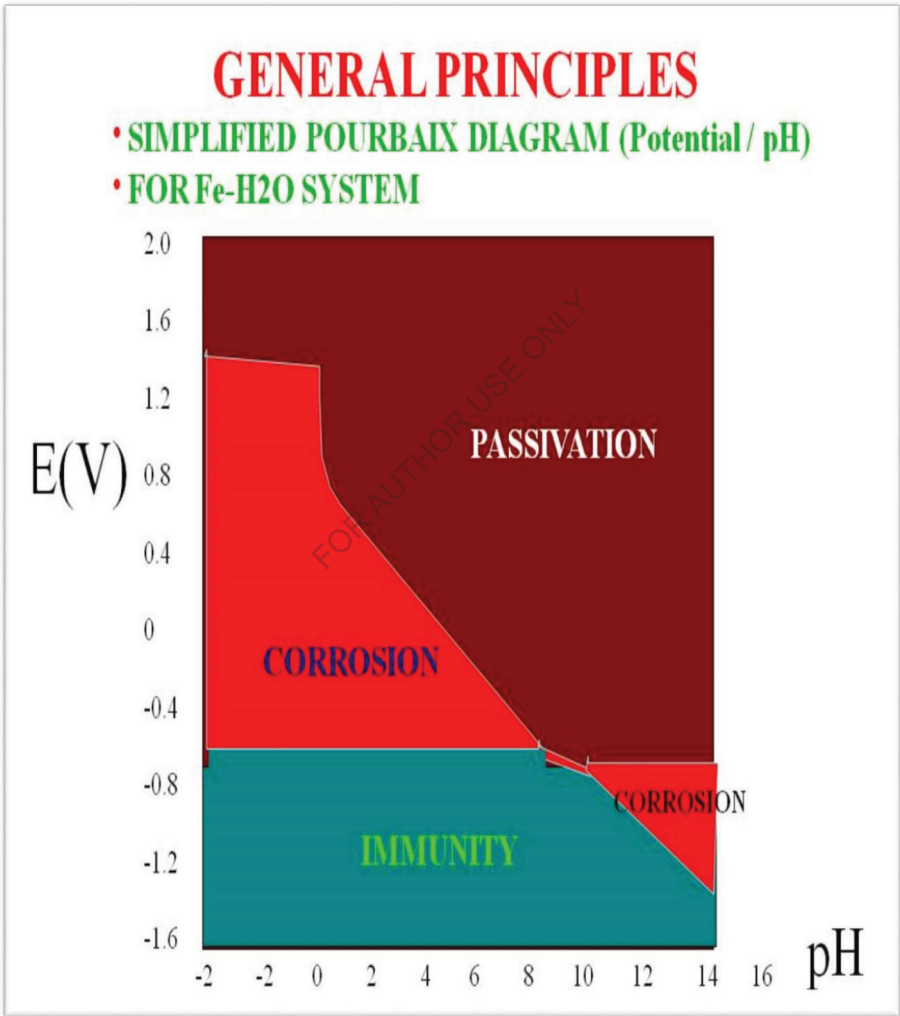


Figure (2.4) pH Diagram

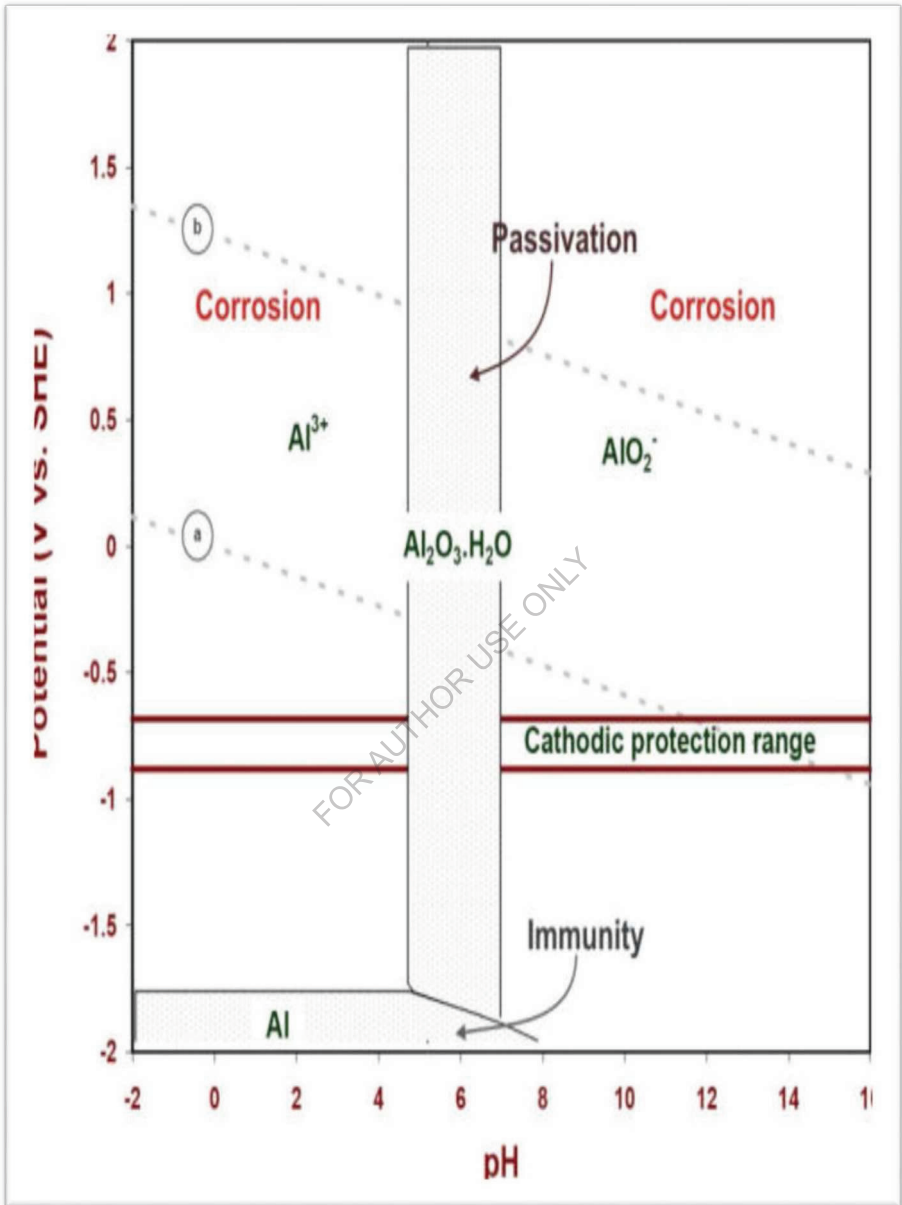


Figure (2.5) Potential / pH Diagram

### 2.7.2.1 The Principles of Cathodic Protection



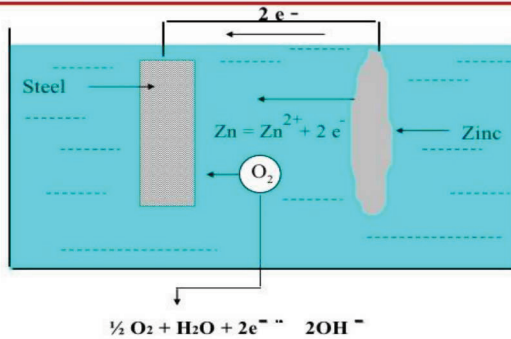
the metal is also protected at a higher current, but hydrogen evolution is possible leading to coating defects or hydrogen embrittlement. The principle above is applied in the real world mainly by two methods. One method involves current supplied to protected metal using a sacrificial metal that is galvanically more active than the protected metal which is termed “sacrificial anode”. The other method involves supply from an external DC current source termed “impressed current” method (Perez. N. (2004).

### **2.7.2.2 Cathodic Protection by Sacrificial Anode**

In cathodic protection, the structure to be protected must be given a cathodic current flow so that it operates as a cathode. The requirement for an external DC current to achieve this can be eliminated by using an anode constructed of a metal that is more active in the galvanic series than the metal to be protected called a sacrificial anode. A galvanic cell is established with the current direction as required.

One example of sacrificial anode material is magnesium or magnesium-based alloys. Magnesium is more active than steel, has a greater tendency to ionize. The open-circuit potential difference between magnesium and steel is about 1 volt. This means that one anode can protect only a limited length of pipeline or over a defined surface area. This low voltage can have an advantage over higher impressed voltages in that the danger of overprotection to some portions of the structure is less and because the total current per anode is limited; the danger of stray-current damage to adjoining metal structures is reduced. Magnesium rods have also been used in steel hot water tanks to increase their service life. The greatest degree of protection is in more conductive electrolyte such as hard waters, compared to soft waters which have lower conductivity. Figure (2.7) shows sacrificial anode cathodic protection (SACP).

## Cathodic Protection Steel protected by a Sacrificial anode



A calcareous deposit is formed on the steel surface

**Figure (2.7) Sacrificial Anode Cathodic Protection (SACP)**

Zinc and Aluminium have been used extensively in seawater applications. Sacrificial anodes for offshore structures in seawater are commonly made of special Aluminium alloys because these anodes are low in cost and provide the highest current output per anode weight. Zinc anodes are used on coated and buried pipelines offshore, where the risk for passivation of Aluminium anodes is higher due to a lower current density requirement. Zinc and Aluminium sacrificial anodes used on ship hulls are usually combined with a paint system. The anodes are placed close to each other on the area around the propeller because the current could leak to the propeller, and the current demand is high due to turbulence around this area. Ballast tanks on tankers and bulk carriers also use Zinc and Aluminium anodes (Bardal, 2004). The energy content and efficiency of these metals are shown in Table (2.4) below. Table (2.4) shows the efficiencies of several common anode materials.



**Table (2.4) Efficiencies of Several Common Anode Materials**

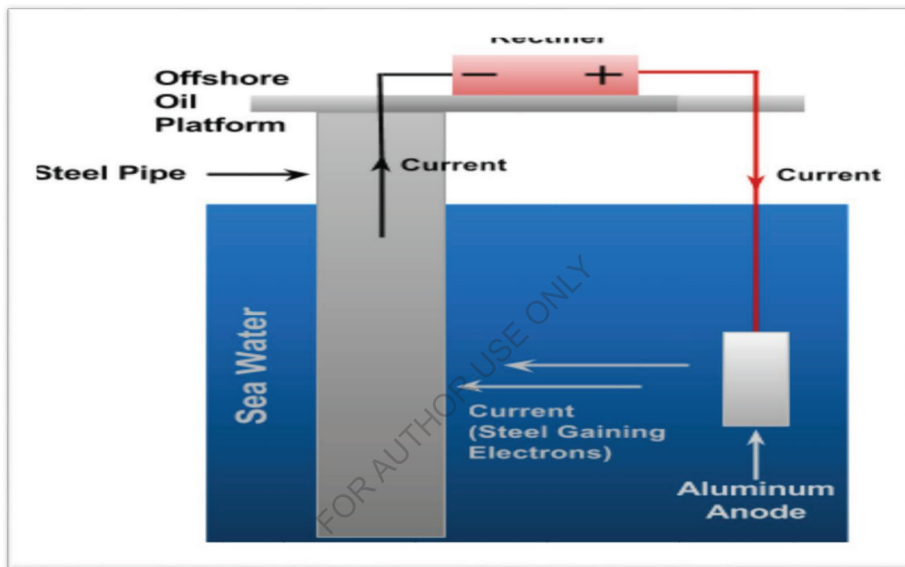
| Energy Content   | Anode material |      |           |
|--|----------------|------|-----------|
|  | Magnesium      | Zinc | Aluminium |
| Theoretical Energy content, ampere-hour per kilogram of mass (Ah/kg)     | 2205           | 816  | 2965      |
| Typical Anode % , Efficiency   | 50             | 90   | 60        |
| Practical Energy content = Theoretical energy x Anode efficiency (Ah/kg) | 1102           | 734  | 1779      |

Each of the anodes have their own limitations. Zinc is more economical to use than magnesium, but because of the relatively small cell voltage it produces, it is primarily useful to protect ships in seawater or to prevent corrosion in systems that require only small currents. Although magnesium is more expensive and consumed faster than zinc or Aluminium, it provides the largest potential and current. Aluminium cannot be used in environments with pH more than 8, since alkaline conditions will make Aluminium self-corrodes rapidly.

### 2.7.2.3 Cathodic Protection by Impressed Current (ICCP)

This system uses external source of electricity. High voltage from the external source is converted to low voltage DC current by means of a transformer-rectifier. This direct current is impressed between buried anodes and the structure to be protected. Use of inert anode is preferred, as this will last for the longest possible time. Typical anodes used are graphite, titanium, silicon and niobium plated with platinum. The applied current is limited by electrolyte resistivity and by the anodic and cathodic polarization. Impressed current system makes it possible to apply the potential level that is necessary to obtain the current density required by means of the rectifier, whatever the value of the potential is. Electric current flows in the soil from the buried anode to the underground structure to be protected. Therefore, the anode is connected to the positive terminal of the rectifier and the protected structure

to the negative terminal. All cables from the rectifier to the anode and to the structure are electrically insulated. If not insulated, wires from the rectifier to the anode can act as an anode and deteriorate rapidly, while cables from the rectifier to the structure may pick up some of the electric current, which would then be lost for protection (Durham & Durham, 2005). Figure (2.8) shows impressed current cathodic protection.



**Figure (2.8) Impressed Current Cathodic Protection**

#### **2.7.2.4 Impressed Current Method Requirements**

Metal to be protected and the environment it is exposed to determine the current density required for complete protection. The applied current density must always be larger than the current density equivalent to the measured corrosion rate under the same conditions. Therefore, as the corrosion rate increases, the impressed current density must be increased to provide protection. Three factors affect current requirements:

1. The nature of the electrolyte

2. Resistivity of the electrolyte.

3. The degree of aeration.

The current requirement increases with increasing acidity of the electrolyte. For example, surroundings with high resistance have a lower cathodic current needed to provide protection. The required current to provide cathodic protection can vary from 5 to 220 mA/m<sup>2</sup> of bare surface. Application of impressed current technique in the real world requires field testing to determine the necessary current density to provide cathodic protection in a specific area. The testing techniques are only some way to obtain approximations. After installation of the system, it is necessary to conduct a potential survey and make the necessary adjustments to provide the desired degree of protection (Zakoski, K and Darowicki, 2004).

### **2.7.2.5 Anode Materials & Surrounding for Impressed Current System**

The determination of anode materials and the surrounding (atmosphere) material used in impressed current systems in different environments and applications play a major role, because these anodes are the mean through which the protective current is delivered to the protected structure or metal. The type of anode is vital in influencing the reactions on the anode surface. For consumable metals such as scrap steel or cast iron, the main reaction is the anodic metal dissolution. Metal dissolution is negligible if the anode has passive surfaces and the main reactions are gas evolutions. For example, oxygen is evolved in the presence of water, and chlorine gas is evolved if the electrolyte contains chloride ions. The gas evolution reactions also happen on non-metallic conducting anodes surfaces such as graphite. On partially passive surfaces, both the metal dissolution and gas evolution reactions could happen. Corrosion product buildup is associated with the metal dissolution reaction.

A wide range of materials can be used for impressed current anodes. The balance between anode performance and costs play a big role in determining the right anode material to be used. The following Table (2.5) shows selected anode materials in general which are used under different environmental conditions (Shrier .L.L & Hayfield, 1986).

**Table (2.5) Anode Materials for ICCP under Different Environments**

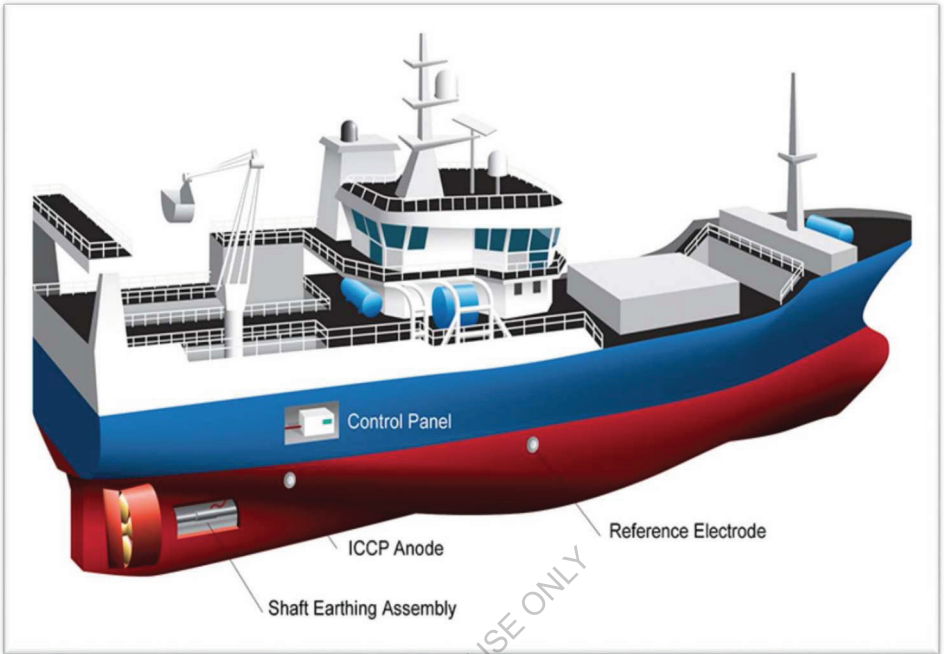
| Anode Materials | Atmosphere (Surrounding) |             |                 |              |              |
|-----------------|--------------------------|-------------|-----------------|--------------|--------------|
|                 | Marine                   | Concrete    | Potable water   | soil         | Pure liquids |
|                 | Platinized               | Platinized  | High-Si iron    | Graphite     | Platinized   |
|                 | surfaces                 | surfaces    | Iron and steel  | High-Si cast | surfaces     |
|                 | Iron and steel           | Mixed-metal | Graphite        | iron         | //           |
|                 | Mixed-metal              | oxides      | Aluminum        | High-Si iron | //           |
|                 | oxides                   | Polymerized | //              | Mixed metal  | //           |
|                 | Graphite                 | //          | //              | oxides       | //           |
|                 | Zinc                     | //          | //              | Platinized   | //           |
|                 | High-Si Cr cast          | //          | //              | surfaces     | //           |
| iron            | //                       | //          | Polymeric, iron | //           |              |

|  |    |    |    |       |    |
|--|----|----|----|-------|----|
|  | // | // | // | steel | // |
|--|----|----|----|-------|----|

The properties of atmosphere that hold the impressed current anodes are also important. To increase the effective anode size and lower the resistance of soil, carbonaceous material such as coke breeze and graphite are used. This type of atmosphere also reduces consumption of the anode material because the anodic reaction is transferred from the anode to the holder atmosphere. Three factors are considered to ensure low resistivity of the surroundings material

1. Composition.
2. Particle size.
3. Degree of compaction.

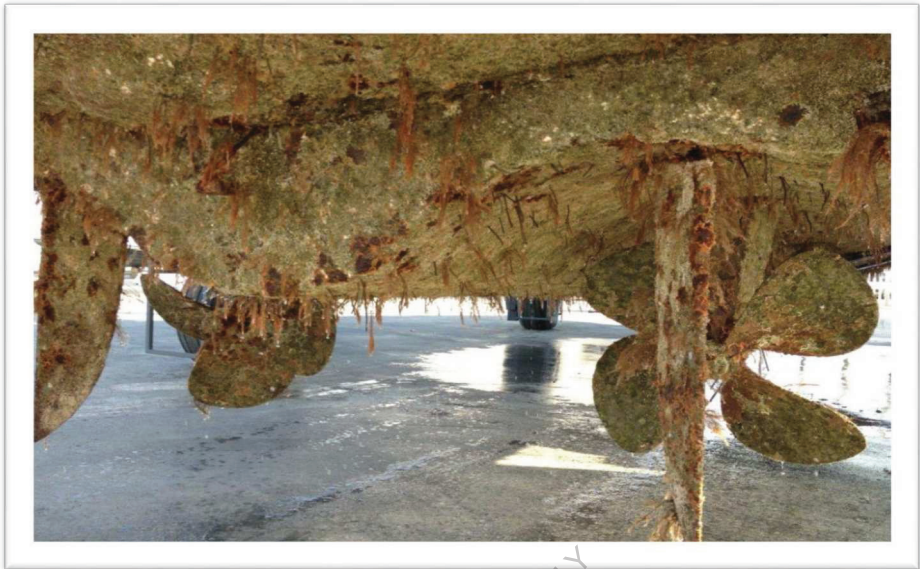
The particle size and degree of compaction also influence how anode-generated gases escape. Since it is quite problematic to properly establish the above surrounding properties properly in the ground, ready-made anodes and atmosphere inside metal containers that are factory-prepared according to the best of the above factors are used. These metal containers will be eventually consumed under operational conditions. A set of parallel cylindrical anode rods placed vertically deep underground are commonly used in the industry (termed vertical deep anode). These provide minimized anode bed resistance and induced stray currents, smaller right-of-way surface area, and improved current distribution. However, vertical deep anodes also incur higher capital expenditure per unit of current output, are difficult to repair in case of any anode damage, and may block gas generated at the anode from escaping (PETRONAS, 1987).



**Figure (2.9) Ship's Hull with ICCP System**

## **2.8 Bio Fouling**

Bio fouling is a complex process which involves the attachment and growth of a community of organisms on a surface in contact with an aqueous medium. For the shipping industry in particular, bio-fouling is a critical problem, leading to the reduction of the maximum speed and upraise of the fuel and maintenance costs. Consequently, as known, higher fuel consumption also translates into higher emission of greenhouse gases such as NO<sub>x</sub> and SO<sub>x</sub>. Also, an increase of at least 50% of CO<sub>2</sub> emissions until 2030, under extreme scenarios, was estimated by the International Maritime Organization (IMO). The settlement and accumulation of marine organisms also leads to the increase of the drag created between the ships' hull surface and the sea water. Drag friction increases up to 40% could be reached. Figure (2.10) below shows fouling and bio corrosion on the hull of a ship.



**Figure (2.10) Fouling and Bio Corrosion on the Hull of a Ship**

Bio-fouling is also associated to bio-corrosion of surfaces, reducing the lifetime of the structures under a marine environment, which is also promoted by the corrosive effect of sea water itself. Microbiological fouling should be strictly controlled since it can create Microbial Induced Corrosion (MIC). For example, Sulphur-reducing Bacteria (SRB) come from the marine sediment and gain energy using electrons from the steel structures, chemically reducing the sulphates from the sea water to sulphides, causing the pitting corrosion of steel surfaces.

Additionally, bio-fouling also contributes to the emigration of certain marine species to other areas, as occurred in Ponta Delgada, Island, and Portugal, where alien species of fouling organisms such as barnacles were found. *Amphibalanus Amphitrite* was one of the species of barnacles detected and it is assumed that it is originated from the Indo-Pacific Ocean. Therefore, it is presumed that due to the fouling propensity of the reported species and given



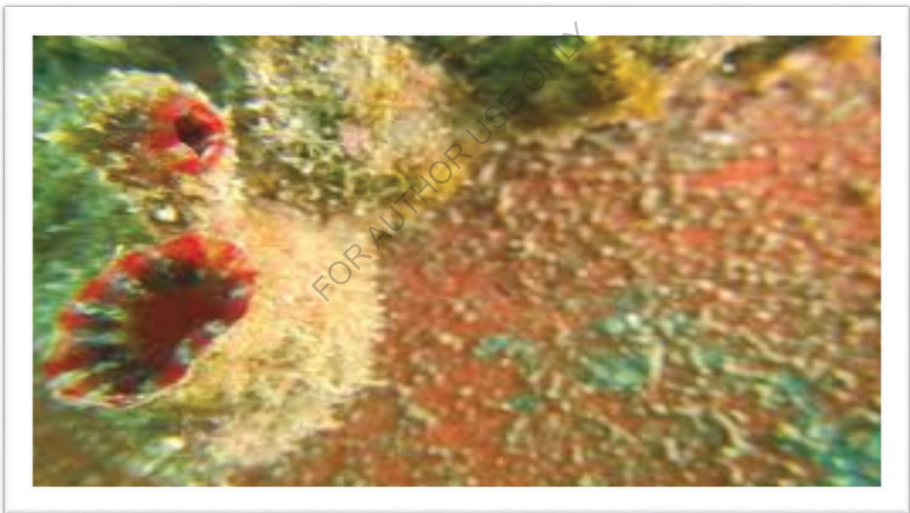
their origin, this reallocation was caused by the increasing boat traffic in the last years.

## **2.9 Types of Bio-Fouling**

The bio-fouling organisms are classified into two different groups. The groups are 'Plant Bio-fouling' and 'Animal Bio-fouling'. The following section elaborates the species of bio-fouling.

### **2.9.1 Plant Fouling**

There are three types of plant fouling species as discussed in the following subsections: Figure (2.11) below shows plant fouling.



**Figure (2.11) Plant Fouling**

#### **2.9.1.1 Bacteria and Bacterial Slimes**

The bacteria which cause bacterial slimes are present in the sea water all the year round; they present a major fouling problem as settlement occurs within minutes of immersion. The slime is generated after the settlement of the bacteria by secretion of mucus, the species of bacteria being classified by



this mucus. Once attached, these bacteria begin to reproduce by cell division, the daughters not normally being released into the sea water but being held in the parents' mucilage thus very quickly the slime thickness and the fouled area increases. The slime thickness can vary from a few microns to several millimeters depending on the conditions, and this thickness directly affects the hull surface roughness and reduce the ship power due to the drag caused by these bacterial slimes. However, these bacterial slimes are important because they can influence the rate at which toxins are released from an antifouling coating by forming a diffusion barrier on the surface. But the slime can also trap spores and larvae of other fouling organisms thus promoting macro fouling and worsen the roughness of hull surfaces.

### **2.9.1.2 Diatoms**

Diatoms are microscopic plants with a characteristic brown color, they are similar to bacteria in size and again secrete mucus through their external siliceous shell although this is less slippery than that produced by the bacteria to those listed above, and it also affects the hull surface and causes drag that reduce ship performance.

### **2.9.1.3 Seaweeds**

Diatoms cause similar problems. These are algae and three main classes are found; namely, green, brown, and red seaweeds .

The commonest species of green seaweed is enteromorpha (seagrass) and this is found near the waterline forming a carpet up to 10 centimeters thick and extending to a depth of several meters on the hull. Its success as a fouling organism stems from its ability to tolerate a wide spectrum of toxins and also its worldwide distribution. This marine algae exists as long 'grass like' filaments which contain up to five million cells in an average frond 7-8 centimeters long, each cell being capable of producing eight zoospores

(reproductive spores). These spores leave the parent cell as free swimming zoospores directed by four flagellae, they settle preferentially in surface irregularities. When the zoospore makes contact with the surface the flagellae act as brushes and clean the point of settlement, a cement is released and within seconds the organism is firmly bound to the surface. It is at this stage that it is most vulnerable to toxins as it is surrounded by only a thin membrane, but within four hours a protective wall is formed and the zoospores begin to develop into the mature algae, after a few days it is already a few millimeters long and a centimeter or more within two weeks.

The most common brown seaweed is ectocarpus which reproduces in a similar fashion to enteromorpha and again has worldwide distribution. The plant is composed of two parts, the rhizoidal, a root-like part and an upright part supporting the spore bearing structure, this being branched and limp. Each plant is capable of producing  $40 \times 10$  spores and each of these spores have two flagellae. They swim in the sea until a suitable settlement site is found (usually in surface defects) where they attach themselves and begin to develop a protective wall, this occurring at a slower rate than with enteromorpha; usually taking 24 hours, after which time growth of the new plant will have started. These seaweeds are found lower down on the hull than enteromorpha.

The commonest red seaweeds found are ceromium and polysuphonia, their reproduction and settlement behavior is similar to that described above but these seaweeds are highly branched and much larger than either of the other two species; they are found much lower down on the hull where the light intensity is very low. It has been shown that these fouling organisms, like the other seaweeds are most vulnerable to toxins during their settlement period; the resistance of the mature seaweeds to toxins is considerably higher than that of animal fouling organisms.

## 2.9.2 Animal Fouling

The second type of bio-fouling is 'Animal Fouling' which is sorted into seven groups: Figure (2.12) below shows animal fouling.



**Figure (2.12) Animal Fouling**

### 2.9.2.1 Arthropods

This is a class of the animal kingdom which includes all organisms with chitinous external skeleton and joined appendages, many of these have a skeleton which is hardened by calcareous deposits .

The barnacle (cirripedia), of which there are many different types, is the most common arthropod to be found on a ship's hull. It is a hermaphrodite, but sexual reproduction is preferred, a sexual reproduction occurring only under adverse conditions. The eggs are produced in the parent shell, when the conditions are correct the nauplii (free swimming) larvae are liberated, and depending on the species they metamorphose up to eight times, the

final transformation producing the cypris (settling) larvae. The cypris larvae either swim or crawl around until they find a suitable area in which to settle, this is often a site which has previously been inhabited by a barnacle community. A protein, arthropodine, is secreted by mature barnacles and it is this which acts as a reference for renewed settlement.

The settling stage is the most vulnerable period for the young barnacles, the toxins in conventional anti-fouling coatings effectively kill the majority at this stage, and hence on recently painted ships there is no serious fouling problem due to barnacles. If they do survive and grow to their adult form not only do they cause increased surface resistance but also their shells tend to cut through the underlying coatings causing a corrosion problem.

A particularly difficult type of barnacle fouling is that produced by the goose barnacle: its settlement and growth occurring rapidly and vigorously even in the open sea.

There are many other arthropods found in the sea, these include isopods, amphipods, crabs, shrimps and insects, but these only foul static structures and therefore do not present a fouling problem on seagoing vessels.

### **2.9.2.2 Tubeworms (Annelids)**

The coral effect on fouled underwater surfaces results from the activity of tubeworms. Reproduction can be either sexual which results in free swimming larvae and thus a new area of infestation, or asexual when the parent acts as host to the new larvae which eventually bore holes through the calcareous shell of the parent and grow as new entities although still attached to the parent. This process produces a random frosted effect on the surface. As the creature grows the shell is extended; this continues until the death of the animal, by which time there may be a large hard calcareous growth which remains attached to the surface and this can only be removed

by abrasive treatments such as grit blasting. The presence of tube worms can be used as a good indication of the state of exhaustion of the matrix toxins in antifouling paints as they are normally vulnerable to toxins.

### **2.9.2.3 Mussels (Pelecypods)**

The mussel is one of the few shellfish which foul vessels since generally shellfish are very susceptible to toxins not only during settling but also in the adult organism. This is due to their method of feeding and also the susceptibility of the settling larvae to toxins. Many mussels reproduce sexually although some species are reproduced asexually, the resulting fertilized eggs being either held within the parent which releases free swimming larvae or the eggs are liberated into the water and hatch to produce the free swimming larvae. These larvae initially settle by means of a foot followed by the formation of a byssus (a web like system of roots) which firmly secures the adult. Again the shell remains attached to the surface after the death of the organism and is difficult to remove.

### **2.9.2.4 Bryozoa**

These may be divided into three main groups depending on their pattern of growth. Encrusting Bryozoa grow over the substrate to produce a network of shell growth similar to tube worms. Erect Bryozoa grow outwards from the substrate, and Stolunate Bryozoa have an intermediate pattern of growth. Reproduction is again sexual or asexual, the fertilized eggs either being retained by the parent or existing in the sea. Settlement occurs several hours after hatching, then the adult develops. The most susceptible time for poisoning Bryozoa is during the settling period, after which time it is difficult to kill this species of fouling .

### **2.9.2.5 Sea Squirts**

These produce free swimming larvae which become attached to a surface before metamorphosis can occur. The parent is a very lowly form of vertebrate existing as a sack through which water is filtered. They are not a common fouling organism on ships as, like mussels, they feed via filtration of water and so are very susceptible to toxins.

### 2.9.2.6 Hydroids

The free swimming hydroid larvae, produced either sexually or asexually, cements itself to a hard surface and grows into the adult. The adult is very firmly attached to the surface and resembles seaweed; it is quite resistant to toxins unlike the young free swimming hydroid which is easily poisoned.

### 2.9.2.7 Protozoa

These are single cell animals which range in size from 0.002 mm to several centimeters. Their small size and their inability to form large colonies render them unimportant as fouling organisms. They do however provide, like the micro fouling organisms in the plant kingdom, sites for settlement of other fouling organisms.

Generally plants are more resistant to toxins than animals because their method of feeding involves the absorption of nutrients by osmosis which prevents the ingestion of the toxin whereas animals take in food and toxins directly and are therefore more easily killed. The resistance of fouling organisms to commonly used toxins is shown in Table (2.6) below.

**Table (2.6) Resistance of Fouling Organisms towards Toxins**

| No | Resistance | Organism             |
|----|------------|----------------------|
| 1  | Very High  | Bacteria and Diatoms |

|   |           |   |
|---|-----------|---|
| 2 | Very High | Ectocarpus, Enteromorpha, Hydroids, Barnacles and Polyzoans           |
| 3 | Moderate  | and Barnacles Tubeworms, Hydroid                                      |
| 4 | Low       | Weeds (Green & Red), Sea Squirts, Mussels and Oysters Sea Squirts and |

## 2.10 Bio-Fouling Mechanism

There are some factors affecting the settlement of fouling organisms; the more important factors being the geographical location, the season, the movement of the water relative to the surface, the texture of the surface, the intensity of illumination and the presence of slime films.

The geographical and seasonal influence are of major importance as the reproduction of the fouling organism is governed by the water temperature consequently, in some areas of the world's oceans no fouling may occur during the winter. The longer the summer season the greater the fouling as the reproduction of fouling organisms is far more prolific during the warmer season. Wherever there is a warm water current, excessive fouling can be expected, as is found in the Gulf Stream. One of the implications of the geographical and seasonal factors is that it may be necessary to have several different types of anti-fouling paint that are suitable for the different areas in which ships operate.

The first step in fouling is settlement and this cannot occur when the ship is moving above 13 km, thus a stationary ship is an ideal site for fouling. The majority of fouling occurs when the ship is in harbor, as there is a higher water temperature, consequently a larger fouling population and the flow of water past the hull is usually very slow. Ships which spend a very short time in harbor are found to be relatively free from animal fouling although they

have a large amount of plant fouling, this being due to the ease and rapidity of settlement of the latter.

The surface texture of the coating is important because imperfections in the surface provide sheltered environments where the fouling organisms can settle and be protected from the flow of water past the hull. The settlement of fouling on a moving ship is thought to be due to a combination of static flow patterns created on certain areas of the ship and also micro fouling organism's entrapping the settling larvae of macro fouling organisms in their mucilage, thus enabling the larvae to grow into the adult form.

The light intensity plays an important role in plant fouling as this can only exist where there is sufficient light to allow photosynthesis to occur. Consequently the seaweeds requiring most light (green) are found near the water line, whereas those requiring less light (brown and red) are found lower down on the hull. Animal fouling is independent of the light intensity although some animal fouling organisms settle preferentially near the water line.

## **2.11 Stages of Bio-Fouling**

Bio-fouling is characterized by four main stages throughout the time. The first stage initiates after the earliest minutes of immersion, where the physical adhesion of organic molecules of proteins, polysaccharides, glycoproteins and others, occur. In this stage, Van der Waal's forces and electrostatic interactions promote this adsorption phenomenon. The movement of water leads to the contact and colonization between the microorganism and the surface. This attachment leads to the second phase, after 24 hours of immersion, where the reversible adsorption of bacteria and unicellular algae occurs. Bacteria and other colonizing microorganisms secrete Extracellular Polymeric Substances (EPS) to enclose and hold



the substrate, forming a microbial film. Consequently, the local surface chemistry is altered, being propitious to stimulate further growth and settlement of macro-organisms.

This microbial film feeds spores of microalgae, allowing their attachment, which will constitute a bio-film (1 week, third stage). The bio-film generated is a mass of microorganisms and the EPS secreted creates a gel matrix providing enzymatic interaction and high resistance to biocides. Also, the arrangement of the microorganisms in the biofilm protects them from the predators and from environmental variations, facilitating the obtainment of the nutrients necessary for the settlement of other microorganisms. This bio-film is capable of attracting more particles and organisms as larvae of marine macro-organisms, characterizing the fourth stage, after 2 or 3 weeks of immersion. The roughness of the surface created by the irregular microbial communities will also help the accommodation of the new attracted organisms. All of these conditions will contribute to the adhesion and attachment of macro algae and marine invertebrates.

## **2.12 Antifouling Coating Formulation and Methods**

### **2.12.1 Coating System**

The coating system on a ship is required to prevent corrosion and fouling, this being achieved by using an anticorrosive paint and an antifouling paint.

#### **2.12.1.1 Formulation of Anti Fouling Paints**

There are two sets of criteria which must be applied when formulating antifouling paints, one set applying to the toxin and the other to the paint film. With current conventional antifouling coatings toxins are the most important ingredients, since they are the components which prevent fouling. They function by controlled release of toxin from the paint matrix into the

laminar sub layer thus in theory killing the fouling organism before settlement. The important characteristics of the toxins are:

- A. They should have a low solubility in sea water but, not of course be totally insoluble,
- B. They should have a wide spectrum of toxicity to marine fouling organisms,
- C. They should not create an ecological problem,
- D. They should be compatible with the paint medium in which they are placed and stable,
- E. They should be of reasonably low price, and
- F. They should not present an application problem .

Many toxins are patented each year most of which are of little use to the antifouling chemist as the above criteria are not satisfied. The main biocides which are used in commercially available anti-fouling today are: copper I oxide, copper I thiocyanate, zinc oxide, and tripheny l tin fluoride, often a combination of these being used to broaden the range of toxicity of the coating.

The role of the paint film is that it must be able to release the toxin at a rate which allows the prevention of fouling, while retaining its structural integrity so that its ability to adhere to the hull and withstand mechanical stresses is not reduced .

The paint formulation is dependent on the toxin and also the mode of release of the toxin. The compounds used in a successful paint formulation have generally been selected on the basis of a trial and error approach as there is at

present no satisfactory method by which the antifouling nature of the paint can be predicted .

The ultimate test for an antifouling is to paint a ship's hull but prior to this cheaper and less expensive tests are conducted. Test panels coated with the new antifouling are immersed in sea water, usually under a raft in an estuary, the flow of water past these panels simulating the ship's passage through water. This tests the ability of the coating system to prevent fouling and also gives a guide to its active life and to the integrity of the film after prolonged exposure. If a new coating system appears to be promising, the next stage in testing is to attach coated bilge keel panels to a ship in service, the last stage before full scale ship trials are test patches (50-100m) painted on various ships. The expense involved in each of the test methods increases. Therefore, it is essential that only antifouling which are virtually certain to prove adequate are applied as test patches. The development of a new antifouling can take up to six or seven years due to the lengthy testing periods required.

The leaching of toxins from an antifouling coating can be determined very easily in the laboratory as can the lethal dose to the fouling organism, although it is impossible to apply this data to the real situation; generally a much higher leaching rate is required in practice than would be predicted on the basis of laboratory estimates. This illustrates that the factors which influence leaching rates form a complex matrix of interacting physical and chemical parameters impossible to quantify.

## **2.13 Antifouling Methods**

The advice to protect the ship hulls from marine bio-fouling, to avoid material damages and excessive fuel consumption, has led to an intensive research for economical and environmentally friendly solutions. Therefore, a

"traditional" and "modern" antifouling methods are elaborated in the following subsections.

### **2.13.1 Traditional Antifouling Methods**

Marine bio-fouling has been an annoyance for more than 2000 years. At that time due to the lack of advanced technology and in order to overcome this problem, natural products were used to resist corrosion and biofouling.

For example, Phoenicians and Carthaginians were said to have used pitch and possibly copper sheathing on ship hulls, whereas other ancient cultures used wax, tar and asphalt. The use of coatings made with arsenic and sulphur mixed with oil were also used to resist shipworms, in the past.

A brief description of the ancient (old) antifouling methods is presented below:

#### **2.13.1.1 Lead Sheathing**

As mentioned above, pitch, copper sheathing, wax, tar, asphalt or a mixture of arsenic and sulphur with oil, were applied to protect ship hulls. Alternatively, lead sheathing was also used for this purpose.

Lead sheathing consisted of covering the ship hulls with lead patches in order to protect them from biofouling and corrosion. Ancient cultures such as Phoenicians employed this prevention method in 700 B.C., while the Greeks were reported to use lead sheathing and tar and wax, in the 3<sup>rd</sup> (third) century B.C. Greeks and Romans also used copper nails to secure the sheathing.

In the period between 45 and 125 A.D., Plutarch mentioned the method of scraping the ship's sides to remove weeds, slime and filth, in order to facilitate the motion of the ship on the water.

Later, in 10 A.D, Vikings occasionally used seal tar. From the 13th to 15th century, the use of pitch was abundant, being sometimes mixed with oil, resin or tallow.

In the 16th century, lead sheathing was largely adopted, being employed by Spain, France and England, although wood sheathing was more usual.

However, the British Admiralty discarded the use of lead sheathing, in 1682, due to the corrosion caused on the iron components of the ships. Subsequently, lead sheathing was then alternated with wood sheathing. After applying the latter, it was painted with several mixtures such as tar, grease, pitch and brimstone and then nailed with large headed copper or iron nails very adjacently, in order to form a metallic sheathing.

### **2.13.1.2 Copper Sheathing**

The first reference regarding to the underwater use of copper was in 1618, during the reign of the Danish King Christian IV, who used a coppered keel.

However, the first reference regarding the use of copper as an antifouling agent was patented by William Beale, who used a mixture of cement, powdered iron and a copper compound (copper sulphates or copper arsenic ore).

The use of copper sheathing was firstly reported in 1758 on 'His Majesty's Ship' (HMS) Alarm frigate, whose success motivated other ships to use copper, mostly the British Navy, around 1780. The application of copper on wooden ships was so successful that England prohibited the exportation of this metal.

Only in the 19th century, Humphrey Davy showed that the fouling prevention was attained due to the dissolution of copper in the sea water.

Anyhow, the use of copper sheathing on iron ships (introduced late in the 18th century) was discontinued, due to the uncertainty of its antifouling action and corrosion effects on iron.

### **2.13.1.3 Other Sheathing Elements**

Due to the introduction of iron ships and the abandonment of copper sheathings on this type of boats, more alternatives were tried, to obtain protection against bio-fouling.

Sheathings of zinc, lead, nickel, arsenic, galvanized iron and alloys of antimony, zinc and tin and coppered wooden sheathings were the alternatives tested. Non-metallic alternatives such as soaking felt in tar or using cork, rubber and plain brown paper were often applied to separate the copper sheathing from the iron hull. Wooden sheathings were also tested on these ships, although without success, due to its high cost.

### **2.13.2. Modern Antifouling Methods: Protective Paints**

Novel antifouling systems were developed to overcome the limitations of the ancient methods. These systems consisted of paints such as enamels, varnishes, primers, sealers and many others. The majority of antifouling coatings is mainly composed by a primer (anticorrosive) and a topcoat. The latter incorporates anti-foulants to protect the hull from bio-fouling.

#### **2.13.2.1 Antifouling Paints**

In the mid of 1800, different paints were created, by dispersing a toxicant in a polymeric base. These toxicants consisted of copper oxide, arsenic and mercury oxide, whereas the solvents used were turpentine oil, naphtha and benzene. Linseed oil, shellac varnish, tar and diverse types of resin were employed as binders.

Nevertheless, these paints required the application of a primer in order to protect the steel hull from the pigments used, since its direct utilization on the hull caused corrosion.

In the meantime, more paints were launched, such as “hot plastic paints” consisting of copper sulphates in a metallic soap composition, shellac based paints (rust preventive) and “cold plastic paints” which used diverse synthetic resins or natural products either solely or in mixtures. The latter effectively decreased fouling and were easily applicable due to “airless” spraying, enabling dry docking periods of up to 18 months.

However, the antifouling industry changed after the Second World War, leading to the appearance of new synthetic petroleum based resins with improved mechanical characteristics. Also during this period, organometallic paints were introduced and contained tin, arsenic, mercury and many others, which after several developments, led to tributyltin (TBT) based paints. The TBT based paints revealed to be remarkably efficient against bio-fouling.

Additionally, more paints’ technologies were developed to overcome the environmental issues of organometallic based paints, and classified according to the chemical properties of the binder and by their water solubility: soluble matrix and insoluble matrix paints.

### **a) Soluble Matrix Antifouling Paints**

Soluble matrix antifouling paints contain rosins and their derivatives as binders and toxic pigments (copper, iron, zinc oxides, arsenic and mercury). The toxic compounds can dissolve in sea water, forming a thin leached layer which easily releases the toxic material as the sea water penetrates. The thickness of the leached layer decreases when the ship speed increases, which consequently leads to an exponential increase of the release rate. On the other hand, at static conditions, the settlement of organisms is

accentuated and the insoluble salts can block the coating's pores, which consequently decreases the release rate of the biocides. In addition, these paints are less mechanically resistant than the insoluble paints due to the brittleness of the resin and its instability to oxidation and as consequence, the life span of these paints is short (12 to 15 months). Nonetheless, they present the advantage of being easily applied on smooth bituminous-based primers.

### **b) Insoluble Matrix Antifouling Paints**

Insoluble matrix antifouling paints have a polymeric matrix such as acrylic, vinyl or chlorinated rubber, which are insoluble in sea water. When the coating is immersed in sea water, the soluble toxic materials dissolve and consequently leave a multiporous layer known as leached layer, which enables the further penetration of the water and the release of more poisonous compounds. The advantage of this type of paint is the high mechanical resistance and stability to oxidation and photo degradation. Although the coatings are thick to increase the content of toxic material, at some stage, the efficiency will decrease due to the gradual release of the toxic compounds. Consequently, the empty space left by the dissolved biocides will modify the roughness of the surface and capture pollutants from the sea water, which will restrain the water penetration and as a result decrease the release rate, leading to the reduction of the life span of this type of paint to 12 to 24 months.

### **c) Tributyltin Self-Polishing Copolymer Coatings**

Since the insoluble and soluble matrix paints have some drawbacks, alternative coatings have been developed in order to improve these paints.

The first tributyltin self-polishing copolymer (TBT-SPC) technology was patented by Milne and Hails, in 1974, revolutionizing the entire shipping industry. Organic tin and its derivatives have been generally used as



antifoulants due to their broad-spectrum characteristic. Tributyltin oxide (TBTO) and tributyltin fluoride (TBTF) were the organotin compounds used, also known as powerful fungicides, completely capable of inhibiting the growth of most fouling organisms at a very low concentration.

As known, every paint contains pigments to confer the desired color. Usually, metallic copper, copper thiocyanate and cuprous oxide are the dominant copper pigments used in antifouling paints. However, the copper ions as  $\text{Cu}^{2+}$  have a major role in antifouling, yet they can only target specific fouling organisms.

TBT-SPC paints were based on acrylic polymer (usually methyl methacrylate) with TBT groups tethered to the polymer backbone by an ester. When immersed in water, the soluble pigment particles such as zinc oxide (ZnO) or copper oxide (CuO) would begin to dissolve.

The water penetration was prevented by the hydrophobic nature of the polymer of TBT methacrylate and methyl methacrylate. Thus, the water could only fill in the pores created by the dissolution of the soluble pigment particles. Furthermore, the carboxyl-TBT bond is easily hydrolyzed in slightly alkaline environments as sea water (pH of 7.5 to 8.5), which slit the TBT portion from the copolymer and then released the biocides into the water. As the TBT portions were split, the partially reacted brittle polymer backbone became prone to be washed off by the moving sea water, exposing a fresh coating surface. The hydrolysis process provided a low hull roughness (about  $100 \mu\text{m}$ ), which did not influence significantly the drag friction of the ship's hull.

One of the advantages of this kind of coating was the control of the polishing rate by the manipulation of the polymer chemistry, being possible to balance the high effectiveness and a long life span in function of the ships' operating

conditions and sailing speed. Studies have proven that the release rate of TBT in the sea water is almost constant with the sailing speed, which confers a high antifouling performance even at static or low speed. Additionally, TBT-SPC paints had high mechanical resistance, high stability to oxidation and short drying times.

This type of paint was widely applied in the shipping industry due to its high efficiency and versatility.

Consequently, the extensive use of TBT introduced high levels of contamination in the environment and thus negatively affected the marine communities. TBT is extremely toxic to non-target organisms ranging from bacteria to fish and mammals, affecting their growth, development, reproduction and survival. For example, before the 1980's, populations of gastropods were ceased due to the presence of TBT compounds in the sea water. This disappearance is explained by the fact that TBT causes a hormonal imbalance, which leads to the development of male sex organs on female gastropods, which hinders the breeding of gastropods.

In 2001, IMO (International Maritime Organization) (IMO) banned the use of TBT in the manufacturing of paints from 1st January 2003 and the presence of these paints on ship hulls from 1<sup>st</sup> January 2008. However, this ban did not apply to copper, since it is an essential element needed for the growth of all plants and animals, besides being naturally present in the sea water. It is also lipophilic and thus less bio accumulative. Nevertheless, it is possible that copper based paints may end up facing the similar regulations as TBT. For instance, Sweden, Denmark and USA are planning to strengthen the legislations regarding the use of copper-based antifouling paints, since the excessive boat traffic can lead to the contamination of the marine environment.

### **2.13.2.2 Environmentally Friendly Antifouling Paints**

Due to the ban of the most efficient and versatile TBT-SPC paints, the paint producers felt the urge to develop new and less environmentally harmful paints. Therefore, Tin-free SPC technology was developed and commercially introduced.

The tin-free coatings can be divided into three categories: tin-free controlled depletion paints (tin-free CDPs), tin-free self-polishing copolymers (tin-free SPCs) and hybrid paints (conjugation between the CDPs and SPCs).

Despite the fact that these paints are free of TBT, their mechanism consists of biocide release, whose action has not always been fully explained. Considering this, the development of fully biocide-free antifouling paints is still in course.

#### **a) Tin-Free Controlled Depletion Paints (Tin-Free CDPs)**

The tin-free CDPs are an improved version of the traditional soluble matrix paints, where organically synthesized resins reinforce the binder, although presenting the same antifouling mechanism as the conventional rosin matrix paints. The synthesized resins are more resistant than rosins and control the dissolution of the soluble binder.

These paints are also known as ablative/erodible paints, containing polymeric compounds capable of controlling the relative rate of dissolution/erosion. They also contain a large proportion of a non-toxic binder, which is soluble in sea water. The biocide content is high and dissolves in the sea water, in conjunction with the soluble binder. The rate of erosion becomes constant after short time of immersion.

However, these paints transform into an empty matrix, due to the dissolution of the soluble compounds incorporated in the paint into the sea water, affecting their behavior. Consequently, a high amount of copper and co-biocide is needed, which rises the concern towards the environment. Also, as the compounds dissolve, the roughness of the coating increases, thus promoting biofouling formation. The leached layer formed may be removed prior to recoating.

Regarding to the lifespan of these paints, these confer a protection a bit longer than 3 years. They do not require a tie coat when repainted and are less expensive than TBT-based self-polishing paints.

Usually, leisure boats and small ships with short service time apply these paints.

### **b) Tin-Free Self-Polishing Copolymer Paints (Tin-Free SPCs)**

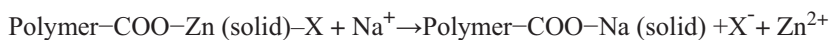
The tin-free SPCs contain an acrylic copolymer matrix combined with booster biocides, where different pendant groups are linked to the polymeric backbone and released after the contact with sea water. This process resembles the hydrolysis of TBT-SPC paints.

In this type of paint, the antifouling activity is induced as the chemical reaction through hydrolysis of copper, zinc or silyl acrylates occurs, forming an acidic polymer, which is soluble in sea water and can be washed from the surface.

The hydrolysis process is followed by the loss of the dissolved layer of polymer, smoothening the surface.

These paints present a life span 3 to 5 years, due to their high polishing rate. Anyhow, they are not as efficient as TBT-based-self-polishing paints.

For instance, when insoluble Zn acrylate is used, it hydrolyzes to soluble acidic polymer and the following reaction is assumed:



The  $\text{Zn}^{2+}$  is released into the sea water for antifouling properties and the soluble acidic polymers can be washed from the surface. Currently, metallic copper, copper thiocyanate and cuprous oxide are the dominant compounds used in antifouling paints.

In comparison with the TBT antifouling paints and as mentioned before, copper-containing coatings can only target specific fouling organisms. To improve the antifouling properties and thereby the selectivity to macro algae, barnacles and bryozoans, booster biocides such as Irgarol 1051, Diuron, copper pyrithione, zinc pyrithione, isothiazolone, Zineb, Ecomea and many others are added, as an alternative to TBT derivatives. Although the toxicity of the majority of the biocides aforementioned has not been fully assessed, zinc pyrithione and Zineb seem to be the least toxic, whereas Irgarol and Diuron are reported to be more poisonous.

### **a) Hybrid Paints**

The antifouling mechanism of hybrid paints is a conjunction of the mechanisms of both CDPs and TF-SPCs. The leached layer, cost and the performance of these paints is intermediate.

An example of these hybrid paints are the microfibers incorporated in paints, by Hempel.

### **b) Biocide-Free Coatings**

Due to the toxicity of the biocides used in the antifouling paints, novel biocide-free technologies have been investigated to replace the biocide based coatings.

Non-stick “fouling-release” coatings, containing fluoro polymers and silicone, have been tested regarding to the release of macro fouling organisms, using robust hydrodynamic conditions. Apparently, fluoro polymers and silicone appear to possess the desired properties to promote antifouling by release. Some low surface energy coatings have also been prepared with modified acrylic resin and nano-SiO<sub>2</sub>. Moreover, accumulated fouling organisms are not easily released, being difficult to develop an environmentally friendly and simultaneously effective coating.

Additionally, these methods have some drawbacks such as high cost, poor mechanical properties and the difficulty of recoating.

Recently, researchers have been focusing in combining “fouling-release” coatings with hydrogel technology. For example, Hempel has been investing in this technology by modifying the surface of commercial PDMS (polydimethylsiloxane) coatings in order to generate a hydrogel in contact with water, with weak adhesion properties. This layer promotes its detachment from the former paint layer together with any attached bio-fouling (e.g. slime or algae) on the coating. Experiments were also performed on ships, showing that this new coating is able to keep the surface clean even at low speeds.

In summary, despite the fact that hydrogel based “fouling-release” coatings are showing positive results on the bio-fouling prevention, their durability and effect on the environment are still unknown, which should motivate a deep research in this field in order to develop an effective, durable and non-toxic coating.

For this purpose, advanced characterization techniques should be performed to evaluate the mechanical characteristics and the environmental

compatibility, to proceed to further improvements and finally introduce new potential benign products in the market.

## **2.14 Characteristics of Antifouling Paints**

After developing the desired polymeric matrix of the coating, it is necessary to proceed to characterization tests in order to check if the coating is in accordance with the standards.

Generally, the requirements for an optimal antifouling coating consist of being anticorrosive, environmentally acceptable, economically viable, durable, smooth, compatible with the underlying system, resistant to abrasion, biodegradation and erosion.

### **2.14.1 Anti-Corrosiveness**

If the substrate (ship's hull) is steel, the paint should protect it from corrosion caused by the exposure to the marine environment.

To prevent this problem, at least one coating of primer or anticorrosive paint is applied before the layer of antifouling paint. The latter may contribute materially to the protection of the hull from corrosion, depending primarily on the thickness of the antifouling coating and its resistance to the ingress of sea water. Thus, thick paints impede corrosion and provide the necessary toxic storage for extended fouling prevention. The adequate thickness is generally specified by the paint providers in the technical data sheet of the product. For instance, Jotun's antifouling paints' thickness ranges from 75 to 150  $\mu\text{m}$ , whereas the primers' thickness ranges from 40 to 250  $\mu\text{m}$ .

Also, the chemical compounds added into the coating should be taken into account, since they might tend to quicken the corrosion effect. For instance, common toxic pigments such as metallic copper and salts of copper and

mercury have the tendency to intensify corrosion if they are applied directly on the hull.

### **2.14.2 Durability**

The durability of a coating is dependent on its resistance to mechanical damage, on the erosion caused by the water motion and on the components present in the paint formulation. If it contains any biocide, the coating disintegration must be also taken into account, since it degrades as the sea water penetrates and releases the toxic biocide. Therefore, a balance between toxicity and durability should be established.

The resistance to the erosive effect of the water motion is a notable problem in high speed vessels, such as motor torpedo boats and hydroplanes. Considering this, it is necessary to develop suitable paints, which can confer a hard and thus resistant surface to overcome this drawback.

The loss of durability is more accentuated near the waterline, due to the mechanical damage caused by the floating debris and the alternation between the wet and dry conditions and also due to the exposure to the sun. These factors intensify the coatings' cracking, being necessary to develop a paint which can resist all of this harm.

### **2.14.3 Adhesion**

The adhesion is an important property, since the paint should adhere adequately to the substrate where it is applied, regardless of the natural conditions existing during this procedure. This means that the paint should adhere suitably either when it is applied during winter (high moisture and low temperature) or summer (low moisture and high temperature).

Low adherence may lead to the disintegration of the coating and therefore exposes the hull to the marine environment, leaving it unprotected.

### **2.14.4 Abrasion**



The assessment of the abrasion resistance of antifouling paints is a relevant factor, since it can indicate the paints' resistance to friction caused by moving particles transported by the wind or water. These particles can erode the paint, when the ship is in motion or in the port, compromising the durability of the coating.

### **2.14.5 Smoothness**

The paint must be applied uniformly to confer a smooth surface, which, therefore, will create less frictional drag and bio-fouling attachment.

Additionally, it is also desirable that paints with a high viscosity (needed to form thick coatings) have sufficient elasticity to fill up the minor irregularities present on the ship's surface.

### **2.14.6 Drag Friction**

As known, a ship must be designed to move efficiently through the water with a minimum of external force. However, when it is propelled through the water, it has drag associated with it, which must be overcome by thrust to move forward.

Drag is defined as the force that opposes forward motion through the fluid and is parallel to the direction of the free-stream velocity of the fluid flow. When moving on the water, the drag of a ship presents two major components: wave-making drag and skin frictional drag. The frictional drag typically accounts 60-90% of the total resistance and can be reduced by applying an appropriate surface coating, which softens the surface. The roughness of the surface and, thereby, the frictional resistance is influenced by different factors such as the age or condition of the ship hull, the surface preparation, the paint application, the paint system and marine fouling.

The skin frictional drag is increased when microbial communities, present in the sea, attach to the surface of the coating, leading to extreme fuel and

maintenance costs of the ships and CO<sub>2</sub> emission. Several papers have studied the effect of marine fouling on the hydrodynamic performance of a surface. For example, Bohlander (1991) performed full scale power trials on a frigate and concluded that microfilms of bio-fouling increased the drag friction by 8 to 18%.

For this purpose, it is of utmost importance to assess the coating regarding the drag friction effect, to avoid excessive fuel consumption and subsequent penalties .

Several experiments have been applied to measure the drag friction of the coatings, including a rough plate or a rotating disc or cylinders.

It is important to mention that the selection of the coating type does influence the drag friction effect. Several studies have been carried out to compare the drag resistance of silicone based “foul release” coatings with tin-free self-polishing coatings. The former has shown positive results in comparison with the latter, mainly due to its surface texture (less rough).

### **2.14.7 Wettability**

The wettability of a solid by a liquid can be determined by measuring the contact angle (or wetting angle),  $\Theta$ . The contact angle is described as the angle between the surface of the liquid and the outline of the contact surface, when an interface between a liquid and a solid exists.

## **2.15 Environmental Risk Assessment**

Since the main mechanism of action of the majority of antifouling paints consists of releasing biocide into the sea water, a severe environmental compatibility assessment should be carried out before the introduction of these paints in the market.

After the ban of TBT based paints, alternative biocides have been used in conjunction with copper, which can be less or equally harmful .

For instance, the leaching of copper from the antifouling paints on Swedish boats tends to be harmful to the Baltic Sea's key-species bladder wrack and *Fucus vesiculosus*, leading the Swedish Chemicals Agency to restrain the use of paints leaching excessive copper and prohibit copper based paints on leisure boats (length < 12 m).

Another example is regarding a study carried out in Hong Kong, which consisted of testing the toxicity of five commonly used booster biocides (Irgarol, Diuron, Zinc pyrithione, Copper pyrithione and Chlorothalonil) on the growth or survival of 12 marine species, concluding that Irgarol is even more toxic than TBT and copper pyrithione is as toxic as TBT.

Considering this, it is important to perform an accurate evaluation of the environmental risks that these paints can pose to the marine species, by carrying out biodegradability tests or mechanical tests that enable the collection of leachates for toxicity analysis.

## **2.16 The Hull Friction (Drag) and Roughness**

The frictional resistance to a ship's movement through water (Drag). The total resistance to a ship's movement through water is normally defined as the force required to tow a ship at a given speed in calm waters. The total resistance is the sum of the frictional resistance and the residual resistance, the latter being a feature of the ship's design whereas the former is due to the tangential shear forces caused by the movement of water parallel to the ship's hull. It can be seen that only the frictional resistance can be influenced by the surface coatings or surface treatment.

In 1874 Froude showed experimentally that the frictional resistance for towed planks could be expressed by the equation:

$$R_f = f \cdot s \cdot v^n$$

Where  $R_f$  = frictional resistance,  $f$  = frictional coefficient,  $s$  = the wetted surface area,  $v$  = the velocity, and  $n$  = a number nearly equal to 2.

From the results Froude obtained that it was obvious that the frictional resistance depends on the nature of the surface, the values of  $n$  being very nearly equal to two whereas the values of ' $f$ ' varied greatly depending on the smoothness of the surface; these observations were not utilized until well into the twentieth century.

### 2.16.1 Flow around a Ship's Hull

The resistance caused by the flow of water around a ship's hull, the residual resistance, is governed by the hull geometry and operational speeds, this can be approximated to the flow around a plane plate for which the formulation below is applicable:

$$Re = \frac{v_1 l}{\nu}$$

Where  $v$  = the velocity of the flow past the hull,  $l$  = the distance from the bow of the ship and  $\nu$  = the kinematic viscosity which is the ratio of the viscosity to density, the units being Stokes and the dimensions being  $l^2 t^{-1}$ .

"Re" is called the Reynolds Number a dimensionless parameter, which provides a useful indicator of the type of flow around the hull: when its value is below  $5 \times 10^5$  laminar flow is observed, whereas at a value  $\geq 10^7$  the flow is turbulent,  $5 \times 10^5$  and  $10^7$  are critical values of "Re" between which the flow changes from laminar to turbulent.

It has been shown by Izubuchi from tests on the Japanese destroyer 'Yudachi' that at normal operating speeds the residual resistance forms a relatively small proportion of the 0 total resistance. These results were in agreement

with those obtained by the U.S. Navy using the U.S. Destroyer 'Hamilton' as the test craft. More recent work has demonstrated that the relative contribution of each of these resistance components to the total resistance depends on both the size and the speed of the vessel.

The reduction of frictional resistance is of major importance for efficient operation, the residual resistance only becomes important at relatively high operating speeds and is affected by the design and building of the vessel; most commercial vessels operate in the 10-20 KN range. A vast amount of research has been and continues to be conducted on design whereas, the frictional resistance can be very significantly lowered, with consequent economic benefit, by the application of a high performance antifouling.

The water around the hull of a ship moving at low speed can be divided into two parts; a laminar sub layer which is a continuous layer of water adjacent and parallel to the ship's hull and moving with the ship, the thickness of this layer being dependent on the speed of the ship; at greater distance from the hull flow becomes turbulent due to the shear forces created by the passage of water around the hull; the faster the ship moves the thinner the laminar sub layer. At a low Reynolds Number for a given ship operating under standard conditions a relatively thick laminar sub layer is present, with increasing speed (and therefore increasing Reynolds Number) the thickness of the laminar sub layer decreases and between certain Reynolds Numbers the laminar sub layer becomes discontinuous.

The smoother the hull, the lower the kinematic viscosity and so the greater the Reynolds Number. The increase in resistance created by turbulent flow (i.e. the energy required to produce turbulence) is thus related to the surface roughness and is directly proportional to the Reynolds Number.

A surface is considered to be rough if the peaks of roughness protrude through the thickness of the laminar sub layer, if the peaks are smaller and remain within the laminar sub layer the surface is considered to be hydrodynamically smooth.

The thickness of the laminar sub layer is dependent on the velocity of the hull and it has been determined that for a ship operating at  $V$  knots a hydrodynamically smooth hull occurs when the surface roughness is less than or equal to  $\frac{230}{V} \mu$ . This criterion is very rarely satisfied even for a freshly painted hull.

## **2.16.2 Sources of Hull Roughness**

Hull roughness is directly related to the frictional resistance and may be affected by numerous factors, these being described in the following sections.

### **2.16.2.1 Structure of the Paint**

As a consequence of the cost of dry docking and repainting, ship owners have sought shorter dry-docking times.

This has led paint manufacturers to compromise between adhesive paints that spray smoothly, but sag easily when sprayed thickly, and thixotropic paints which tend to ripple on the surface but can be applied in thicker coats without sagging. Both of these paint systems cause hull roughness, the former being less than the later.

### **2.16.2.2 Inadequate Surface Preparation**

The removal of fouling organisms and the repair of surface defects to provide a smooth finish to which the new antifouling is to be applied is of

major importance in producing a smoothly painted hull. This, however, is not always realized because of the cost of preparation, consequently in many instances surface roughness is built in this way, the roughness increasing with each repainting.

### **2.16.2.3 Poor Application Standards**

The application of any coating system is really a skilled job but due to working conditions and pay, the average worker is either unskilled or untrained and consequently the manufacturer ~ spraying instructions are often not followed closely. The environment also plays an important role; for example, variations in humidity and wind speed can result in poor application.

### **2.16.2.4 Failure of the Paint System**

This occurs when the ship is in service and the main problems are: blistering, detachment and corrosion.

### **2.16.2.5 Mechanical Damage**

This includes berthing and grounding damage as well as that incurred from cable chafing.

### **2.16.2.6 Fouling**

This is the major cause of hull roughness, it is caused by an ineffective or exhausted antifouling coating, thus the roughness caused by fouling increases with time.

## **2.17 Measurement of Hull Roughness**

Surface roughness of a ship's hull is expressed as the maximum peak height to minimum valley depth over a distance of 50 mm, this is more commonly known as the mean apparent amplitude or MAA per 50 mm. This method of measurement gives reasonable correlation between hull roughness and ship's resistance.

Many instruments are available to measure surface roughness in the laboratory, Talysurf, Surfometer, Electron Microscope, etc. but it is only recently that the British Ship Research Association (BSRA) have developed an instrument which can measure the surface roughness of a ship's hull in dry dock. The instrument (B.S.R.A. Roughness Gauge) consists of three wheels supporting a carriage through which protrudes a stylus. When the apparatus is pushed across the hull the stylus records the surface profile. The gauge's sample length is 50 mm and it measures the maximum peak to minimum trough distance.

This apparatus gives reasonable correlation with the standard laboratory instruments but it does not account for waves with a large wavelength as the sampling distance per measurement is too short and there is no fixed reference.

The results obtained by measuring a ship's roughness have to be corrected for defects which cause residual resistance, i.e. plate curvature, welds, etc. and then the surface roughness of the hull may be calculated, this being displayed usually as a histogram.

To measure the ship's roughness in practice the hull is divided up into sections and each section is measured using the B.S.R.A. gauge before painting, the same procedure is followed after painting, sufficient measurements being taken to ensure a random sampling. The data may then



be correlated to the ship's performance before and after painting to provide evidence for the increased fuel consumption due to surface roughness.

Scott has shown that the cost of surface roughness for a typical ship results in a one per cent increase in power to maintain the ship at a constant speed for every  $10\mu$  of roughness above  $100\mu$ . The surface roughness of a new ship is generally about  $130\mu$ , this figure increasing with service time for a ship painted with a conventional anti-fouling preparation as was shown by the Norwegian Ship Research Institute.

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# Chapter Three

## Research Methodology

### 3.1 Introduction

This chapter deals with methods of data collection on the phenomenon of vessels hull protection. It gives an overview about the case study to show how ship's hull corroded in Sudan Navy, Red Sea State (Port Sudan). Then, it shows the suggested method of corrosion protection using Impressed Current Cathodic Protection (ICCP). Finally, the chapter shows the procedures of designing ICCP system using multi physics software program (Comsol 5.3a).

### 3.2 A Case Study

This study is intended to investigate the problems of corrosion on vessels hull. A case study is taken from Sudanese's Navy. The ship type called Zamzam which is considered as an arbitrary model affected by corrosion. The ship's hull is made of naval iron. The length of the ship is 42 meters and the width is 4 meters. Also, the ship type called Almaz is taken as a case study due to its massive affection by corrosion. They are three in number constructed of naval iron. The length of the ship is 41 meters and the width is 4.8 meters.

### 3.3 Methods

The research use two different methods to conduct the study. The first method used in this study is Impressed Current Protection modeling simulation using (Comsol 5.3a) program. Impressed Current Cathodic Protection (ICCP) is a commonly employed strategy to mitigate ship hull corrosion, by which an external current is applied to the hull surface,

polarizing it to a lower potential. Although there are various parameters such as salinity, temperature, hull surface coating that contribute to the demand for current, the area of bare metal (mainly propeller) is the most governing parameter. In this model, ship's hull structure represent (Cathode), the sea water represent the surrounding atmosphere, and anode boundaries i.e. a metal which is higher in potential than the Cathode (Hull) are used. The second method is coating. The researcher created the program to show the effect of ICCP system for coated and non-coated structure. Figure (3.1) below shows ICCP system.

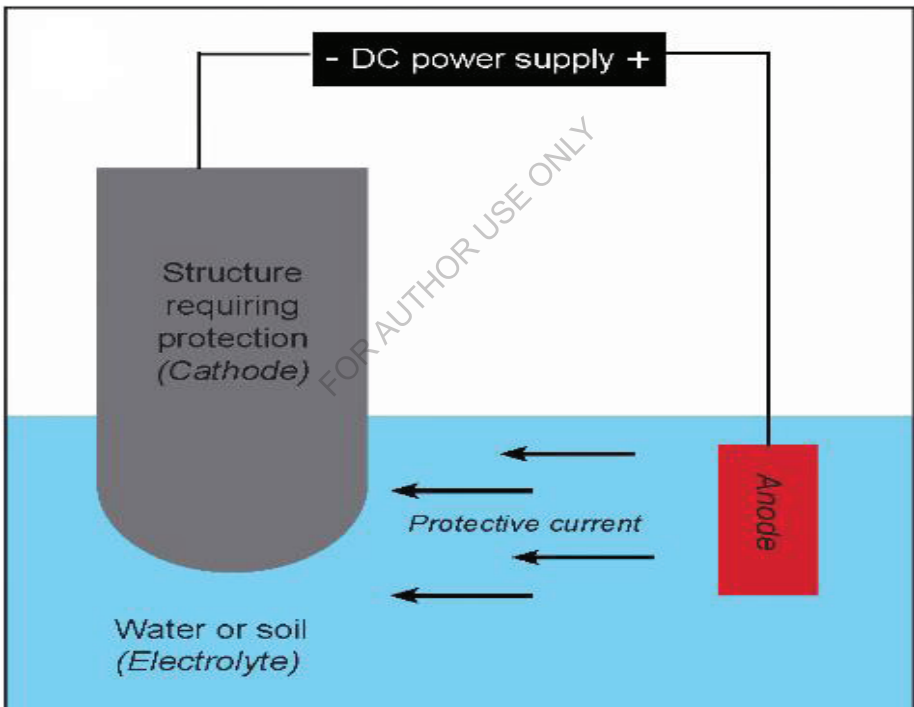


Figure (3.1) ICCP System

### 3.4 Program Parameters

The researcher used the following parameters to design the ICCP model to protect the ship's hull efficiently and effectively. Table (3.1) below shows ICCP Parameters.

**Table (3.1) ICCP Parameters**

| <b>Name</b>  | <b>Expression</b>            | <b>Value</b>            | <b>Description</b>                                       |
|--------------|------------------------------|-------------------------|--|
| Evsref       | -0.85[V]                     | -0.85 V                 | Ship hull potential vs reference, imposed by ICCP system |
| sigma        | 4[S/m]                       | 4 S/m                   | Sea water conductivity                                   |
| Eeq_prop     | -0.31[V]                     | -0.31 V                 | Equilibrium potential of propeller vs. Ag/AgCl           |
| i0_prop      | 1.5E-02[mA/cm <sup>2</sup> ] | 0.15 A/m <sup>2</sup>   | Exchange current density of propeller                    |
| alphaa_prop  | 0.78                         | 0.78                    | Anodic transfer coefficient of propeller                 |
| alphac_prop  | 0.45                         | 0.45                    | Cathodic transfer coefficient of propeller               |
| Eeq_shaft    | -0.18[V]                     | -0.18 V                 | Equilibrium potential of shaft vs. Ag/AgCl               |
| i0_shaft     | 1.3E-04[mA/cm <sup>2</sup> ] | 0.0013 A/m <sup>2</sup> | Exchange current density of shaft                        |
| alphaa_shaft | 0.44                         | 0.44                    | Anodic transfer coefficient of shaft                     |
| alphac_shaft | 0.57                         | 0.57                    | Cathodic transfer coefficient of shaft                   |
| ilim         | 5[A/m <sup>2</sup> ]         | 5 A/m <sup>2</sup>      | Limiting current density at cathodes                     |

### 3.5 Procedures

The research creates the Impressed Current Cathodic Protection simulation through metaphysics software program (comsol 5.3a). The procedures are as follows:

#### 3.5.1 Create Corrosion Model Wizard

In the New window Comsol 5.3a program, click Model Wizard to build the Corrosion Model: **1.** In the Model Wizard window, click 3D. **2.** In the Select Physics tree, select Electrochemistry> Primary and Secondary Current Distribution>Secondary Current Distribution (cd). **3.** Click Add. **4.** Click Study. **5.** In the Select Study tree, select Preset Studies>Stationary. **6.** Click Done.

### 3.5.1.1 Build Ship Hull Geometry

To build the geometry of the ship hull from a geometry file:

#### a. Import 1 (imp1) geometry file

1. On the Home toolbar, click Import. 2. In the Settings window for Import, locate the Import section. 3. Click Browse. 4. Browse to the model's Application Libraries folder and double-click the file ship\_hull\_geometry.mphbin. 5. Click Import.

#### b. Mesh Control Faces 1 (mcf1)

The geometry is divided into two domains, use a mesh control face to remove this split when setting up the physics. This will reduce the number of geometry entities that can be selected when setting up the physics. 1 On the Geometry toolbar, click Virtual Operations and choose Mesh Control Faces. 2 On the object fin, select Boundaries 9–12 and 15 only. 3 On the Geometry toolbar, click Build All. 4 Click the Transparency button on the Graphics toolbar. 5 Click the Zoom Extents button on the Graphics toolbar. The geometry should now look like **Figure 1** (see chapter 4). Select Zoom Box and a region closer to propeller. The zoomed in geometry should now look like **Figure 2** (see chapter 4).

### 3.5.1.2 Global Definitions

#### Parameters: Load the Model Parameters

1. In the Model Builder window, under Global Definitions click Parameters. 2. In the Settings window for Parameters, locate the Parameters section. 3. Click Load from File. 4. Browse to the model's Application Libraries folder and double-click the file ship\_hull\_parameters.txt.

## Definitions

Create explicit selections for the propeller base, propeller blades, shaft, anode, reference electrode and hull surfaces. Then create a selection for the ship hull surface by using a union. The selections will be used later on when specifying the physics, setting up the mesh and when plotting and evaluating the results.

### Explicit 1

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 19-21 in the Selection text field. **6.** Click OK. **7.** Right-click Explicit 1 and choose Rename. **8.** In the Rename Explicit dialog box, type Propeller base in the new label text field. **9.** Click OK.

### Explicit 2

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 22, 24-25, and 39-40 in the Selection text field. **6.** Click OK. **7.** Right-click Explicit 2 and choose Rename. **8.** In the Rename Explicit dialog box, type Propeller blades in the new label text field. **9.** Click OK.

### Explicit 3

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 37, 38 in the Selection text field. **6.** Click OK. **7.** Right-click

Explicit 3 and choose Rename. **8.** In the Rename Explicit dialog box, type Shaft in the new label text field. **9.** Click OK.

#### **Explicit 4**

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 17 in the Selection text field. **6.** Click OK. **7.** Right-click Explicit 4 and choose Rename. **8.** In the Rename Explicit dialog box, type Anode in the new label text field. **9.** Click OK.

#### **Explicit 5**

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 18 in the Selection text field. **6.** Click OK. **7.** Right-click Explicit 5 and choose Rename. **8.** In the Rename Explicit dialog box, type Reference electrode in the new label text field. **9.** Click OK.

#### **Explicit 6**

**1.** On the Definitions toolbar, click Explicit. **2.** In the Settings window for Explicit, locate the Input Entities section. **3.** From the Geometric entity level list, choose Boundary. **4.** Click Paste Selection. **5.** In the Paste Selection dialog box, type 6-14, 16, 23, 26-36, 41, 43-46 in the Selection text field. **6.** Click OK. **7.** Right-click Explicit 6 and choose Rename. **8.** In the Rename Explicit dialog box, type Hull surface in the new label text field. **9.** Click OK.

#### **Union 1**

1. On the Definitions toolbar, click Union. 2. In the Settings window for Union, locate the Geometric Entity Level section. 3. From the Level list, choose Boundary. 4. Locate the Input Entities section. Under Selections to add, click Add. 5. In the Add dialog box, in the Selections to add list, choose Propeller base, Propeller blades, Shaft, Anode, Reference electrode, and Hull surface. 6. Click OK. 7. Right-click Union 1 and choose Rename. 8. In the Rename Union dialog box, type Ship surface in the new label text field. 9. Click OK.

### **Union 2**

1. On the Definitions toolbar, click Union. 2. In the Settings window for Union, locate the Geometric Entity Level section. 3. From the Level list, choose Boundary. 4. Locate the Input Entities section. Under Selections to add, click Add. 5. In the Add dialog box, in the Selections to add list, choose Propeller base, Propeller blades, and Shaft. 6. Click OK. 7. Right-click Union 2 and choose Rename. 8. In the Rename Union dialog box, type Propeller and Shaft in the new label text field. 9. Click OK.

### **3.5.1.3 Secondary Current Distribution (Cd)**

Now, set up the Secondary Current Distribution interface for the case of a coated propeller. Start with the electrolyte conductivity.

#### **Electrolyte 1**

1. In the Settings window for Electrolyte, locate the Electrolyte section. 2. From the  $\sigma_1$  list, choose User defined. In the associated text field, type sigma.

#### **Reference Electrode 1**



The ICCP system will control the potential of the ship hull vs a reference electrode, located at mid-ship. In this model we set all Equilibrium potential with reference to Ag/AgCl. The equilibrium potential of this reference is hence 0. **1.** On the Physics toolbar, click Points and choose Reference Electrode. **2.** Select Point 49 only.

### **Electrolyte Potential 1**

In this model we will not explicitly define the anode reaction kinetics. Instead we will use a potential (primary) condition for the anode potential and ground it to zero. The value of the anode electrolyte phase potential is arbitrary since we will define the ship hull potential with respect to the reference electrode. **1.** On the Physics toolbar, click Boundaries and choose Electrolyte Potential. **2.** In the Settings window for Electrolyte Potential, locate the Boundary Selection section. **3.** From the Selection list, choose Anode.

### **Electrode Surface 1**

Now specify the electrode potential and the kinetics for the shaft surface. **1.** On the Physics toolbar, click Boundaries and choose Electrode Surface. **2.** In the Settings window for Electrode Surface, locate the Boundary Selection section. **3.** From the Selection list, choose Shaft. **4.** Locate the Boundary Condition section. From the Boundary condition list, choose Electrode potential. **5.** In the  $E_{vsref}$  text field, type  $E_{vsref}$ . **6.** From the  $\phi_{s,ref}$  list, choose Electric reference potential (cd/refel1).

### **Electrode Reaction 1**

**1.** In the Model Builder window, expand the Electrode Surface 1 node, then click Electrode Reaction 1. **2.** In the Settings window for Electrode Reaction, locate the Equilibrium Potential section. **3.** In the  $E_{eq}$  text field, type

Eeq\_shaft. **4.** Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler-Volmer. **5.** In the  $i_0$  text field, type  $i0\_shaft$ . **6.** In the  $\alpha_a$  text field, type  $alphaa\_shaft$ . **7.** In the  $\alpha_c$  text field, type  $alphaa\_shaft$ . **8.** Select the Limiting current density check box. **9.** In the  $i_{lim}$  text field, type  $ilim$ .

## Definitions

The Electrode Surface node will declare a global variable ( $cd.phis\_eebii1$ ) for the electron phase potential of the ship hull. Now add a variable to for the ship hull potential as measured vs a reference electrode located in the electrolyte. The variable will be used later for post processing of the solution.

## Variables 1

**1.** In the Model Builder window, under Component 1 (comp1) right-click Definitions and choose Variables. **2.** In the Settings window for Variables, locate the Variables section. **3.** In the table, enter the following settings:

| Name   | Extension | Unit | Description |
|--------|-----------|------|-------------|
| E_hull |           |      |             |

**4.** Locate the Geometric Entity Selection section. From the Geometric entity level list, choose Boundary. **5.** From the Selection list, choose Ship surface. **6.** Locate the Variables section. In the table, enter the following settings:

| Name   | Extension         | Unit | Description               |
|--------|-------------------|------|---------------------------|
| E_hull | .phis_eebii1-phil | V    | Hull potential vs Ag/AgCl |

## Secondary Current Distribution (Cd)

Add an Infinite Electrolyte to describe an infinite extension of the electrolyte. Use symmetry planes to describe the ocean surface and the mid-ship symmetry planes.

### **Infinite Electrolyte 1**

1. On the Physics toolbar, click Boundaries and choose Infinite Electrolyte. 2. Select Boundaries 1–3 and 5 only. 3. In the Settings window for Infinite Electrolyte, locate the Electrolyte section. 4. In the  $\sigma_1$  text field, type sigma. 5. Click to expand the Symmetry planes section. Locate the Symmetry Planes section. Select the yz-plane check box. 6. Select the xy-plane check box.

No more boundary conditions are needed for study with the coated propeller since Insulation condition is applied by default, including the coated propeller surfaces.

### **Initial Values 1**

Provide an initial value for the electrolyte potential to reduce the computational time. 1. In the Model Builder window, under Component 1 (comp1)> Secondary Current Distribution (cd) click Initial Values 1. 2. In the Settings window for Initial Values, locate the Initial Values section. 3. In the *phil* text field, type 0.5.

### **Mesh 1**

Build a mesh with a finer resolution at the propeller, shaft and hull surface. Mesh the domain around the propeller first.

### **Free Tetrahedral 1**

1. In the Model Builder window, under Component 1 (comp1) right-click Mesh 1 and choose Free Tetrahedral. 2. In the Settings window for Free Tetrahedral, locate the Domain Selection section. 3. From the Geometric entity level list, choose Domain. 4. Select Domain 2 only.

### Size 1

1. Right-click Component 1 (comp1)>Mesh 1>Free Tetrahedral 1 and choose Size. 2. In the Settings window for Size, locate the Element Size section. 3. From the Predefined list, choose Extra fine. 4. Click the Custom button. 5. Locate the Element Size Parameters section. Select the Maximum element size check box. 6. In the associated text field, type 1.5. 7. Select the Minimum element size check box. 8. In the associated text field, type 0.01.

### Size 2

1. Right-click Free Tetrahedral 1 and choose Size. 2. In the Settings window for Size, locate the Geometric Entity Selection section. 3. From the Geometric entity level list, choose Boundary. 4. From the Selection list, choose Propeller and Shaft. 5. Locate the Element Size section. From the Predefined list, choose Extra fine.

### Size 3

1. Right-click Free Tetrahedral 1 and choose Size. 2. In the Settings window for Size, locate the Geometric Entity Selection section. 3. From the Geometric entity level list, choose Boundary. 4. From the Selection list, choose Propeller base. 5. Locate the Element Size section. From the Predefined list, choose extremely fine. 6. Click Build Selected.

### Size 1

**1.** In the Model Builder window, right-click Mesh 1 and choose Free Tetrahedral. **2.** Right-click Free Tetrahedral 2 and choose Size. **3.** In the Settings window for Size, locate the Element Size section. **4.** From the Predefined list, choose Finer.

## **Free Tetrahedral 2**

**1.** In the Model Builder window, under Component 1 (comp1)>Mesh 1 click Free Tetrahedral 2. **2.** In the Settings window for Free Tetrahedral, click Build Selected. The mesh should look like **Figure 3** (see chapter 4) (toggle the transparency button in order to see the mesh better).

## **Study 1**

Now, solve the model for the coated propeller case. **1.** In the Settings window for Study, type Study: Coated Propeller in the Label text field. **2.** On the Home toolbar, click Compute.

## **Results**

Several plots are added by default. Now, add a surface plot for hull potential to the electrode potential versus adjacent reference plot.

## **Electrode Potential vs Adjacent Reference (cd)**

**1.** In the Model Builder window, under Results click Electrode Potential vs Adjacent Reference (cd). **2.** In the Settings window for 3D Plot Group, locate the Plot Settings section. **3.** Clear the Plot data set edges check box. **4.** Locate the Color Legend section. From the Position list, choose Left.

## **Surface 1**

**1.** In the Model Builder window, expand the Electrode Potential vs Adjacent Reference (cd) node, then click Surface 1. **2.** In the Settings window for

Surface, locate the Coloring and Style section. **3.** Clear the Color legend check box.

### **Electrode Potential vs Adjacent Reference (cd)**

**1.** In the Model Builder window, under Results click Electrode Potential vs Adjacent Reference (cd). **2.** On the Electrode Potential vs Adjacent Reference (cd) toolbar, click Surface.

#### **Surface 2**

**1.** In the Model Builder window, under Results> Electrode Potential vs Adjacent Reference (cd) click Surface 2. **2.** In the Settings window for Surface, locate the Expression section. **3.** In the Expression text field, type E\_hull. **4.** On the Electrode Potential vs Adjacent Reference (cd) toolbar, click Plot. The surface plot of the potential for the ship surface with the coated propeller should look like **Figure 6** (see chapter 4).

### **Electrolyte Current Density (cd)**

Select Zoom Box and a region closer to propeller. The surface plot of the total current density for the zoomed in region near the coated propeller should look like **Figure 7** (see chapter 4).

### **Secondary Current Distribution (CD)**

Now, set up the problem for an uncoated propeller case by describing the electrode kinetics at the propeller base surfaces using the Electrode Surface boundary feature and at the propeller blade surfaces using the Thin Electrode Surface boundary feature.

#### **Electrode Surface 2**

**1.** On the Physics toolbar, click Boundaries and choose Electrode Surface. **2.** In the Settings window for Electrode Surface, locate the Boundary Selection section. **3.** From

the Selection list, choose Propeller base. **4.** Locate the Boundary Condition section. From the Boundary condition list, choose Electrode potential. The potential of the electronic phase of the propeller base is the same as for the shaft. **5.** In the  $E_{vsref}$  text field, type Evsref. **6.** From the  $\varphi_{s, ref}$  list, choose Electric reference potential (cd/refell).

### **Electrode Reaction 1**

**1.** In the Model Builder window, expand the Electrode Surface 2 node, then click Electrode Reaction 1. **2.** In the Settings window for Electrode Reaction, locate the Equilibrium Potential section. **3.** In the  $E_{eq}$  text field, type Eeq\_prop. **4.** Locate the Electrode Kinetics section. From the Kinetics expression type list, choose Butler-Volmer. **5.** In the  $i_0$  text field, type i0\_prop. **6.** In the  $\alpha_a$  text field, type alphaa\_prop. **7.** In the  $\alpha_c$  text field, type alphac\_prop. **8.** Select the Limiting current density check box. **9.** In the  $i_{lim}$  text field, type ilim.

### **Thin Electrode Surface 1**

**1.** On the Physics toolbar, click Boundaries and choose Thin Electrode Surface. **2.** In the Settings window for Thin Electrode Surface, locate the Boundary Selection section. **3.** From the Selection list, choose Propeller blades. **4.** Locate the Boundary Condition section. From the Boundary condition list, choose Electrode potential. The potential of the electronic phase of the propeller blade is the same as for the shaft. **5.** In the  $E_{vsref}$  text field, type Evsref. **6.** From the  $\varphi_{s, ref}$  list, choose Electric reference potential (cd/refell).

### **Electrode Reaction 1**

**1.** In the Model Builder window, expand the Thin Electrode Surface 1 node, then click Electrode Reaction 1. **2.** In the Settings window for Electrode Reaction, locate the Equilibrium Potential section. **3.** In the  $E_{eq}$  text field, type Eeq\_prop. **4.** Locate the Electrode Kinetics section. From the Kinetics

expression type list, choose Butler-Volmer. **5.** In the  $i_0$  text field, type  $i0\_prop$ . **6.** In the  $\alpha_a$  text field, type  $alphaa\_prop$ . **7.** In the  $\alpha_c$  text field, type  $alphac\_prop$ . **8.** Select the Limiting current density check box. **9.** In the  $i_{lim}$  text field, type  $ilim$ .

### 3.5.1.4 Study: Coated Propeller

Now, disable the Electrode Surface 2 and Thin Electrode Surface 1 boundary nodes in study for the coated propeller and add a new study to solve the model for the uncoated propeller case.

#### Step 1: Stationary

**1.** In the Model Builder window, under Study: Coated Propeller click Step 1: Stationary. **2.** In the Settings window for Stationary, locate the Physics and Variables Selection section. **3.** Select the Modify model configuration for study step check box. **4.** In the Physics and variables selection tree, select Component 1 (comp1)> Secondary Current Distribution (cd)>Electrode Surface 2. **5.** Click Disable. **6.** In the Physics and variables selection tree, select Component 1 (comp1)> Secondary Current Distribution (cd)>Thin Electrode Surface 1. **7.** Click Disable.

#### Add Study

**1.** On the Home toolbar, click Add Study to open the Add Study window. **2.** Go to the Add Study window. **3.** Find the Studies subsection. In the Select Study tree, select Preset Studies>Stationary. **4.** Click Add Study in the window toolbar. Click Add Study again to close the Add Study frame. **5.** On the Home toolbar, click Add Study to close the Add Study window.

#### Study 2

### 3.5.1.5 Study Uncoated Propeller



**1.** In the Settings window for Study, type Study: Uncoated Propeller in the Label text field. **2.** On the Home toolbar, click Compute.

## Results

Several plots are added by default for the uncoated propeller case. The surface plot of the total current density for the zoomed in region near the uncoated propeller should look like **Figure 9** (see chapter 4). Now, add a surface plot for hull potential to the electrode potential versus adjacent reference plot.

### Electrode Potential vs Adjacent Reference (cd) 1

**1.** In the Model Builder window, under Results click Electrode Potential vs Adjacent Reference (cd) 1. **2.** In the Settings window for 3D Plot Group, locate the Plot Settings section. **3.** Clear the Plot data set edges check box. **4.** Locate the Color Legend section. From the Position list, choose Left.

### Surface 1

**1.** In the Model Builder window, expand the Electrode Potential vs Adjacent Reference (cd) 1 node, then click Surface 1. **2.** In the Settings window for Surface, locate the Coloring and Style section. **3.** Clear the Color legend check box.

### Electrode Potential vs Adjacent Reference (cd) 1

**1.** In the Model Builder window, under Results click Electrode Potential vs Adjacent Reference (cd) 1. **2.** On the Electrode Potential vs Adjacent Reference (cd) 1 toolbar, click Surface.

### Surface 4

**1.** In the Model Builder window, under Results> Electrode Potential vs Adjacent Reference (cd) 1 click Surface 4. **2.** In the Settings window for

Surface, locate the Expression section. **3.** In the Expression text field, type E\_hull. **4.** Click the Zoom Extents button on the Graphics toolbar. **5.** On the Electrode Potential vs Adjacent Reference (cd) 1 toolbar, click Plot. The surface plot of the potential for the ship surface with the uncoated propeller should look like **Figure 8** (chapter 4).

## **1D Plot Group 9**

Now, create a Line Plot along the keel of the hull potential for both the coated and uncoated propeller cases. **1.** On the Home toolbar, click Add Plot Group and choose 1D Plot Group. **2.** In the Settings window for 1D Plot Group, type Potential along Keel in the Label text field. **3.** Locate the Data section. From the Data set list, choose none.

## **Line Graph 1**

**1.** Right-click Potential along Keel and choose Line Graph. **2.** In the Settings window for Line Graph, locate the Data section. **3.** From the Data set list, choose Study: Coated Propeller/Solution 1 (sol1). **4.** Select Edges 119, 121, and 123–125 only. **5.** Locate the y-Axis Data section. In the Expression text field, type E\_hull. **6.** Locate the x-Axis Data section. From the Parameter list, choose Expression. **7.** In the Expression text field, type y. **8.** Click to expand the Legends section. Select the Show legends check box. **9.** From the Legends list, choose Manual. **10.** In the table, enter the following settings:

## **Legends / Coated Propeller**

### **Line Graph 2**

**1.** Right-click Results>Potential along Keel>Line Graph 1 and choose Duplicate. **2.** In the Settings window for Line Graph, locate the Data section. **3.** From the Data set list, choose Study: Uncoated Propeller/Solution 2

(sol2). **4.** Locate the Legends section. In the table, enter the following settings:

### **Legends / Uncoated Propeller.**

#### ***Potential along Keel***

**1.** In the Model Builder window, under Results click Potential along Keel. **2.** In the Settings window for 1D Plot Group, click to expand the Title section. **3.** From the Title type list, choose Manual. **4.** In the Title text area, type Potential along keel. **5.** On the Potential along Keel toolbar, click Plot. The potential comparison plot for the coated and uncoated propellers should look like **Figure 10** (chapter 4).

### **Derived Values**

Finally, evaluate the magnitude of the current imposed by the ICCP anode by integrating the current density over the anode area.

#### **Surface Integration 1**

**1.** On the Results toolbar, click More Derived Values and choose Integration > Surface Integration. **2.** In the Settings window for Surface Integration, locate the Data section. **3.** From the Data set list, choose Study: Coated Propeller/Solution 1 (sol1). **4.** Locate the Selection section. From the Selection list, choose Anode. **5.** Click Replace Expression in the upper-right corner of the Expressions section. From the menu, choose Component 1>Secondary Current Distribution>cd.nII - Normal electrolyte current density. **6.** Click Evaluate.

#### **Surface Integration 2**

**1.** Right-click Surface Integration 1 and choose Duplicate. **2.** In the Settings window for Surface Integration, locate the Data section. **3.** From the Data set list, choose Study: Uncoated Propeller/Solution 2

(sol2). 4. Run the Program ICCP computation will take place Figure 5 (see chapter4).

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# Chapter Four

## Data Analysis and Discussions

### 4.1 Introduction

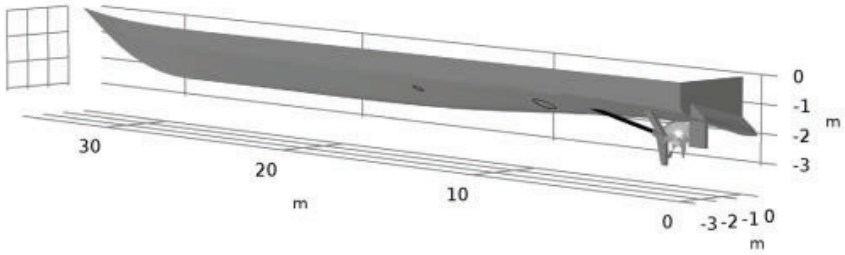
Impressed current cathodic protection (ICCP) is a commonly employed strategy to mitigate ship hull corrosion, by which an external current is applied to the hull surface, polarizing it to a lower potential. Although there are various factors such as salinity, temperature, hull surface coating that contribute to the demand for current, the area of bare metal (mainly propeller) is the most governing parameter. This model example simulates the effect of propeller coating on the current demand and is based on a paper by Huber and Wang, however using slightly different geometry and polarization data. Two different cases are investigated; a coated and an uncoated propeller.

### 4.2 Results and Discussions

This part deals with the result of the data analysis, it shows the equations, the ship hull geometries required for protection which were set in chapter 3. It depicts the final output to calculate the current density for the hull protection in both coated and uncoated situations.

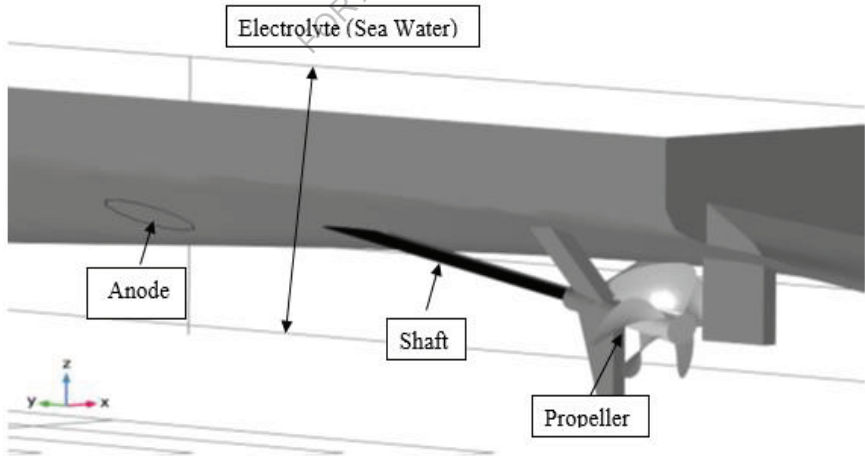
#### 4.2.1 Ship Hull Atmosphere

The geometry of the ship hull considered in this example is shown in Figure (4.1). The model geometry is created by adding rectangular block outside the hull geometry to represent the ocean. Figure (4.1) below shows the geometry of the ship hull surface, which is exposed to the sea water.



**Figure (4.1) the Geometry of the Ship Hull Surface, which is exposed to the Sea Water**

The following shape which shows the zoomed-in model geometry highlighting the propeller features is shown in Figure (4.2) where the anode, shaft and propeller surfaces and the electrolyte (sea water) domain are highlighted.



**Figure (4.2) the Zoomed-in Model Geometry of the Ship Hull Surface Highlighting Anode, Shaft, Propeller Surfaces and Electrolyte Domain**

The Secondary Current Distribution interface is used to solve the electrolyte potential,  $\phi_l$  (SI unit: V), over the electrolyte domain according to:

$$i_l = -\sigma_l \nabla \phi_l$$

$$\nabla \cdot i_l = 0$$

Where,  $i_l$  (SI unit: A/m<sup>2</sup>) is the electrolyte current density vector and  $\sigma_l$  (SI unit: S/m) is the electrolyte conductivity of the sea water which is assumed to be a constant at 4 S/m

The Electrode Surface boundary node at the shaft electrode surfaces is used to add electrode reactions and set the boundary condition for the electrolyte potential to

$$n \cdot i_l = i_{loc}$$

Where  $i_{loc}$  (SI unit: A/m<sup>2</sup>) is the local individual electrode reaction current density.

Butler-Volmer expression is used to model the electrode reaction at the hull surface and the propeller surface in case of uncoated propeller. This sets the local kinetic current density to

$$i_{kin} = i_0 \left( \exp\left(\frac{\alpha_a F \eta}{RT}\right) - \exp\left(-\frac{\alpha_c F \eta}{RT}\right) \right)$$

Where the over potential is calculated as

$$\eta = \phi_{s, ext} - \phi_l - E_{eq}$$

The electrode reaction considered on the metal surfaces is oxygen reduction. Also enable a limiting current density of 5 A/m<sup>2</sup> to the electrode kinetics expressions, since oxygen transport in the seawater is limited by the rate of

transport to the surface. This will result in the following local current density expression

$$i_{loc} = \frac{i_{lim}i_{kin}}{i_{lim} + i_{kin}}$$

The ICCP system controls the hull potential versus the reference electrode. Describe this in the model by adding a Reference Electrode node, and then setting the electrode phase potential,  $\Phi_{s,ext}$ , of the Electrode Surface nodes to -850 mV versus the potential of the Reference Electrode. The propeller and the shaft are considered to be made up of nickel aluminum bronze (NAB) alloy and Alloy 625, respectively. The electrode kinetics parameters used in the Butler-Volmer expression for the shaft and propeller are shown in Table (4.1).

**Table (4.1) Electrode Kinetics Parameters**

| Parameter                                 | Unit               | Nab Propeller       | Alloy 625 Shaft     |
|---|--------------------|---------------------|---------------------|
| Equilibrium potential, $E_{eq}$           | V vs Ag/AgCl       | -0.31               | -0.18               |
| Exchange current density, $i_0$           | mA/cm <sup>2</sup> | $1.5 \cdot 10^{-2}$ | $1.3 \cdot 10^{-4}$ |
| Anodic transfer coefficient, $\alpha_a$   | -                  | 0.78                | 0.45                |
| Cathodic transfer coefficient, $\alpha_c$ | -                  | 0.44                | 0.57                |

In case of uncoated propeller, use the Electrode Surface boundary node at the propeller base surfaces and use the Thin Electrode Surface boundary node at the propeller blades surfaces to add electrode reactions. Note that the Thin Electrode Surface boundary feature allows to prescribe the electrode kinetics at both the upside and downside of the propeller blades.

Since the anode kinetics of this model is not known (and of minor interest for this analysis), use an Electrolyte Potential node for the anode surface and set the potential to 0 V. Note that the choice of potential level is at this



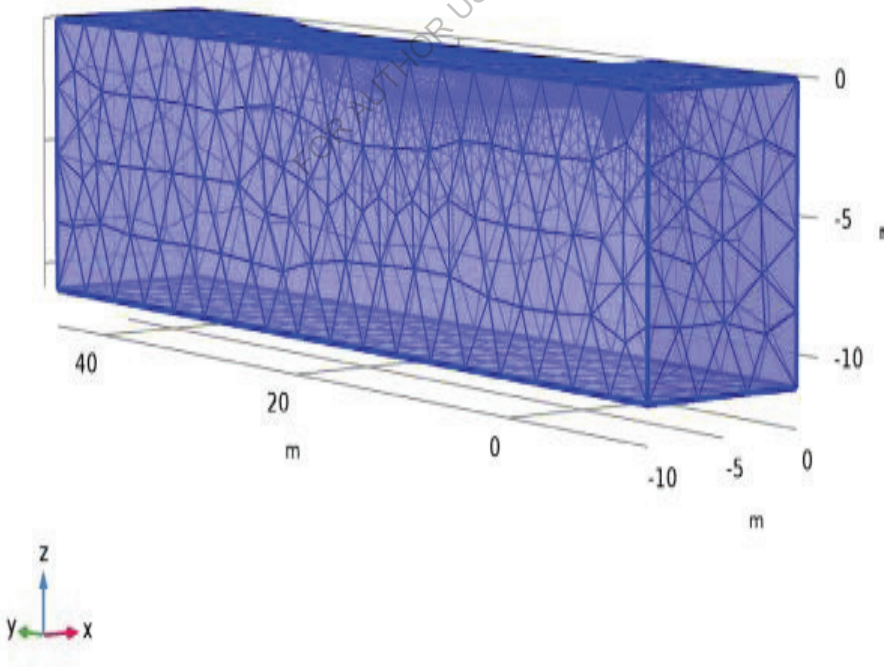
boundary arbitrary and only serves to “boot strap” (ground) the potentials of the model.

Use the default Insulation condition for all boundaries of the ship hull surfaces:

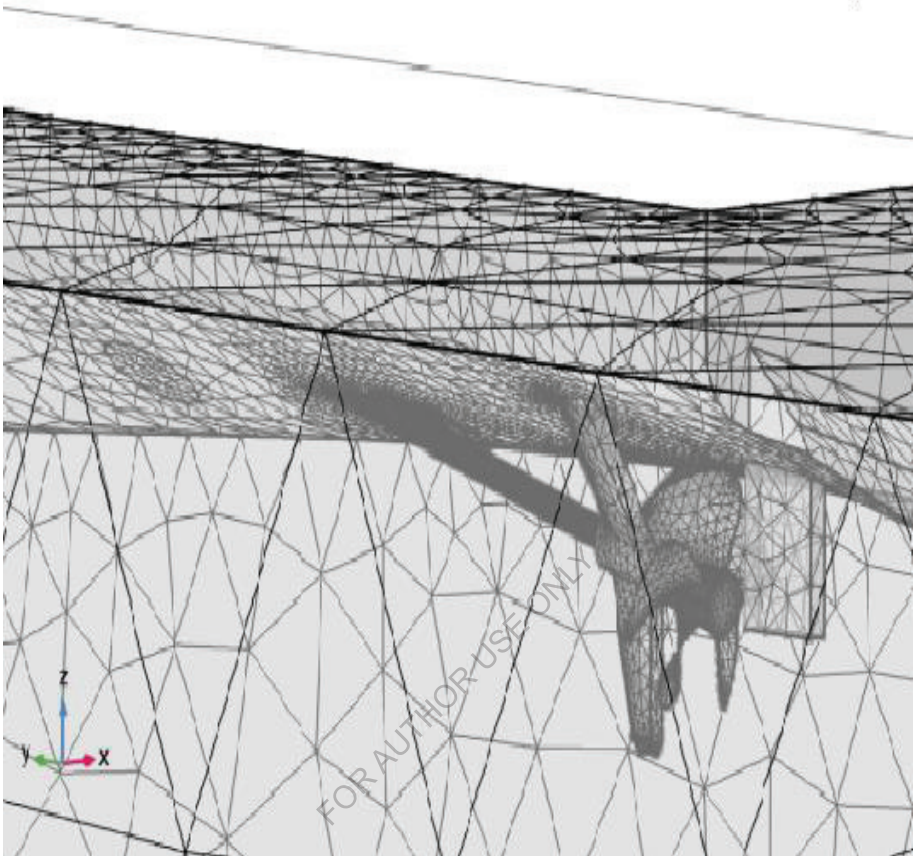
$$\mathbf{n} \cdot \mathbf{i}_t = 0$$

Where  $\mathbf{n}$  is the normal vector, pointing out of the domain.

Use an Infinite Electrolyte condition on the external boundaries to the Electrolyte domain to describe the infinite extension of the ocean. Specify the ocean surface and mid ship plane as symmetry planes. This models the current conduction outside the drawn geometry, using the boundary element method. The mesh used in the model is shown in Figure (4.3), with a close-up of the propeller shown in Figure (4.4).



**Figure (4.3) the Mesh used in Model**

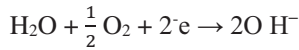


**Figure (4.4) The Mesh used in Model, Zoomed-in around Propeller**

### **4.2.2 Total ICCP Current Demand**

The research is about an Impressed Cathodic Current Protection (ICCP) for a naval vessel. In ICCP, an active anode electrode is used to impress a cathodic current on the protected metal, thereby lowering the potential of the surface into a regime wherein little or no corrosion occurs. The magnitude of the impressed current is controlled by monitoring the potential of the protected metal body versus a reference electrode, placed in the vicinity of the protected body.

The designed program investigate the behavior of the ICCP system used to protect the ship hull. When the ICCP system is operating as intended, the only active electrode reaction on the hull, propeller, and shaft is oxygen reduction:



The hull is coated, whereas the propeller and shaft are bare, implying that the governing factors for the ICCP behavior are the kinetic parameters for oxygen reduction on the latter surfaces.

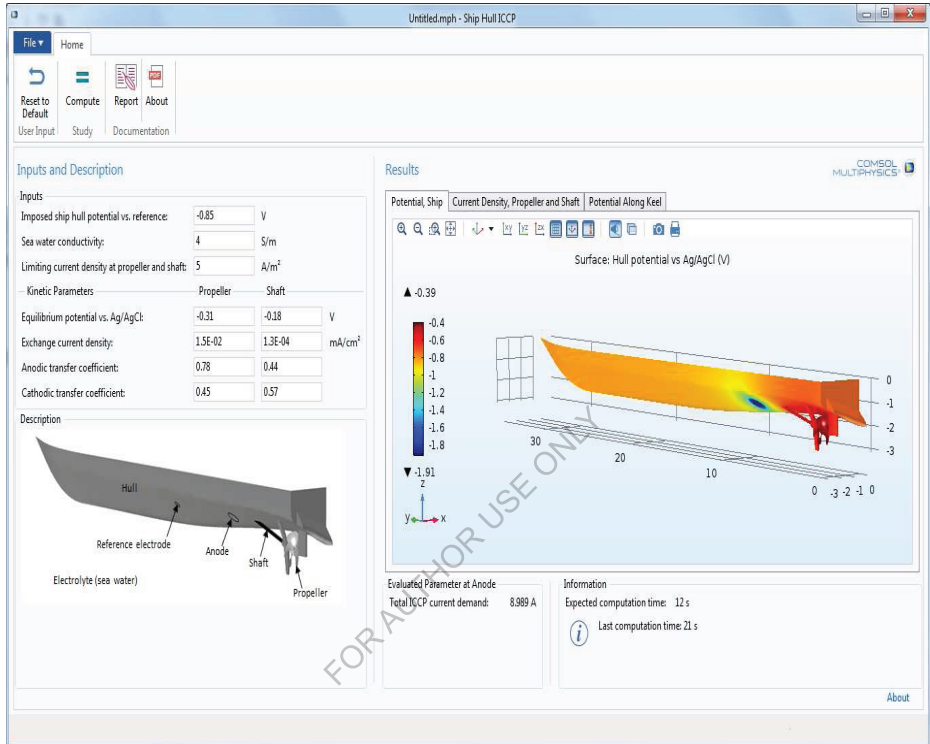
An important factor is also the limiting current for oxygen reduction due to transport limitations of the dissolved oxygen molecules in sea water. For instance, you would expect the limiting current density on the propeller to rise when the propeller is rotating as compared to when the ship is moored with the engine shut off.

The Ship Hull ICCP program lets you vary the following parameters:

1. Control potential of the ICCP system to protect the ship hull.
2. Sea water conductivity.
3. Limiting current for oxygen reduction.
4. Electrode kinetics of the propeller and shaft.

The objective is to keep the hull potential low, but at the same time avoid excessively high impressed currents, since these induce wear on the anode as well as increase the power demand of the system.

The figure below (Figure (4.5)) summarizes the graphical user interface of the program.



**Figure (4.5) Graphical User Interface of the Ship Hull ICCP Simulator**

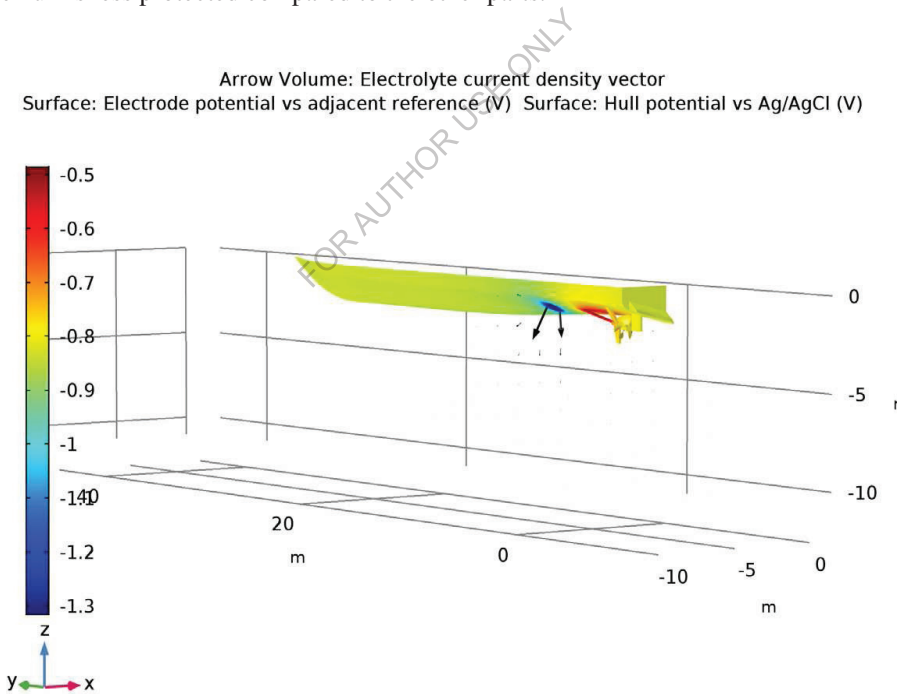
The program evaluates the total ICCP current demand at the anode. Additionally, potential distribution across the ship hull surface and current density distribution at the shaft and propeller surfaces are plotted.

For the default imposed ship hull potential of  $-0.85\text{ V}$  versus the reference electrode, it can be seen that the surface plot of the potential distribution across the ship hull surface is non-uniform, which may increase the risk of portions of the hull being unprotected to corrosion or being subjected to hydrogen evolution. Similarly, the hull potential plotted along the keel of the

ship shows that the largest potential difference along the keel is around 450 mV, which is within the maximum 500 mV difference that is considered safe. A negative local current density seen in the surface plot for the shaft and propeller surfaces confirms cathodic reaction at both of these surfaces.

### 4.2.3 Analysis of Hull Potential with Coated Propeller

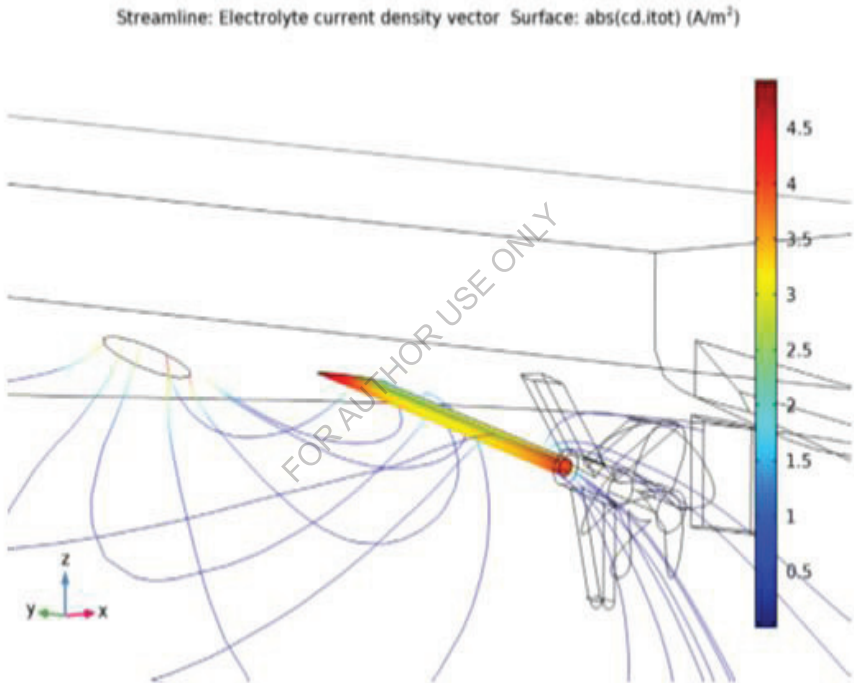
A surface plot of the hull potential for the case with a coated propeller is shown in Figure (4.6). It can be seen that the potential distribution across the ship hull surface is quite uniform, except in the region close to the anode surface and the propeller and shaft surfaces. The potential is higher near the shaft compared to the rest of the ship hull surface, indicating that this part of the hull is less protected compared to the other parts.



**Figure (4.6) a Surface Plot of the Hull Potential for the Case with a Coated Propeller**

#### 4.2.4 Analysis of Current Density to the Shaft for Coated Case

The following Figure (4.7) shows a streamline plot of electrolyte current density and a surface plot of absolute value of the total current density over the shaft surface for the case with the coated propeller. The ionic current flow from the anode surface to the shaft surface can be seen in Figure (4.7) below.

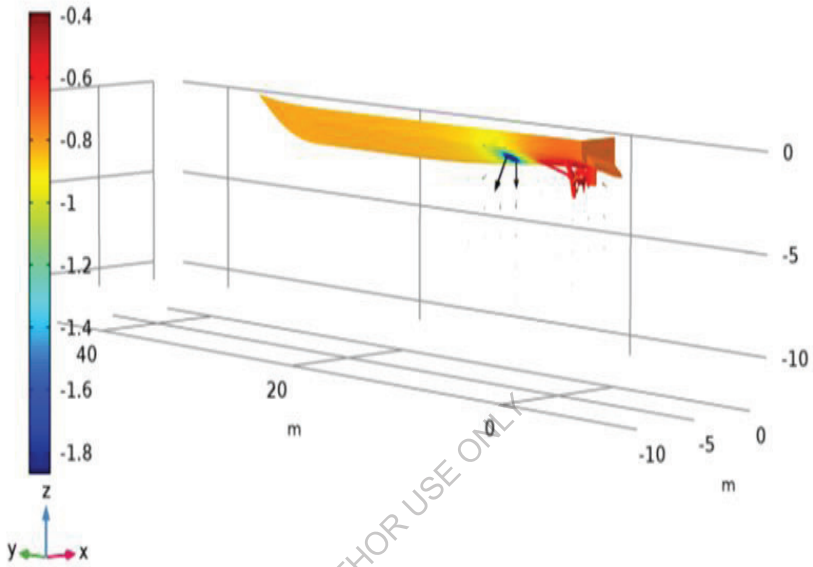


**Figure (4.7) a Surface Plot of the Total Current Density for the Case with a Coated Propeller**

#### 4.2.5 Analysis Hull Potential with Uncoated Propeller

Figure (4.8) below shows the potential for the case with an uncoated propeller. It can be seen that the potential distribution across the ship hull surface is less uniform compared to the coated propeller case.

Arrow Volume: Electrolyte current density vector  
 Surface: Electrode potential vs adjacent reference (V)  
 Surface: Electrode potential vs adjacent reference (V)  
 Surface: Electrode potential vs adjacent reference (V) Surface: Hull potential vs Ag/AgCl (V)



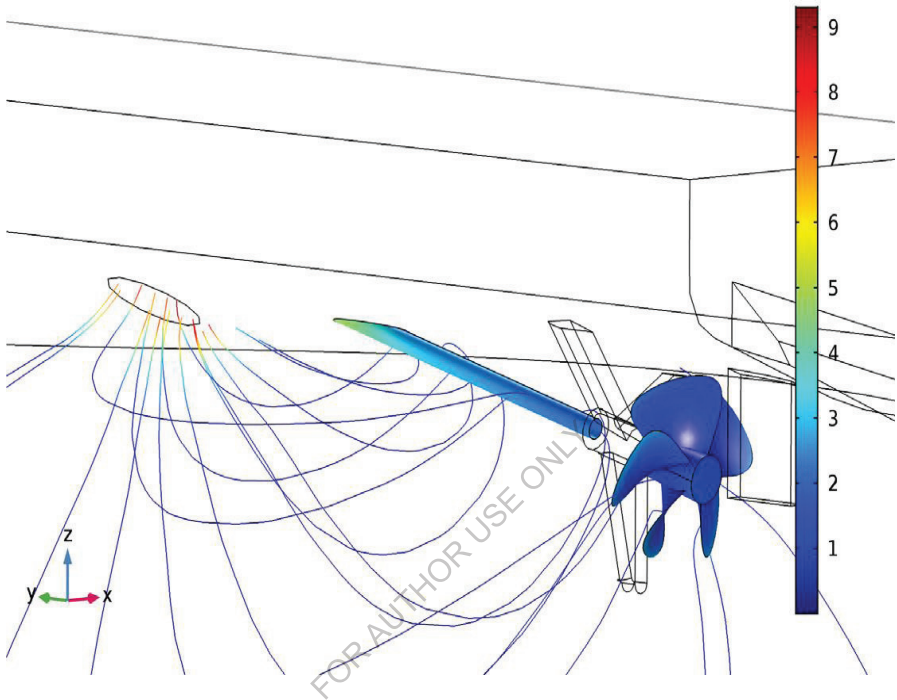
**Figure (4.8) a Surface Plot of the Hull Potential for the Case of an Uncoated Propeller**

#### **4.2.6 Analysis of Current Density to the Shaft for Uncoated Case**

A streamline plot of electrolyte current density and a surface plot of absolute value of the total current density over the shaft and propeller surfaces for the case of the uncoated propeller is shown in Figure (4.9). The ionic current flow from the anode surface to the shaft and propeller surfaces can be seen in Figure (4.9). The total current demand is found to be higher in case of the uncoated propeller compared to the coated propeller case, which could be attributed to the higher cathode surface area in case of the uncoated propeller.



Streamline: Electrolyte current density vector Surface: abs(cd.itot) (A/m<sup>2</sup>)  
Surface: abs(cd.itotu) (A/m<sup>2</sup>) Surface: abs(cd.itotd) (A/m<sup>2</sup>)

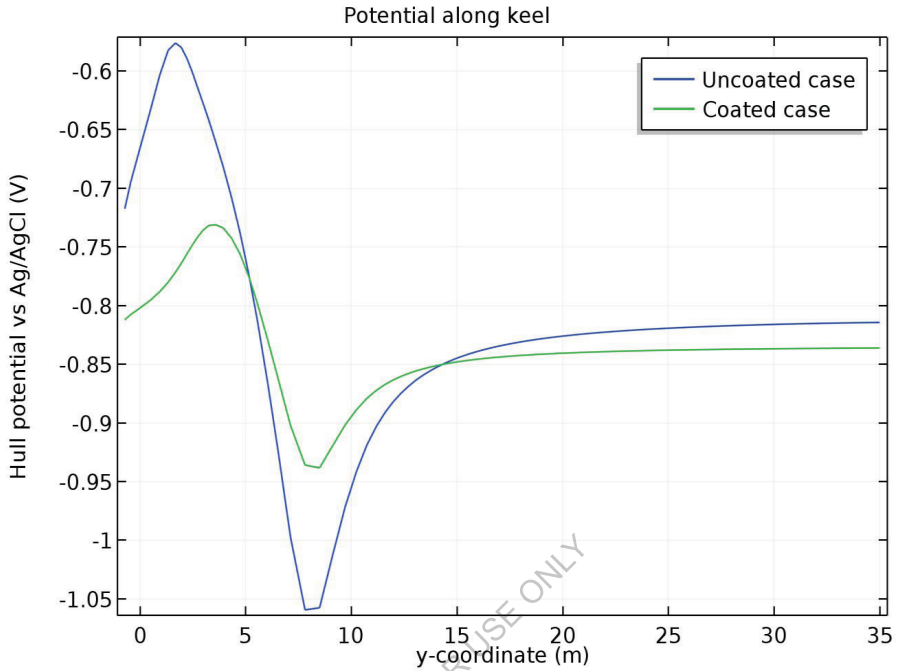


**Figure (4.9) a Surface Plot of the Total Current Density for the Case of an Uncoated Propeller**

#### **4.2.7 Electrode Phase ICCP Potential Plot**

Figure (4.10) shows the electrode phase potential along the keel of the ship for both coated and uncoated propellers. It can be seen that the potential in the regions closer to the anode and the propeller surfaces deviates significantly from the potential at the rest of the ship hull surface in case of uncoated propeller. This deviation is less significant in the case of a coated propeller. Thus, the potential distribution across the length of ship hull surface is found to be considerably uniform in case of coated propeller and non-uniform in case of uncoated propeller.





**Figure (4.10) the Electrode Potential Variation along the Keel of the Ship for both Coated and Uncoated Propellers**

Finally, the integrated anode current is evaluated for the two cases. For the coated case the current is 4 A, and for the uncoated case the current is 9 A.

## Chapter Five

### Conclusions, Recommendations and Suggestions for Further Studies

This chapter presents the conclusions of the study, recommendations and suggestions for further studies.

#### 5.1 Conclusions

The purpose of this study is to increase the ships' performance by reducing the drag which is caused by fouling and corrosion. The researcher used two ways to achieve this goals, first the vessel hull coating is used to eliminate the drag caused by fouling and Impressed Current Cathodic Protection system (ICCP) is designed using 'comsol 5.3a ' multi physic software program. The program calculated the current density for hull protection in both coated and uncoated states. This experiment also provided an estimate that the range of cathodic potentials. The system shows that the largest potential difference along the keel is around 450 mV, which is within the maximum 500 mV difference that is considered safe and can ensure hull protection. For the coated propeller the demanded current for protection is 4 A. In this case the potential distribution across the ship hull surface is quite uniform, except in the region close to the anode surface and the propeller and shaft surfaces. For the uncoated case, the value of the total current density over the shaft and propeller surfaces is 9A. The potential distribution across the ship hull surface is less uniform compared to the coated propeller case. There is high ionic current flow from the anode surface to the shaft and propeller surfaces which lead to oxidization of the anode more than the coated case. It could be true to say that the total current demand is found to

be higher in case of the uncoated propeller compared to the coated propeller case. .

## **5.2 Recommendations**

The findings of this study reveals some recommendations as following:

1. ICCP should be used in corrosion protection of the ship hull to increase the ship performance and to prolong the vessel structure to its maximum allocated lifetime.
2. The anode material is consumed base on the current density the higher current the more consuming of anodes, therefore, the research recommend for coated cases to reduce the amount of the protection current, this lead to less consuming of anodes.
3. It is important to set a periodic time to check the serviceability of the anodes to ensure the structure protection from corrosion.
4. The protection current density should be checked periodically to its limit to ensure vessels' hull protection from corrosion.

## **5.3 Suggestion for Further Studies**

1. It is suggested to perform study on bacterial attachment and viability on metal surfaces to be controlled by potential polarization.
2. Since calcareous deposit is a significant feature of cathodic protection at more negative potentials, it is proposed to study the mechanism of calcareous deposition under cathodic protection and effects of bio-films on this mechanism and vice-versa.

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## Appendices

### Photographs of Marine Workshop Complex and Slipway in Port Sudan, Sudan



**Photograph (1)**



**Photograph (2)**



**Photograph (3)**



**Photograph (4)**





**Photograph (5)**



**Photograph (6)**





**Photograph (7)**



**Photograph (8)**



**Photograph (9)**



**Photograph (10)**



**Photograph (11)**

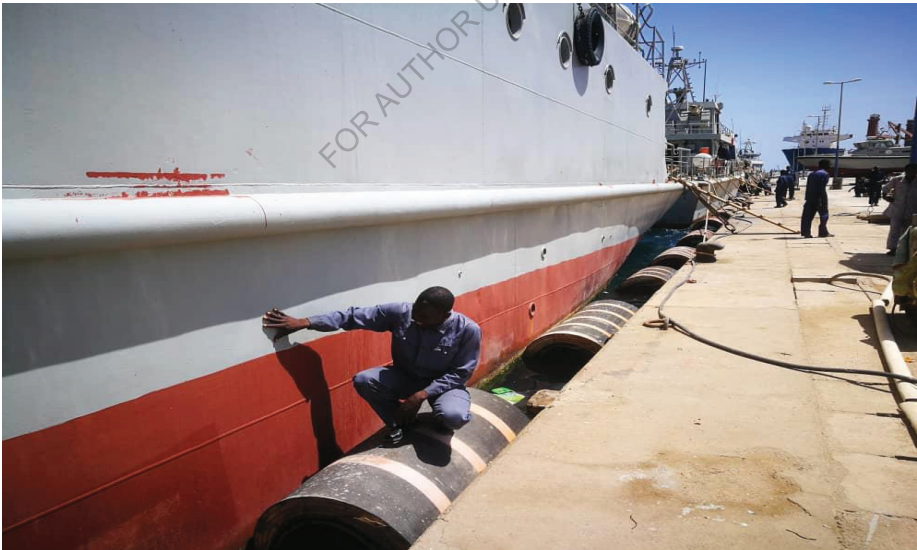


**Photograph (12)**





**Photograph (13)**



**Photograph (14)**



**Photograph (15)**



**Photograph (16)**



**Photograph (17)**



**Photograph (18)**





**Photograph (19)**



**Photograph (20)**



**Photograph (21)**



**Photograph (22)**





**Photograph (23)**

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