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DIPLOMA THESIS:
Battery Vessels and Corrosion due to DC Stray Currents

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Introduction

Green energy has been challenging the global economy lately. In the maritime industry, the green transition concerns mainly the decarbonisation of energy sources. New technologies are already being implemented on most European ships and ports with the objective of either reducing or completely switching from GHG fuels to green fuels. A few examples are the application of hybrid and battery propulsion system, the incorporation of photovoltaic panels on deck and the cold ironing system to reduce emissions in ports.

However, the application of these new technologies needs to be studied in terms of various issues such as efficiency and effectiveness, cooperation with the installed structure and corrosion behavior.

The chemical process of corrosion is a natural phenomenon that is necessary to maintain the natural balance from an environmental point of view. However, from the engineer's point of view, corrosion can be considered as a destructive attack of nature on metal. This destruction causes significant material losses, resulting in economic consequences in terms of productivity, maintenance, repair and restoration costs. The consequences should also include incidental injuries or loss of life associated with failures as a result of corrosion. It can be seen that it is imperative for the engineer to protect steel structures from corrosion.

The present thesis studies the corrosion behavior of hull steel during the operation of battery propulsion system. The use of direct current (DC) increases the risk of corrosion from leakage currents at the points where they leave the electrical circuit. This problem can be caused by inadequate design and selection of materials or by deterioration of the insulation.

The work lists as the first attempt in the archived literature to approach the macroscopic impact of battery propulsion and Photovoltaic oriented DC stray current corrosion. It unfolds by holistically defining the origin of the problem, modelling the problem in commercially available software and discussing the arising implications. Recognition of the impact of corrosion from DC power traction projects has forced stakeholders around the world to consider a variety of design specifications, codes of practice and international standards to ensure that interference from the dispersal current is minimised. These codes and standards are intended to provide designers and utilities with an corrosion management strategy that defines a level of corrosion risk that is acceptable across all infrastructure. Utilizing existing documentation or developing similar corrosion management systems and practices may be necessary for battery vessel owners and port authorities.

Abstract

This thesis aims to study and simulate the stray current corrosion phenomenon in ships using direct current as the main power source. In addition, recommendations and solutions using cathodic protection as a problem-solving factor are provided. The approach to the problem is achieved through three steps: deep understanding of the principles of cathodic protection methods , analysis and understanding of the corrosion and protection phenomenon, study of the structure under protection and finally, simulation of the cathodic protection phenomenon in Comsol Multiphysics 6.1.

The first part presents the regulations and new technologies for green growth. The main focus is on the installation of on-board batteries. Their characteristics, capabilities, specifications, risks, and overall costs are discussed.

In the second stage, the importance of cathodic protection (CP) and the basic electrochemical principles are discussed. Cathodic Protection is the predominant method of protection for ships and floating structures. The two main methods of cathodic protection are the installation of sacrificial anodes (SACP) and the application of imposed current (ICCP). Both methods are applied to the ship's hull , but the former is considered more suitable for ships powered by direct currents.

Using Comsol Multiphysics, a first approach to the problem of battery vessel corrosion was carried out. By introducing the geometry of the ship and the physical parameters of the problem we were able to visualize the risk of stray DC currents. Despite the lack of literature on the field, and consequently the unexpected results in study 2, our findings nevertheless highlight the problem and make suggestions for addressing it.

Περίληψη

Η παρούσα διπλωματική εργασία αποσκοπεί στη μελέτη και προσομοίωση του φαινομένου διάβρωσης από αδέσποτα ρεύματα σε πλοία που χρησιμοποιούν συνεχές ρεύμα ως κύρια πηγή ενέργειας. Επιπλέον, παρέχονται συστάσεις και λύσεις με τη χρήση της καθοδικής προστασίας ως παράγοντα επίλυσης του προβλήματος. Η προσέγγιση του προβλήματος επιτυγχάνεται μέσω τριών βημάτων: κατανόηση των αρχών των μεθόδων καθοδικής προστασίας , ανάλυση και κατανόηση του φαινομένου της διάβρωσης και της προστασίας, μελέτη της υπό-προστασία κατασκευής και, τέλος, προσομοίωση του φαινομένου της καθοδικής προστασίας στο Comsol Multiphysics 6.1.

Στο πρώτο μέρος παρουσιάζονται οι κανονισμοί και οι νέες τεχνολογίες για την πράσινη ανάπτυξη. Το κύριο βάρος δίνεται στην εγκατάσταση μπαταριών επί του πλοίου. Συγκεκριμένα παρουσιάζονται τα κύρια χαρακτηριστικά, οι δυνατότητες, οι προδιαγραφές, οι κίνδυνοι από τη χρήση μπαταριών και το συνολικό κόστος τους.

Στο δεύτερο μέρος, αναλύεται η σημασία της καθοδικής προστασίας (CP) και οι βασικές ηλεκτροχημικές αρχές. Η καθοδική προστασία είναι η κυρίαρχη μέθοδος προστασίας για τα πλοία και τις πλωτές κατασκευές. Οι δύο κύριες μέθοδοι καθοδικής προστασίας είναι η εγκατάσταση θυσιαζόμενων ανόδων (SACP) και η εφαρμογή επιβαλλόμενου ρεύματος (ICCP). Και οι δύο μέθοδοι εφαρμόζονται στη γάστρα του πλοίου , αλλά η πρώτη θεωρείται καταλληλότερη για πλοία που τροφοδοτούνται από συνεχή ρεύματα.

Χρησιμοποιώντας το πρόγραμμα Comsol Multiphysics, πραγματοποιήθηκε μια πρώτη προσέγγιση του προβλήματος της διάβρωσης σε πλοία που χρησιμοποιούν μπαταρίες. Με την εισαγωγή της γεωμετρίας του πλοίου και των φυσικών παραμέτρων του προβλήματος μπορέσαμε να απεικονίσουμε τον κίνδυνο από τα παρασιτικά ρεύματα(stray currents). Παρά την έλλειψη βιβλιογραφίας στον τομέα αυτό και, κατά συνέπεια, τα απροσδόκητα αποτελέσματα της μελέτης 2, τα ευρήματά μας αναδεικνύουν ωστόσο το πρόβλημα και διατυπώνουν προτάσεις για την αντιμετώπισή του.

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CHAPTER 1

I)Target For 2050-Shipping Electrification

Environmental Impact of Shipping

Vessels carry the 80 per cent of consumer goods around the world. Likewise, every other transportation, fossil fuels that are used in marine diesel engines produce gases like CO2, SO2 that accelerate greenhouse warming effect. Those emissions directly contribute to Global Warming Potential (GWP), Acidification potential (AP), Eutrophication potential (EP) and Photochemical Ozone creation potential (POCP). Furthermore, hazardous gases make a bad impact on the level of life near coastal areas and ports. Ferries have a direct effect on human health due to their long stay on the port. EU accounts for more than 70% of human transportation across the sea{19}. In recent times, international regulations have been enforced, with a view to narrowing down the environmental impact of maritime industry.

Rules and Regulations on Maritime Sustainability

Paris Agreement

The goal of the 2015 Paris Agreement – to achieve climate neutrality by the middle of this century – creates the need for numerous decarbonization technologies to be commercially available and affordable across economic sectors, including transport, industry and buildings. The share of renewable energy in the power sector would increase from 25% in 2017 to 85% by 2050. The main aim of the analysis is to limit the global temperature rise to below 2°C until 2025.

IEA-Global Energy Review

In May 2021 the IEA published a scenario of changing energy mix of the total energy supply. As mentioned, currently dominating fossil share (oil, coal, gas) will be mainly replaced by renewable sources. In accordance with survey, over the next 30 years, conventional fossil fuel must be decreased by 73% whereas renewable energy consumptions increases strongly by 360%. Globally, shipping accounts for approximately 3% of all anthropogenic GHG emissions. In the IEA NZE(Net Zero Emissions) scenario shipping emissions are reduced by 6% per year and decrease to 120 million tons (Mt) CO2 in 2050. {1}

EU strategy

On 14 July 2021 the EU announced a series of measures: a) Including ships of 5,000 GT and above in its Emissions Trading System for all intra-EEA voyages and for 50 per cent of voyages starting and ending in the block. b) Establishing greenhouse gas intensity standards for ship fuels. c) Introducing taxes on bunkers sold in the European Economic Area.

MARPOL Annex VI – Regulation 14

Regulation 14 which was imposed by MARPOL Annex VI and NTC 2008 stipulates the following limits:

1) Ships calling at SECA'S ports are obliged to burn fuels not above 0.1% sulphur content while in port. (2015)

2) The sulphur content of any fuel oil used on board ships shall not exceed the following limits 0.50% m/m on and after 1 January 2020.

IMO Regulations

In 2018, the International Maritime Organization (IMO) established the target of reducing total annual GHG emissions in the sector by 50% or more by 2050 against 2008 levels to align with the 2015 Paris Climate Agreement goals.{2,3} Also the aim is by 2030 to reduce carbon by at least 40% and 70% until 2050.

International regulations established by IMO aim to vertical reduction of Maritime GHG emissions. Examples for these measures are:

1. EEDI (Energy Efficiency Design Index) for new ships with regard to the specific CO2 emissions of freight ships. The goal of the EEDI is an improvement in average annual efficiency of 1.5% from 2015 to 2025;
2. SEEMP (Ship Energy Efficiency Management Plan) for existing ships, aiming to increase their energy efficiency in operations; and
3. IMO 2020 to limit the sulphur in fuel (effective from 1 January 2020).
4. EEXI (Energy Efficiency Existing Ship Index): this new index came into force on 1 January 2023. The EEXI is like its predecessor, the Energy Efficient Design Index (EEDI), but is applied to existing ships outside EEDI regulations. Emissions are defined per cargo ton and mile; and
5. CII (Carbon Intensity Indicator): the CII provides ship operators with the factor by which they must reduce CO2 emissions annually to ensure continuous improvement and comply with regulations. The CII must be implemented within each operator's Ship Energy Efficiency Management Plan (SEEMP). The CII will come into effect in 2023. This CII index will be used to rate ships on a five-grade scale: A, B, C, D and E, from best to worst performing. This will lead to the phasing out of the least-efficient vessels, e.g. by technology upgrades.

Nevertheless, the IMO analysis emphasizes that without further efforts, the transport sector will predominantly use fossil thus GHG emissions will not be sufficiently reduced fuels.

Green Power Supply

Developing countries of Middle East and North Africa (MENA) are expected to supply renewable energy to Europe, Asia and North America. As a user and carrier of (net) zero carbon fuels, shipping will underpin and benefit from this transition so it must be adequately supported.

Renewable electricity production must be rapidly increased in order to meet the high energy requirements of ship functionality. Total electric power needs have been calculated up to 3.000 TWh, taking into consideration expected technology efficiencies by 2050 Marine industry should supply an 18-fold increase in the world's existing renewable production capacity to fulfil of these requirements. {1}

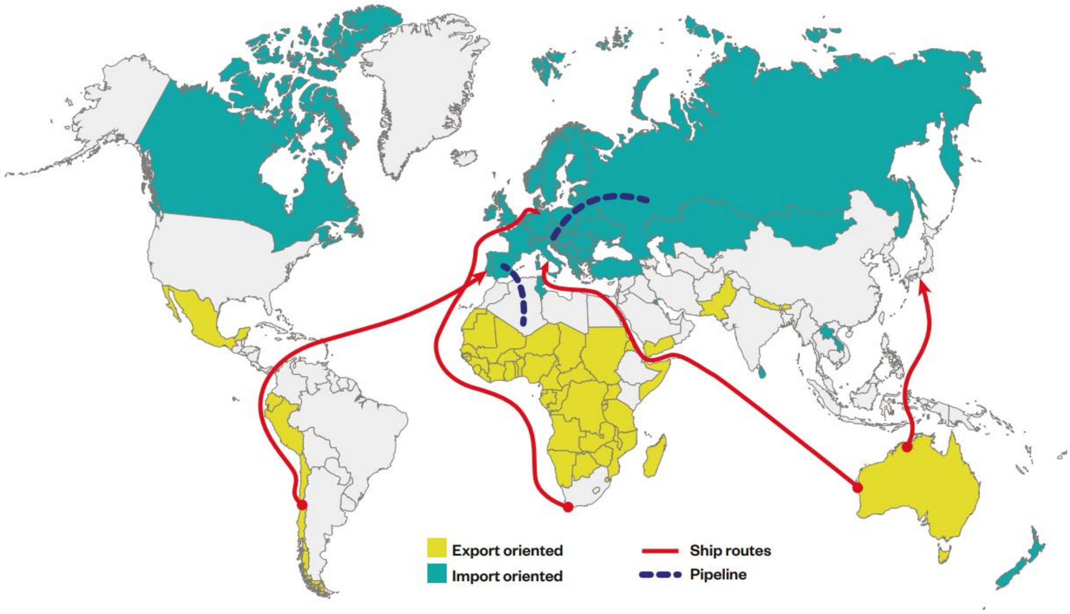


FIGURE 1: MAPPING RENEWABLE ELECTRICITY GENERATION

Sustainable Shipping & Renewable Energy Technologies

The global economy has a very high demand for maritime transport. Similarly, the OECD expects maritime trade to triple by 2050. In Europe there are significant commercial ports and tourists' areas that emit significant amounts of greenhouse gas emissions. The marine industry is undergoing a fourth revolution in propulsion. The replacement of marine diesel engines to more eco-friendly technologies of propulsion and functionality of vessels is a matter that attracts more attention in the field of marine industry.

LNG Vessels

Liquefied natural gas (LNG) and bio-fuels on board commercial ships have been used as alternative fuels, minimizing SOx,NOx emissions. Despite the fact that LNG is more advanced in technology readiness level than battery ships and H2, it does not meet the standards for zero emissions

Lithium Ion Batteries vs Hydrogen Fuel Cells

In recent years, urgent action is needed to accelerate the pace of the global energy transition and decarbonize the global economy. Green hydrogen fuels and batteries will form the backbone for the decarbonising sector.

Electric ships and H2 vessels for passenger and freight transport are the two most promising solutions for decarbonizing international shipping (Table1). Fuels such as hydrogen or ammonia do not contain carbon and consequently will not emit carbon dioxide, leading to the notion of 'zero carbon fuels'.

TABLE 1 EVALUATION OF HYDROGEN AND BATTERY ELECTRIC (FULL/HYBRID) FUEL ALTERNATIVES {6}

	Electric (full)	Elextric Hybrid	Hydrogen
Reduction of GHG	Very High	Moderate-High	Very High
Reduction of NOx	Very High	Moderate	Very High
Reduction of SOx	Very High	Moderate-High	Very High
Investment cost(on vessels)	High	Moderate	High
Fuel Cost	Low	Moderate	High
Availability	Moderate	Moderate	Low
Vessel Adaptation	Very High	Low-Moderate	High
Infrastructure adaptation	Moderate-high	Low	Very High
Market segment suitability	Vessels-short routes	All	All
Importance of regularity	High	Low-High	Low

The battery capacity used in pure electric vessels is in the range of 50–500 kWh, with a median value of 140 kWh, while, in hybrid ships, the range is 500–5000 kWh, with a median of 1000 kWh. From the analysis, it is clear that hybrid technology (used in 69% of the vessels) has an almost 10 times larger battery capacity compared to the pure electric vessels. {4}

Challenges of battery propulsion system

For the accomplishment of vessel's electrification, a tireless endeavor must be made by evaluating factors in shipping. Some of the major problems to be overcome are listed below:

1. Electric capacity is an asset as fully electric ferries must be autonomous during traveling from one port to another.
2. Battery charging from the store.
3. Life length of batteries.
4. The weight of the energy system installed.
5. The lightship weight, which is the total weight of vessel's hull could be reduced by the use of special materials having lower density(carbon fiber).
6. Education and training of the ship's crew to familiarize them with the technical, operational and safety aspects of the new system

The increasing contribution of variable renewable energy sources (VRES) in the energy system is the dominant decarbonization pathway for today's systems. The major disadvantages of green electricity technologies are the storage of energy for long periods of time and balance of electrical grid. In addition, all electric ships, to improve the fuel consumption without the emission of hazardous gases, should use the same electrical network to drive the propulsion as well as the service equipment. Their high price and short life are still a challenge regarding their commercialization.

Using and transporting these new fuels comes with significant operational and safety challenges which will need to be addressed. Defined and agreed global safety and sustainability standards for hydrogen-based fuels and strong safety standards for the transport and use of (net) zero fuels must be developed quickly, to keep pace with the transformation. Seafarers and those in the supply chain will need to be trained and new standards developed to maintain safety and minimise risk.

Decarbonisation measures and opportunities at ports

Cold ironing is a promising eco-friendly technology in the field of decarbonization and reduce emissions like SOx,NOx, particulate matter (PM). While vessels are anchored in port, their auxiliary engines are turned on to fulfill energy requirements of the ship. Renewable sources installed on shore side supply onshore power to the ships. Cold ironing has two main advantages:

1. The electrification of vehicles used for port functionality mitigates emissions from port infrastructure.
2. The use of electric-powered equipment reduces reliance on diesel and fossil fuel-based equipment.

Green Port Standards

A fully green system contains two autonomous power producers that supply electricity to the port store. That plug-in battery ships do not produce emissions during operation Both wind and photovoltaic energy could be harnessed as renewable energy sources. This step is necessary for the elimination of exhaust gases produced by lignite-fired power stations. Wind energy is preferable due to the lack of carbon dioxide which is harmful for humans' health. Islands and areas near ports usually have winds capable of moving the blades of wind turbines. Moreover, renewable energy can also be produced using surface waves that are generated at the surface of the sea. Energy Storage System (ESS) can store the power which is surplus to port energy requirements. In relation to the ship side, propulsion motor will be operated by a dual energy system consisting of battery bank and electric generator as shown in figure 2. A PV array is also installed on the deck of the ship in order to change the battery during daytime. When sunlight strikes the silicon, electric charges are conducted by metal contacts as direct current (DC).

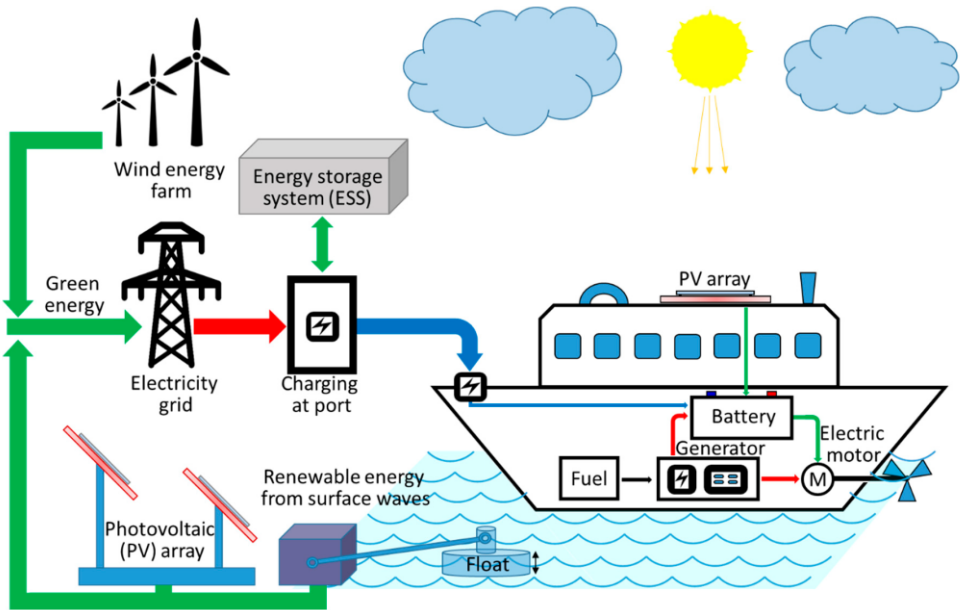


FIGURE 2: REPRESENTATION OF THE SHIP PORT INTERFACE

Green-Vessel Environmental Footprint

Crucially, same vessels yield different environmental performances, regarding the technology of electricity production. For instance, the environmental impact of battery operation in countries which heavily rely on fossil poor generation is greater than in others using natural gas. Into the bargain, it can be seen in Fig. 3 that natural-gas used for electricity production reduces CO2 emissions up to 50%, but does not nullify pollutant emissions nonetheless. More recent surveys show that 64% of total electricity power is generated by carbon-based fuels like coal(38%), natural gas(23%) and oil. {5} The difference between the average values of biogas and renewable energy sources was found to be roughly as large as 1.7 CO2 kg eq./kWh.

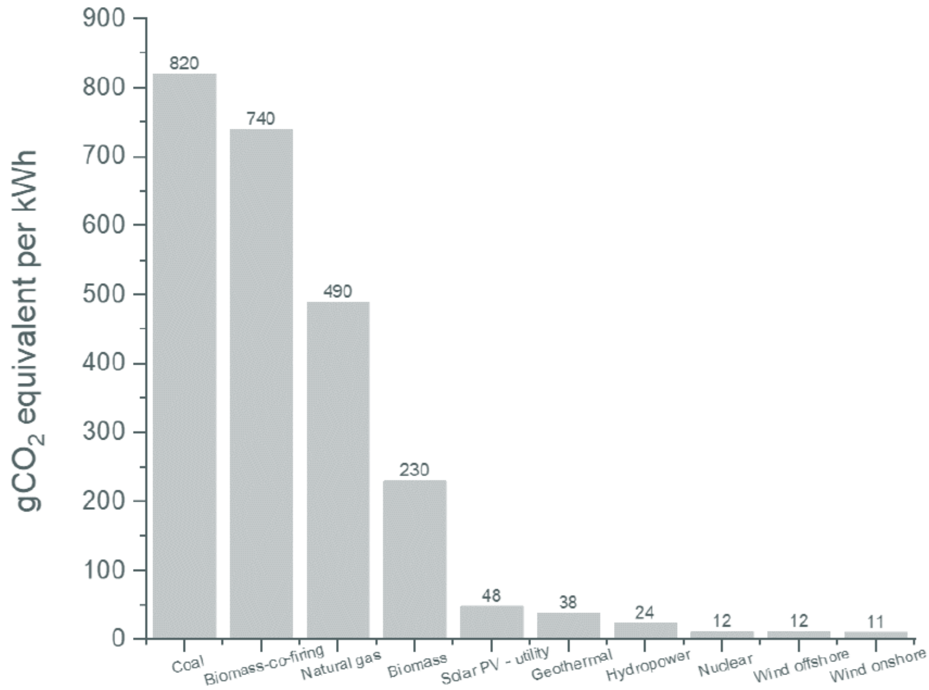


FIGURE 3: CO2 EMISSIONS FOR ELECTRICITY GENERATION BY VARIOUS FUEL TYPES.

Recent developments

International companies, research institutions, local ship-owners and yards are important contributors and often collaborate on the developments of Battery ship technology. More knowledge is needed in order to achieve further advancements in battery production and charging infrastructure solutions.

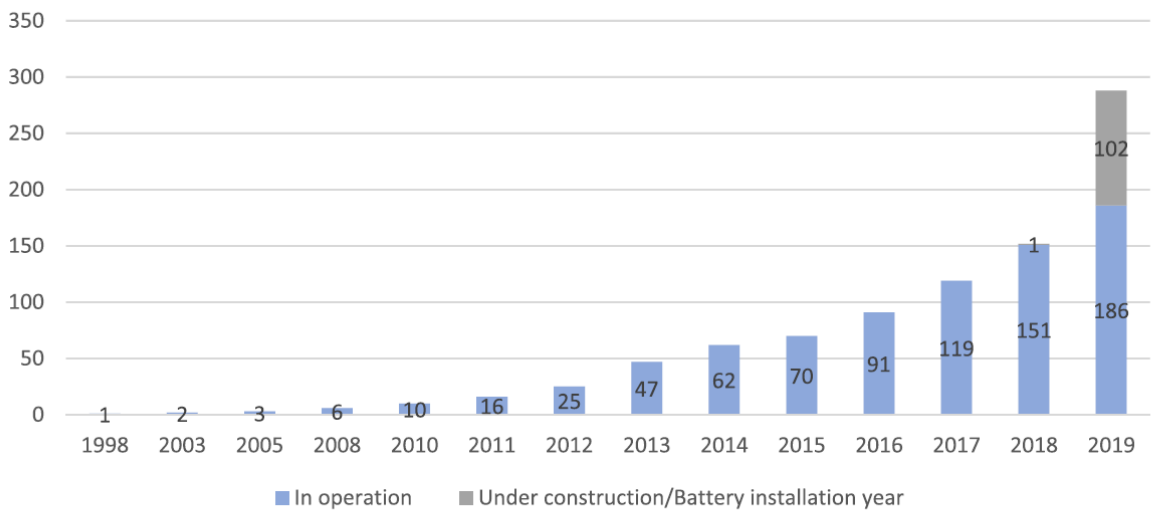
According to Marine forecast to 2050 underlying for the total 1349 alternative fuel ships in operation, there are 926 LNG ships and 396 ships with hybrid/battery propulsion. For the total 1046 alternative fuel ships on order, there are 534 LNG ships and 417 ships with hybrid/battery propulsion.{6} During the last decade the market for marine batteries and electrical installations has expanded rapidly worldwide. Currently, about 40 % of the world's marine battery installations are located on Norwegian ships.{7}

Implementation of full electrical propulsion powered by batteries is currently restricted to smaller vessels with short routes, like ferries. That is a stepping-stone towards implementation of battery technology onboard larger vessels.

Taking into consideration, the modifications to the contractual details regarding fuel costs, where shipowners are gradually undertaking the fuel costs from the companies chartering their ships, are initiating the market formation for battery technology with the aim of cutting-edge savings and reducing fuel consumption. However, the undesirable or unexpected results take on dimensions, such as the long-term risk for ship owners and shipyards, as the repair and replacement of defective parts of the structure does not seem to be guaranteed for the time being.

According to DNVGL (2019), as of March 2019, more than 150 battery-powered ships. Only 20 of them are full battery powered.

FIGURE 4: DEVELOPMENT IN TOTAL NUMBER OF VESSELS WITH INSTALLED BATTERY(GLOBALLY).



Cost of Renewable Energy

Energy-saving technologies encompass waste heat recovery systems, exhaust gas economizers, propeller ducts, pre-Swirl or stator fins, rudder bulbs, rigid sails, air lubrication system, bow enhancement and solar panels. Also, ship owning companies invest in scrubbers which are used to reduce harmful elements from exhaust gases. Nevertheless, total cost of new developments must be considered. As specified in Review of maritime Transport 2021 UNCTAD, it is estimated to require an average annual investment of between $40 and $60 billion in order to achieve IMO goals by 2050. between 2030 and 2050.{3}

Despite the high cost of the green transition, the overall rate of return on investment (ROI) can be very high, with sustainable ocean-based investments yielding benefits at least five times greater than costs as reported in the research "A Sustainable Ocean Economy for 2050, Ocean Panel".{8}. Depending on how prices evolve for renewable electricity in recent decades, a 70–100% absolute reduction in GHG emissions by 2050 can be achievable for a marginal abatement cost of $100–$500/tCO2. By multiplying the cost per tCO2 the total costs (capital and operational were estimated to be $2.3 trillion over 30 years to decarbonise shipping by 100 percent.

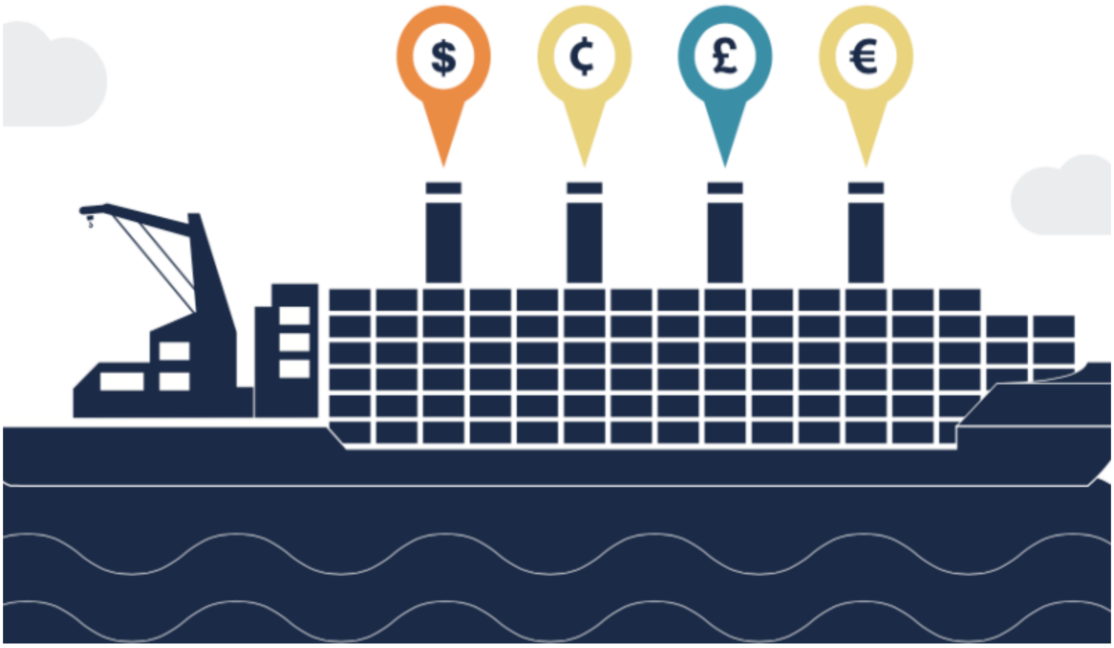


FIGURE 5: APPROACH OF TOTAL COST FOR SHIP DECARBONISATION

II) Battery vessels

A battery is made up of an anode, cathode, separator, electrolyte, and two current collectors. Electrolyte enables ions to be transferred through an the electric circuit between these poles. A separator is used to separate anode and cathode electrode. This process allows energy to be stored or produces in the battery.

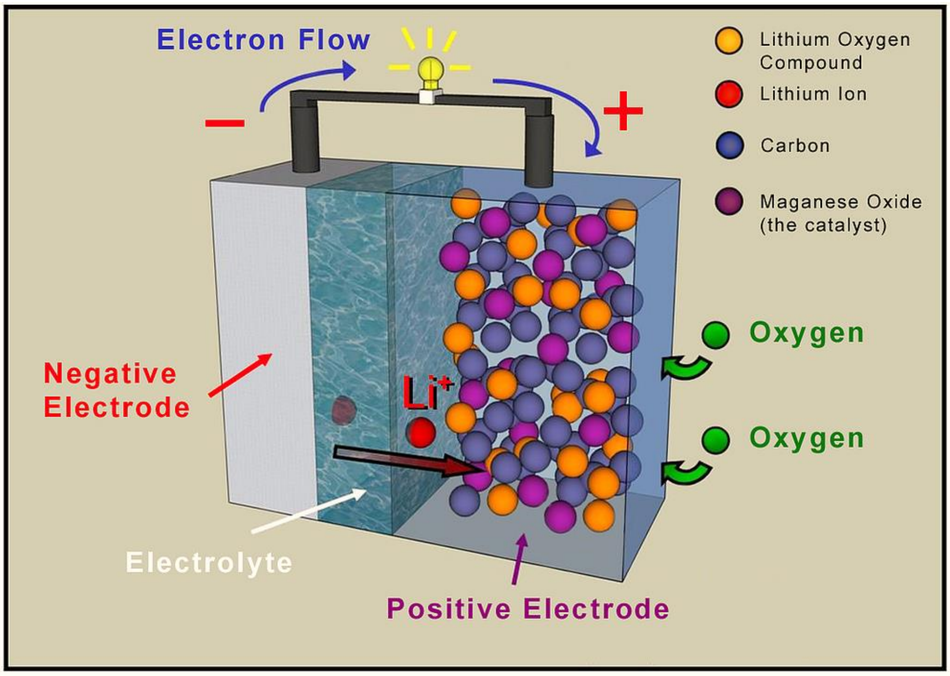


FIGURE 6: SCHEMATIC REPRESENTATION OF A LITHIUM ION BATTERY

The main use of battery for shipping applications can be separated into two main categories. First of all, batteries in shipping have been common elements of vessel, used to supplement the other fuels. More specifically, they have had a supporting role in starting-power to emergency systems, safety equipment, communication and other less energy/ power demanding solutions. The main advantages of maritime battery systems are reduced emissions, improved machinery utilization and flexibility and reduced maintenance cost involving fewer engine running hours, less running on low loads, longer intervals between planned maintenance and less planned maintenance. Secondly, as the zero carbon plan is implemented, batteries are being established as the main energy supplier for the ships' propulsion system. The following pages describe the installation and operation of the battery as the primary and secondary power source for the ship.

Battery propulsion for ships

Full-hybrid diesel-electric propulsion

Figure 7 shows the typical setup combination of a diesel electric and battery hybrid propulsion system. A diesel generator supplies power to the propulsion system whereas the batteries provide a dynamic system that allows for electric propulsion powered by BESS and peak-shaving. Aurora Spirit (Table2) is one of the first tanker which propulsion system combines LNG as a main fuel with battery storage for excess power. The vessel is also equipped with a battery system supplying power to the thrusters also makes the vessel unique in its segment.

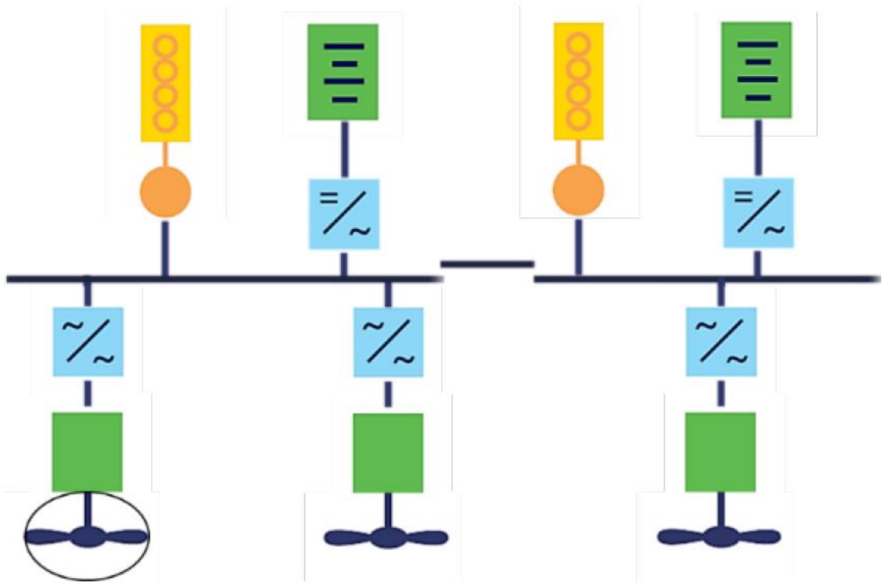


FIGURE 7: FULL-HYBRID DIESEL-ELECTRIC PROPULSION WITH BATTERIES IN A HYBRID SYSTEM

TABLE 2: AURORA SPIRIT GENERAL CHARACTERISTICS

Name	Aurora Spirit
Vessel type	Shuttle Tanker
Gross tonnage	90 000
Deadweight tonnage	125 000
Vessel size	177 m x 46 m x 16,5 m
Payload capacity	137 500 Liquid
ESS capacity	610 kWh

Pure battery-electric propulsion

A system for battery-electric propulsion of a vessel is illustrated in Fig8. In the battery electrical system, the propellers are connected to electric motors, which are powered by the energy stored in a battery system that is usually charged from land. In addition, a smaller diesel generator could be installed to ensure operation in case the batteries do not charge or to enable longer voyages, i.e. when the vessel must be docked.

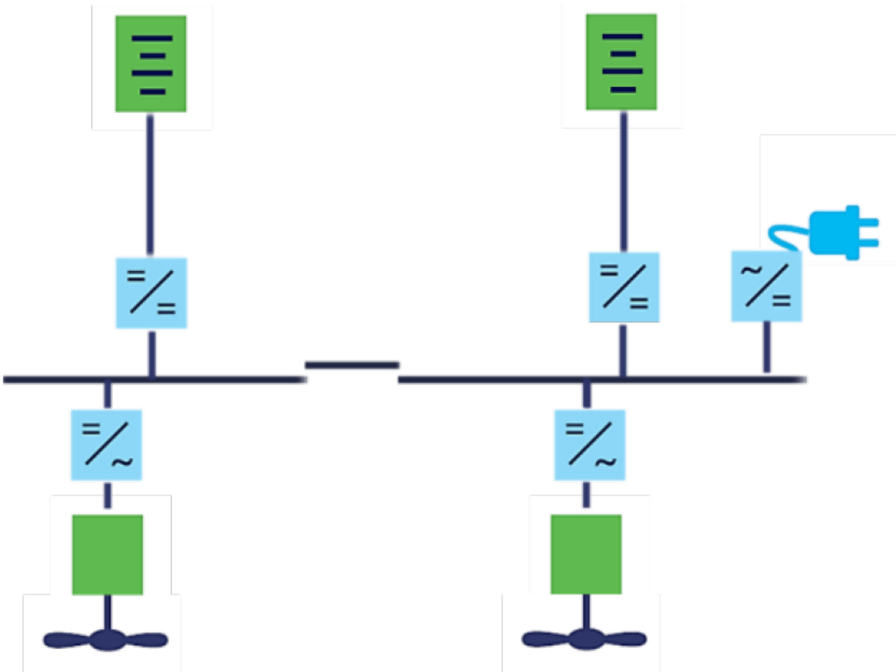


FIGURE 8: PURE BATTERY-ELECTRIC PROPULSION

M/F Tycho Brahe and M/S Aurora af Helsingborg are two sister ships that use batteries as a main propulsion system since 2017. 4.1 MWh of batteries were installed on each vessel, allowing for three full crossings of the 5km strait without charging. The general characteristics of these ships are presented below.

TABLE 3: MF TYCHO BRAHE GENERAL CHARACTERISTICS

Name	MF Tycho Brahe
Segment	Cruise and Ferry
Gross tonnage	11 148
Deadweight tonnage	2500
Vessel size	111,2 m x 28,2 m x 5,5 m
Passenger capacity	1250
Car capacity	240
ESS capacity	6345 kWh

In recent years there has been growing interest in reducing fuel-emission nearby ports. The global known eco-technology that is prevailing in the marine economy is cold ironing. Surprisingly, battery systems offer new competitive opportunities in the field of zero-emission ports. More precisely charging batteries while at sea via a power take-off on the main engine and using the energy in port will not only eliminate emissions during port stays, but also reduce the overall energy consumption. This alternative option should be considered by ship owners as to whether it could be economically preferable to other methods based on current legislation.

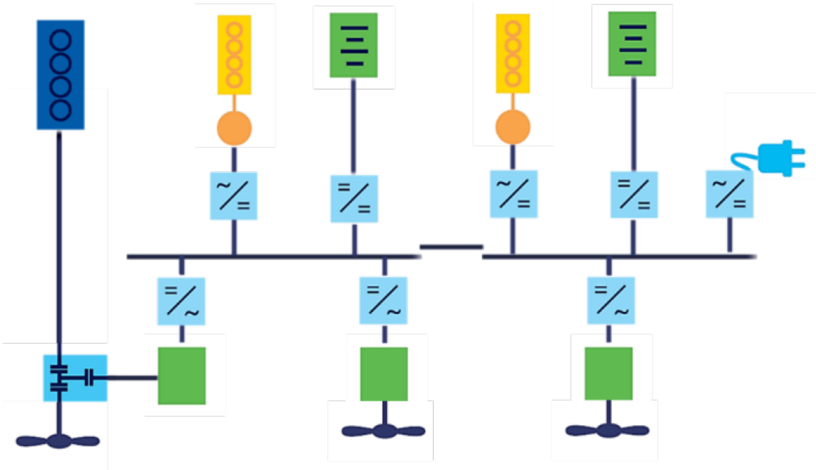


FIGURE 9: FUEL CELL AND BATTERIES

Battery Developments

Developments within battery technology have been vast within recent years. The first battery-electric short-sea ferry headed out in 2015. Nowadays, technology of batteries can be used to provide necessary power for onboard power requirements. Future carbon neutral fuels are expected to be more expensive than the current residual fuels applied for the two-stroke engine. Battery-hybrid systems are, as such, complementary to carbon neutral fuels, and the savings attained by hybrid systems will help to ease the transition towards such fuels and a carbon neutral shipping industry.

Battery technology aims to four key developments up to 2050:

1) Increasing availability of technologies to adopt solid-state electrolyte.
2) Metal-air technology as a key vector for development. It is mentioned that energy density potential could be increased up to 20/30 times higher than current state-of-the-art lithium-ion technology.
3) Battery management systems development expected to incorporate predictive failure
assessment, charging/discharging and state-of-charge monitoring based on machine learning principles.
4) Life-cycle cost reduction of batteries to be improved.

Today the field of batteries is dominated by lithium-ion batteries.

Lithium-ion batteries

The designation of lithium-ion labels the chemical composition of the cathode (the positive electrode). Today the most common types of lithium-ion batteries are:

a. Lithium cobalt oxide (LiCoO2) – first application of lithium-ion technology, most commonly applied in older consumer electronics due to its high energy density. However, it typically displays lower power (rate) capabilities and shorter cycle life. As a result, LICoO2 is not applicable to the maritime industry.

b. Lithium iron phosphate (LiFePO4) – the main benefit of this composition is that the cathode is more stable, which reduces the risk of a thermal runaway. LiFePO4 has lower energy density but longer life and better charging rates than LiCoCO2.

c. Lithium nickel manganese cobalt oxide (LiNiMnCoO2) – preferred for electric vehicles and within the maritime industry as its life cycle is long while the energy density is satisfying. It's strength is the combination of attributes of the constituents of nickel (with a high specific energy), cobalt (high specific energy) and manganese (doped in the layered structure to stabilize it).

d. Lithium manganese oxide (LiMn2O4) –LMO is a somewhat unique cathode chemistry, being a spinel structure, which provides significant benefit in terms of power capabilities offers high charging rates and thermal stability, at the cost of lower energy capacity compared to LiCoO2, and a reduced lifetime why it is not of interest to the maritime industry.

It's worth mentioning that other types of batteries, being presently subject for research, are considered to show significant promises to the marine industry market. The most auspicious of these batteries use a solid-state electrolyte, rather than the liquid which is used in conventional lithium ion batteries. The cathode and anode are the same materials which are used in other lithium-ion batteries. Using solid-state battery improves the packing efficiency of the cells whereas gives freedom ion design of battery geometry.
Although, the production cost is too high in today's market, solid state batteries are most promising technology for both increasing safety as electrolyte is non-flammable, specific energy and practical energy density in marine applications.

Battery concepts and terms

Batteries have been categorized by a set of parameters that reflect their performance.

C- and E-rates

C- and E-rates have been used in order to specify the rate of current and power discharge of a battery. C- rate of a li-ion can be measured by division of Power/Capacity. A 1C rate means that the discharge current will discharge the entire battery in 1 hour whereas 1 1E-rate is the discharge power to discharge the entire battery in 1 hour.

Battery Management System

BMS Battery Management System is the control system dedicated to the battery which monitors individual cell voltages and temperatures, and calculates aspects such as State of Charge, allowable power levels and also incorporates balancing functions between cells.

Stage Of Charge

SOC State of Charge is an indication of how much energy is available in a battery. Typically expressed as a percentage ranging from 0% when empty, to 100% when full.

Delta State of Charge

Delta State of Charge is an indication of the relative size of a battery cycle. For a given battery cycle, it would have been charged or discharged from one SOC level to another. DSOC is the difference in those SOC levels.

Components of Cells and Batteries

Considerable attention must be paid when selecting anode, cathode and electrolyte as well as monitoring over manufacturing process and usage of battery, in order to produce long lasting batteries. Overloading due to high currents has an adverse impact on battery lifetime due to lithium plating and increased temperatures. The desired range of battery temperature is usually from 20 to 30°C.

It seems that an expected lifetime of the batteries of 10 years currently is the marine industry standard, varying somewhat with type and charging profile. This implies that a midlife exchange of the battery pack must be expected if the vessel lifetime is 20 to 25 years. The battery discharge during a transport should not overcome the 80% of the capacity to ensure the battery life. Calendar ageing is affected by storage parameters, namely temperature and state of charge (SOC). Degradation during cycle aging depends on the operating parameters: temperature, state of charge (SOC), current amplitude and depth of discharge (DOD). For both calendar and cycle ageing, the ageing mechanisms are usually investigated by alternating electrochemical characterisation under reference conditions with storage conditions or cycling periods at predetermined conditions. Figure 10 shows the relationship between Capacity Fade and Equivalent Full Cycles (EFC) compared at:

(a) 20 C and 45 C for 1 C charge rate and 1 C discharge rate.

(b) different DOD for 1 C charge and 1 C discharge rate at 20 C.

(c) two different discharge rates cycled at 20 C for DOD of 50% and 100%.

(d) different mean SOC for 50% DOD and 1 C charge rate and 1 C discharge rate.

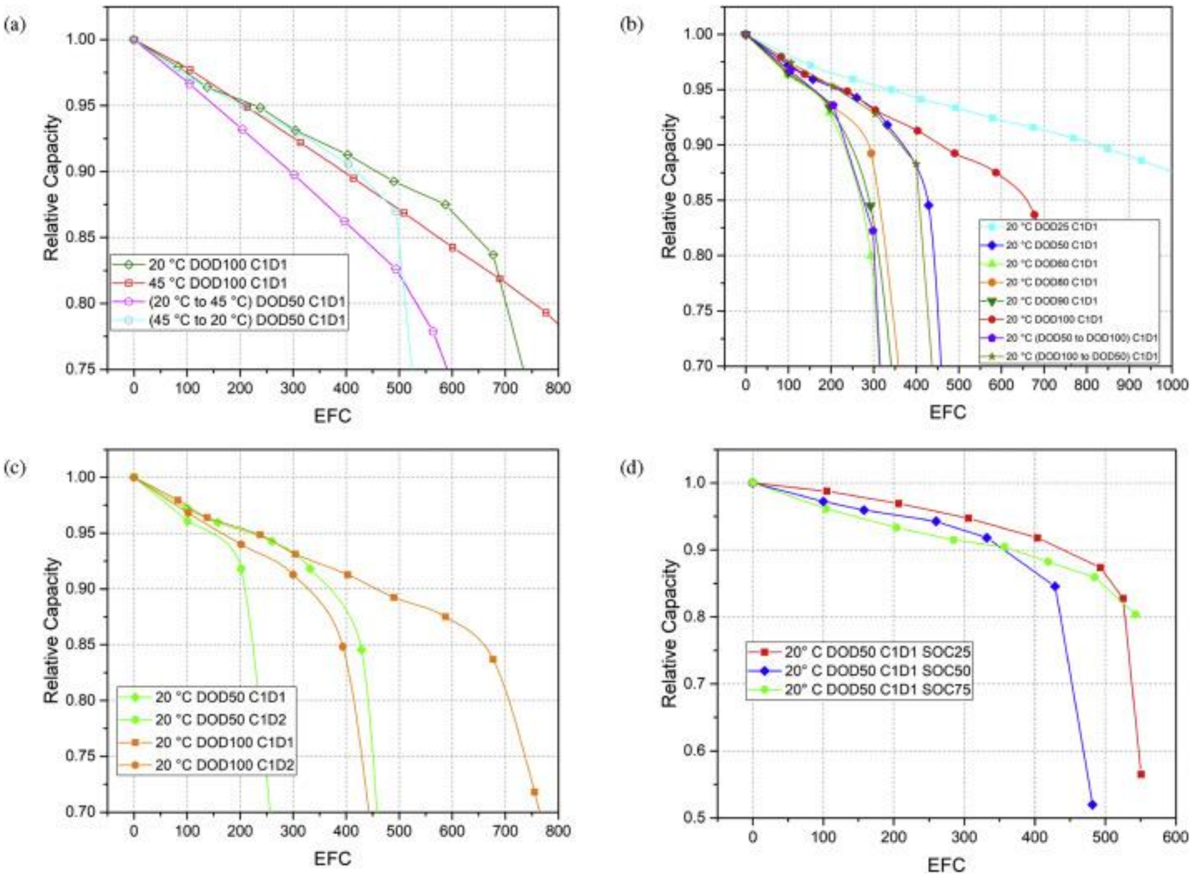


FIGURE 10: CAPACITY FADE VS. EFC TESTED FOR LITHIUM NICKEL MANGANESE COBALT OXIDE-BASED BATTERIES {38}

Battery Room

The main guidelines for the battery installation on vessels are imposed by regulations. First of all the battery must be installed in an enclosed space consisting of hull bulkheads or in a separate special compartment. Secondly, the battery compartment shall not be located forward of the collision bulkhead. In addition, battery compartment must not contain other systems related to the essential services of the ship. Pipes shall not enter the battery compartment, as leakage of the pipe may cause damage to the battery system. {9}

Full electrified vessels must at least consist of two separate independent systems, succeeding electrical supply for ship essential services and services for habitability necessary to provide normal operational conditions of propulsion in case of damage.

In the battery-electric system in Fig. 11, the propellers are connected to electric motors, which are driven by the energy stored in a battery system that is typically charged from shore. In some battery-electric systems, a smaller diesel generator is sometimes included to ensure operation if the batteries fail to charge or to enable longer voyages, i.e. when the vessel has to dock.

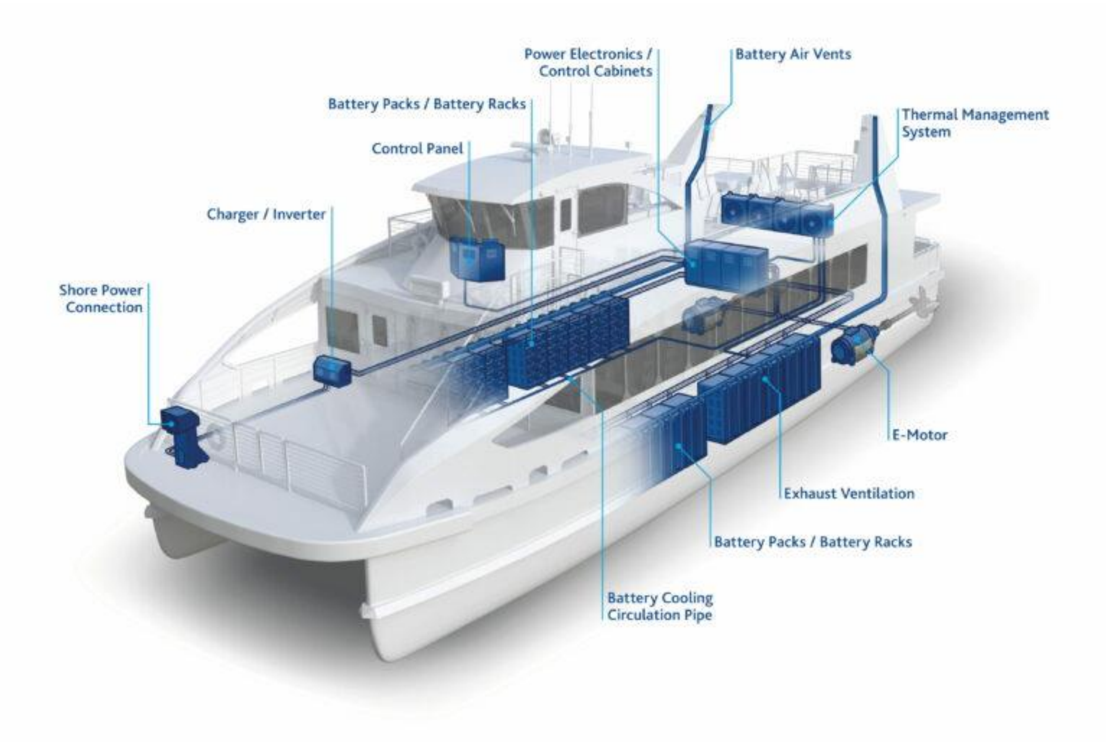


FIGURE 11: ALL-ELECTRIC FERRY DESIGN

The degradation of a lithium-ion battery is governed primarily by two factors: Temperature, and the nature of the cyclic loading of the battery. Parts and related materials used in the battery system shall be flame-retardant and moisture-resistant. Also, materials shall be of a material or coating that is corrosion-resistant to corrosion at the place of installation and at the environmental conditions of use. The conductive material shall be copper, copper alloy, stainless steel or equivalent, with sufficient electrical, thermal and mechanical safety. The battery room must be isolated so as a single failure in the battery system does not affect other systems in the ship.

Basic requirements for battery functionality consist of battery cell, battery module or battery pack and battery system. For each battery cell with a laminated composite metal foil when installed and used, a fixed support shall be provided externally to meet effective ventilation and other requirements. Furthermore, a battery module/battery pack is to be equipped with temperature regulating devices. Battery pack is equipped with a monitor controlling voltage and temperature of each module.

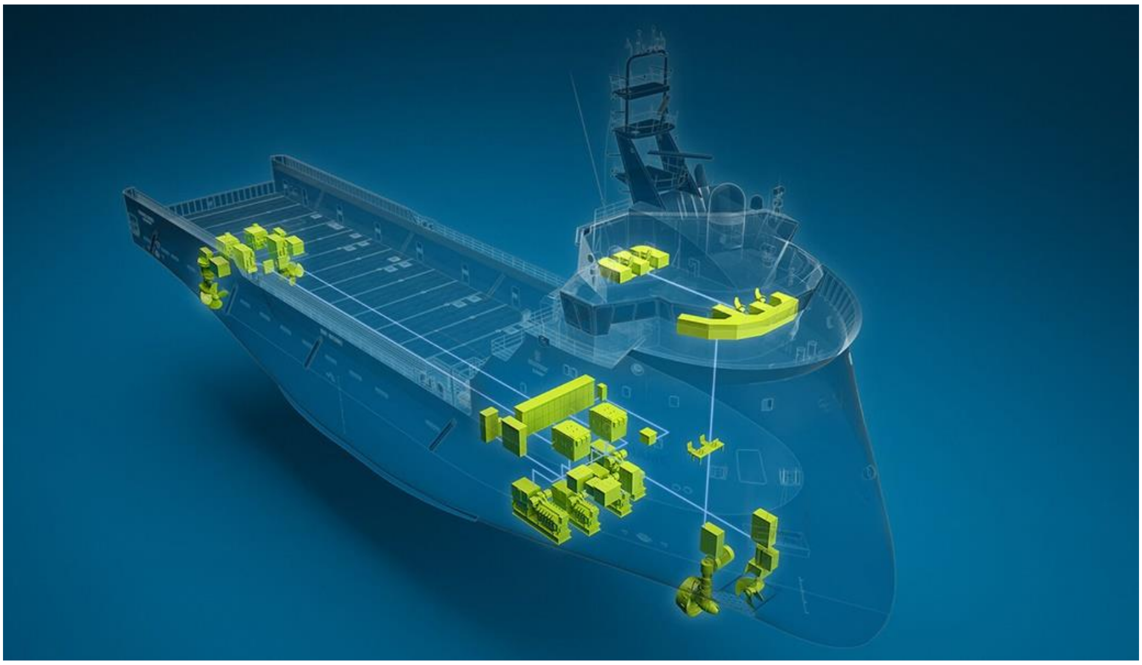


FIGURE 12: ON-BOARD BATTERY REPRESENTATION

Battery Master System

Battery Master System (BMS) is to be powered by another power supplier in order to monitor battery auspiciously. The system can measure and display system voltage, temperature, battery series loop current and system insulation resistance. Thus, it is to set the following visual and audible alarm locally and remotely, whenever the limits are outranged. Moreover, BMS should summarize the information from the battery control unit of battery box and feed the necessary information back to the corresponding management system of the ship and shall be subject to its management. Management system can be the power management system (PMS) or the energy management system (EMS) or the monitoring and alarm system (IAS). {10}

BMS is forced to take control of the following vitally important system functions:

1. Control the balance between battery cells and battery modules.
2. Control the charge, discharge, and charging / discharging equipment of the battery.
3. Overcurrent protection
4. Over the charge and discharge protection
5. Over heat protection
6. Fault protection of self-check function.

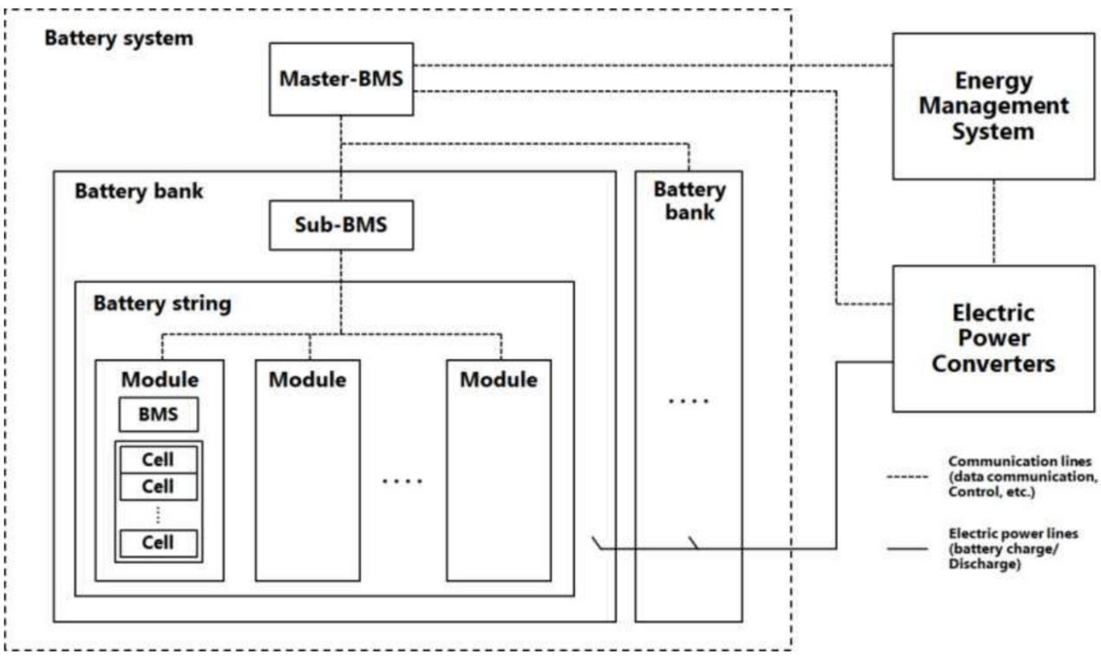


FIGURE 13: BATTERY PACK COMPONENTS

Shore-to-ship power

Port authorities are being forced to promote shore-based power charging systems that will allow ships to fully charge their installed Battery Energy Storage Systems (B.E.S.S.) systems while at anchor through an automatic, convenient, and quick connection at berth. Plug-In automatic charging system is expected to efficiently charge the vessel's power system at the dock. The connection to the vessel's charging cable socket is provided by a shore-based automatic charging system. The funnel of the plug-in socket can be mounted either on the side or aft of the vessel. For avoiding the challenges and limitations of mechanical connection systems for high-power battery charging in marine environments, marine industrial initiative has started the development of technology for contactless inductive power transfer to ships. The technology has already been demonstrated in laboratory environments at power levels exceeding 1 MW, and the first pilot has been installed on the Norwegian double-ended motorcar ferry, the MS Folgefonn since 2017.

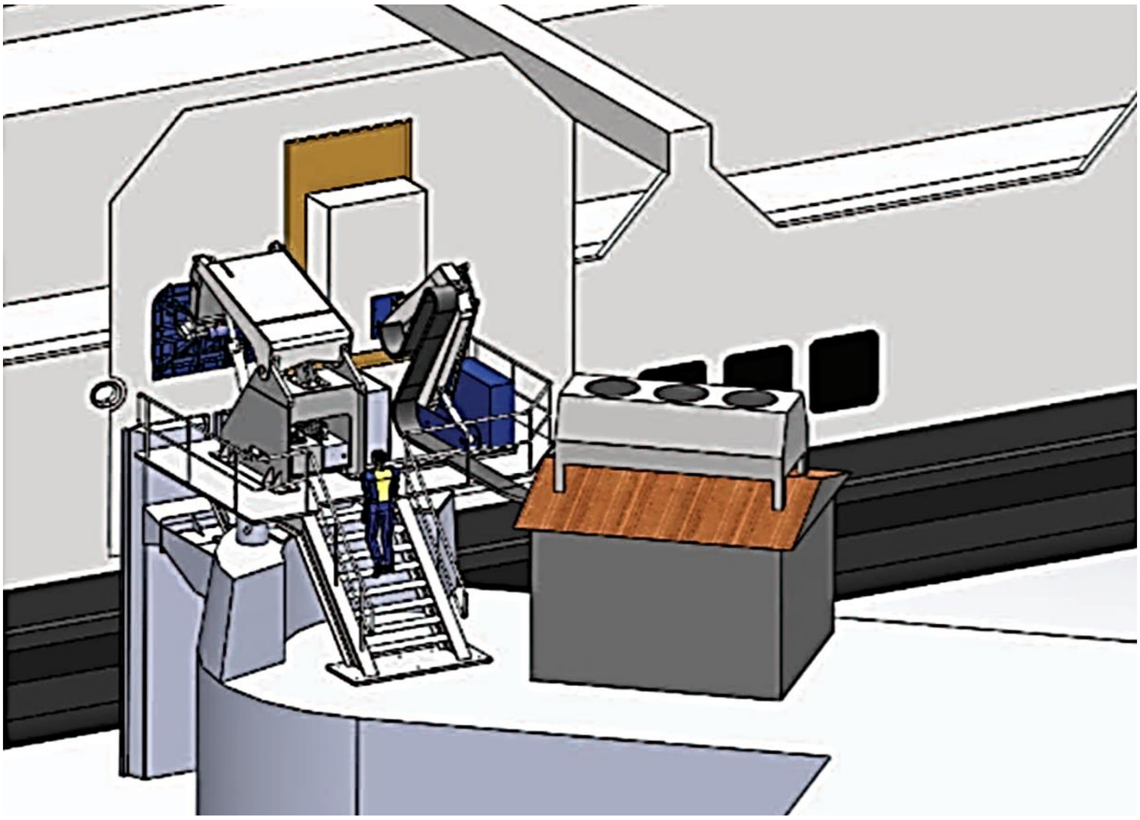


FIGURE 14: SCHEMATIC OF SHORE POWER SYSTEM

Battery System Costs

A system price of 500 USD/kWh, without operational margins, for a system to be implemented in a new building is considered to be the minimum level as of 2019. The price of 250 USD/kWh is included to illustrate if and how a significant drop in price would affect possible areas for marine battery applications.

Safety regulations must also be considered as new applications of battery technology are apt to be introduced into the marine economy. Safety concerns mainly come from two sources. From the one hand is the presence of flammable, unstable electrolyte, while on the other hand is the presence of metal electrodes that can burn and often release oxygen. There are two primary failure modes or impacts that can result from lithium-ion battery misuse: escalating thermal runaway and the release of toxic and flammable gases.

CHAPTER 3

III) Corrosion & Protection Against Corrosion For Ships

Definition of the corrosion problem

Deterioration as a result of corrosion is often accepted as an unavoidable fact of life. As a result, there has been a lack of awareness of the importance of economic aspects of corrosion. Many firms are unable to supply information for corrosion cost being hidden as general maintenance although surveys have estimated this cost scale from 1.5 to 5% of Gross National Product (statistics made in developed countries such as UK and USA). It is remarkable that the expenditure and potential savings as a percentage of total cost in marine industry is up to 20%. A recent survey of the cost of corrosion in the United States has estimated that some 5 percent of the total cost is attributable to stray current effects, mostly due to electrified transit systems. This percentage includes the damage to utility structures operated outside the direct activities of the transit authorities. In other parts of the world electrified rail systems can represent the dominant form of rail transportation for passengers and freight. Not surprisingly, major stray current corrosion problems have also been associated with these systems, again with serious economic implications.

The design priority must ensure that a functional and secure design will be suitably productive and be maintained at reasonable cost for the duration of the installation's life.

Electrochemical Nature of Aqueous Corrosion

As mentioned on the book of Deny a Jones {11} corrosion in salt water has been found to involve electron or charge transfer. The rate of corrosion reaction is related to a change in electrochemical potential or electrical activity or availability at the metal surface of the hull. The reaction which represents the corrosion between hull of the vessel and the aqueous solutions can be separated as follows:

1. Anodic reaction of iron: As iron Fe liberates electrons its valences increase from 0 to 2+.

   $$Fe \rightarrow Fe^{2+} + 2e^{-} \qquad (1)$$

2. Cathodic reaction of salt water: Liberating electrons migrate to the adjoining surface of the hull so as the following reaction takes place. Although dissolution of iron in water with hydrogen evolution is theoretically possible, corrosion of iron in salt water occurs with oxygen depolarization. {12} High Oxygen concentration ensures that the cathodic reaction is one of oxygen reduction. The reaction proceeds rather sluggishly under most circumstances and the accompanying production of hydroxide ions results in the reaction being rate-limiting corrosion reaction in seawater. Under certain circumstances like anaerobic or anoxic seawater or lower pH than normal, hydrogen-evolution cathodic reaction can replace oxygen reduction. This chemical reaction accelerates corrosion rates, hydrogen embrittlement and disbanding of protective coatings. {13}

   $$O2 + 2H2O + 4e- \rightarrow 4\ OH- \qquad (2)$$

The reversible potential of this reaction in a neutral solution in an atmosphere of air (i.e., at a partial oxygen pressure of 0.21 atm) is equal to 0.805 V. The agent (oxidizer) that is reduced on the cathode is defined in the existing corrosion terminology as the depolarizer of the cathodic process. Accordingly, a corrosion process at which a cathodic reaction takes place is termed corrosion with oxygen depolarization. {12}.

Thermodynamics gives us an understanding of the energy changes involved in corrosion. Without using the laws of thermodynamics, we are unable to predict the rate of corrosion. One should use kinetic laws in order to find out how fast or slow the corrosion takes place. The corrosion process involves simultaneous charge and mass transfer at the metal/solution interface. Faraday's law gives the analogy between the mass loss m, in grams, and the current I, in an upward reaction, as in the equation.

Pourbaix Diagrams

The potential/pH Pourbaix diagram represents conditions of solution oxidizing potential and pH for different phases which are stable in an aqueous system. Saltwater pH values within the range of 7.5 to 8.5. In addition, salt water carries the ions of the reaction and is called electrolyte. Seawater has low resistance values which normally ranges from 20 to 36 Ω cm. {13}.

Taking into consideration the Pourbaix diagrams of iron at 25° temperature, it is obvious that immunity phase is preferable in order to prevent the corrosion under seawater environment.

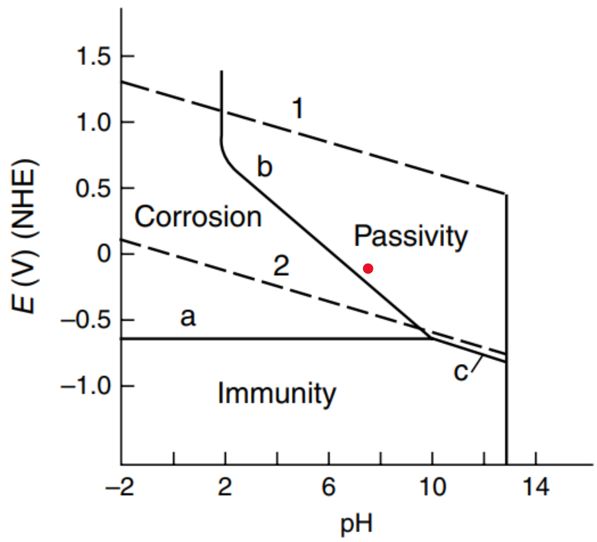


FIGURE 15: POURBAIX DIAGRAMS OF IRON AT 25O TEMPERATURE

Electrode Potential

Electric potential is essential to understand the electrochemical reactions of the corrosion. Iron is the basic chemical component of steel used in marine infrastructures. Potential Ea and Ec of each half cell electrochemical reaction (1) and(2) has been designated experimentally. The half-cell potential $E_{FE/FE2+}$ for anodic reaction of iron is equal to -0,44V versus the Standard Hydrogen Electrode. Reference electrodes such as Standard Hydrogen Electrode (SHE) or Saturated Calomel Electrode (SCE) can be used for this purpose. The potential values depend on the reference electrodes. Figure 14 shows the relative potential values depending on the reference electrode used.

For anodic polarization, electrons are removed from metal whereas for cathodic polarization electrons are supplied to the surface. The total rate of oxidation must be equal to the total rate of reduction.

According to the Nerst equation, the equilibrium potential Ea, is calculated by the mathematical formula:

$$E_\alpha = E_0 + \frac{0.059}{2} \cdot \log \quad \alpha_{fe2+}$$

Where α_{FE2+} is the thermodynamic concentration of the ferrous cation.

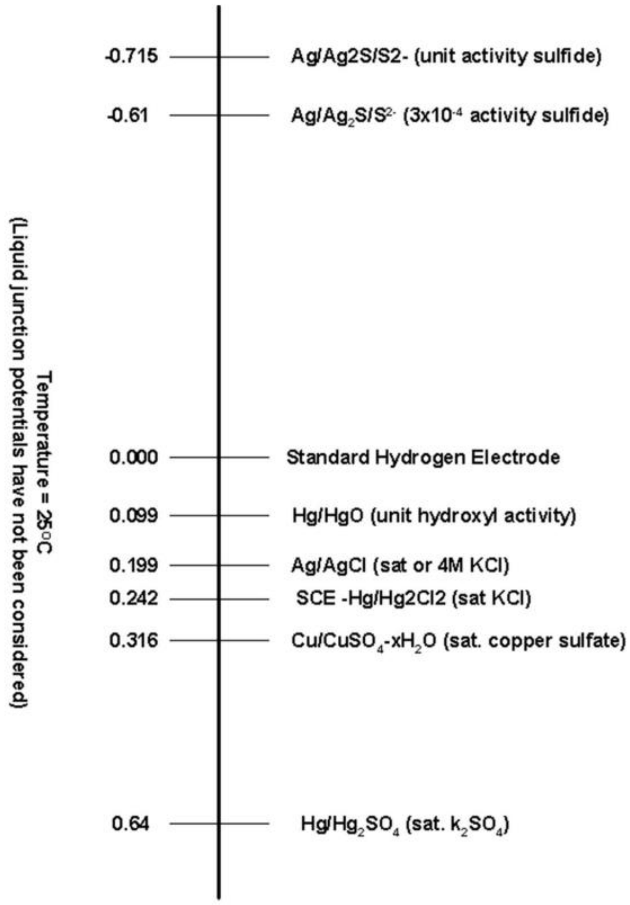


FIGURE 16: ELECTRODE POTENTIAL FOR A HALF-CELL REACTION OF REFERENCE ELECTRODES RELATED TO SHE

Mixed Potential Theory

In conditions of corrosion from the aquatic environment the potential of the steel reaches a steady state potential Ecorr. Corrosion Potential Ecorr is referred to as a mixed potential since it is a combination or mixture of the half-cell electrode potentials for reactions (1) and (2). As the surface potential increases due to the DC stray current for example, steel potential increases too. Considering Figure 13 one can ascertain that increased potential E, leads to at high rates of anodic reaction and corrosion. If the surface potential rises above a critical potential Ep, corrosion rate decreases due to passivity. Passivity is caused by formation of a thin protective corrosion product surface which acts like a barrier to the anodic dissolution reaction.

Faraday’s law

The corrosion rate does not depend on the potential difference between anode and cathode, but mostly on the corrosion current. The rate of electron flow, m, to or from a reacting interface, is a measure of the reaction rate.

$$m = \frac{I \cdot t \cdot \alpha}{nF}$$

where:

- I : the corrosion current. Electron flow is conveniently measured as current, I, in amperes(A)
- t : the time,
- α : the atomic weight of the anode metal,
- n : the number of electrons exchanged of the anode metal and
- F : the Faraday’s constant (96485.33289 Coulomb/mol, corresponds to the charge carried by one mole of electrons)

In addition, another useful physical quantity is the corrosion rate r. The equation indicates a proportionality between the mass loss per unit area per unit time (e.g. mg/dm2/day) and the current density (e.g. μA/cm2).

$$r = \frac{i \cdot \alpha}{nF}$$

where i, defined as current density.

The following table provides an overview of the ratio of corrosion rate and current density for mild steel in sea water.

TABLE 4 :CORROSION PARAMETER OF COATED AND UNCOATED MILD STEELS IMMERSED IN SEAWATER.

Sample	$-E_{corr}$ (mV)	i_{corr} (A cm^{-2})	Corrosion Rate, CR (mm/year)
Naked	650.1	2.06E–04	2.3991
0%	668.5	1.01E–04	1.1733
3%	657.3	5.71E–05	0.6633
6%	394.4	2.49E–05	0.2791
9%	561.0	3.75E–05	0.4361
12%	571.2	1.20E–04	1.3990

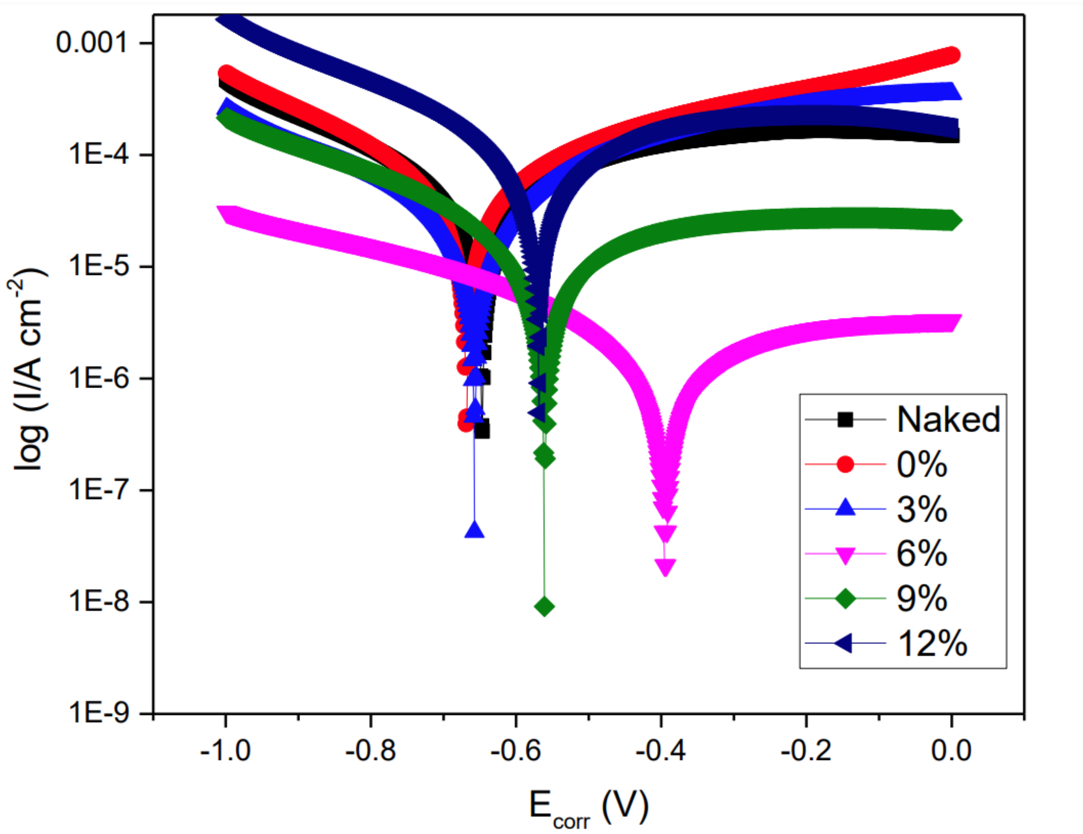


FIGURE 17: TAFEL PLOT FOR COATED AND UNCOATED MILD STEELS IMMERSED IN SEAWATER. THE POTENTIAL IS MEASURED VS SCE REFERENCE ELECTRODE (-242V)

Ship corrosion prevention

There are two principal methods of applying electrons to the surface, implementing cathodic protection: impressed current technique and use of sacrificial anodes. Moreover, coatings are usually used as a third part which separates the affected structure and the corrosive environment.

Cathodic Protection on ships

Cathodic protection has been used on ship hulls and tanks. Sea water used for ballast or other purposes corrodes the internal tank space. For this reason, anodes, like platinized titanium or lead-platinium, are supplied to vessels bulkhead. The first 'full hull' installation on a vessel in service was applied more than 200 years ago, when the frigate HMS Sumarung in 1824 had been Equipped with four groups of cast iron.

Corrosion of solar panels installed on vessels upper deck remains an open problem in the area. However, this subject could be analyzed in another chapter.

Impressed Current Cathodic Protection (ICCP)

Cathodic protection reduces the corrosion rate by cathodic polarization of a corroding metal surface. The circuit comprises the power source, an auxiliary or impressed current electrode, the corrosive solution, and the structure to be protected. More particularly, positive current, produced by the power supplier, drives from the impressed current anode through the corrosive saltwater solution and onto the protected hull. Finally, the current returns through the circuit to the power source.

The ICCP system reduces the rate of the anodic reaction with an excess of electrons which also increases the rate of oxygen reduction. Cathodic current polarizes the surface to more noble potentials that suppress the anodic dissolution rate. If additional electrons were introduced at the metal surface, the cathodic reaction would speed up to consume the electrons while the anodic reaction would be inhibited because of the high concentration of electrons. This is the basis of cathodic protection as it leads to lower rates of metal dissolution.

The low electrical resistivity of seawater enables greater cathodic/anodic surface area ratios to become active in corrosion processes, thereby promoting pitting mechanisms in vulnerable materials whereas it enables cathodic protection to be applied with relative ease.

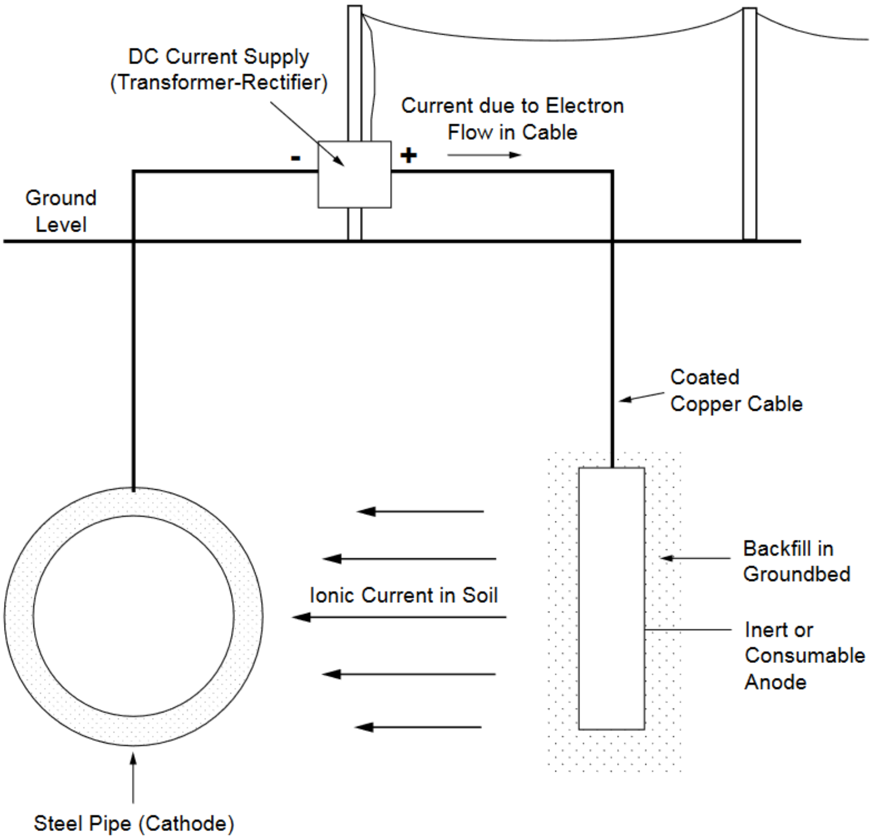


FIGURE 18: SCHEMATIC OF PRINCIPLE OF CATHODIC PROTECTION WITH IMPRESSED CURRENT

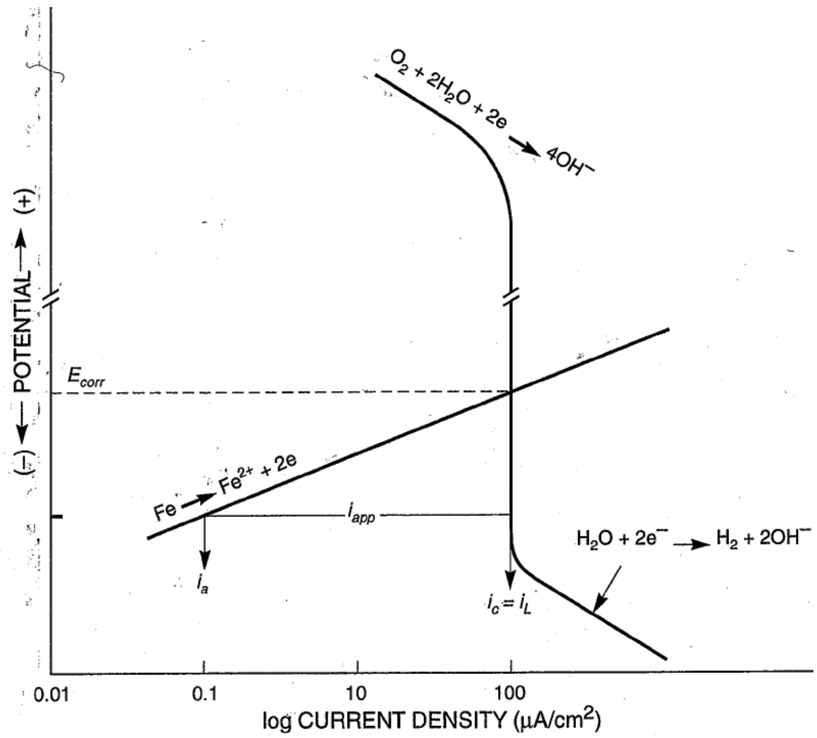


FIGURE 19: CATHODIC PROTECTION BY IMPRESSED CURRENT DENSITY FOR STELL IN NEUTRAL AERATED WATER

Figure 17 helps us understand the way corrosion rates can reach low values by use of ICCP. The unpolarized corrosion rate ic reduces to ia while ICCP apply current, iapp to the system current. More precisely, reduction of the potential Ecorr to a new value E', well known as cathodic polarization, causes the oxidation reaction taking place near point A. It may also be apparent that, if the potential is maintained below E' the metal dissolution rate remains zero, but a cathodic current greater than I:must be supplied; more current is supplied without achieving a benefit in terms of metal loss. In fact, if the applied current leads to a potential lower than E', entails a substantial increase in current of corrosion and significantly more hydrogen evolution. In conclusion, the basic principle of the ICCP system is to provide more negative potential, so that the metal will move into the immune zone.

Tafel equations and cathodic protection

The actual values of the diagram can be measured by Tafel equations. The cathodic protection applied after localized corrosion initiation requires polarizations enough to reach the immunity potential E', which is typically 200-300 mV lower than the pitting potential {14}.
In addition, Tafel constants βa give us the exact values of the decrease. A potential reduction near value of βa decreases corrosion rate by factor of 10. Neutral aerated seawater controls the corrosion due to the diffusion of dissolved oxygen to the corroding surface of hull. Oxygen is not very soluble in aqueous solutions(10 ppm in cool seawater). As follows the cathodic reaction rate is then controlled by the rate of arrival of oxygen at the surface. This matter of fact is often referred to as mass transfer control.

The anodic reaction of steel represented at figure 17 by a straight line with positive inclination. Tafel equation of steel is as follows.

$$n_\alpha = \beta_\alpha \cdot \log \frac{\iota_\alpha}{\iota\beta}$$

Total cathodic polarization of seawater environment, $n\mathbf{T,c}$, is the sum of activation and concentration polarization:

$$\mathrm{n}\mathbf{T,c} = \boldsymbol{\beta}\mathbf{c}\ \mathbf{log}\ \frac{ic}{i_0} + \frac{2.3\ \mathrm{RtT}}{\mathrm{nF}}\ \mathbf{log}[\mathbf{1} - \frac{ic}{i_l}]$$

where:

- n : the number of electrons exchanged of the anode metal and
- F : the Faraday's constant (96485.33289 Coulomb/mol, corresponds to the charge carried by one mole of electrons)

Design of ICCP

The ICCP system is divided into zones which consist of a group of anodes, controlling reference cells and associated controller/power supplies. However, hull is the common ground point so each system can influence the operation of the other{15}. The first zone, composed of the reference cells, is usually placed nearby those areas which require cathodic protection due to their location on the hull surface.

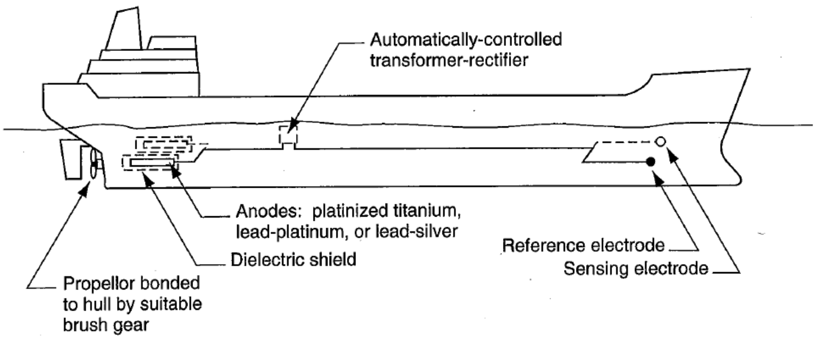


FIGURE 20: DESIGN OF IMPRESSED CURRENT CATHODIC PROTECTION SYSTEM FITTED ON SHIP

Protection Criteria

Cathodic protection system should abide by regulations which specify the desired values of potential and the current density that is applied. In particular, excess of current can cause hydrogen embrittlement or disbonding of coatings, while corrosion rates can be increased if the ICCP supplies too little current.

The following list of protection criteria have been proposed for steel used on marine offshore pipelines and ships:

1. 850 mV vs. Cu/CuSO4 NACE Standard RP0675-75. If Ag/AgCl/seawater is used as reference electrode the protection potential for iron is 800Mv.{13}

2. Minimum negative 300-mV shift under application of CP NACE Standard RP0675-75

3. Minimum positive 100-mV shift when depolarizing (after CP current switched off). This shift criterion may be useful for preventing overprotection.

Many research and experimental measurements indicate that in clean aerated sea water at approximately 25 °C, full cathodic protection is achieved at steel/sea water interface potentials more negative than -0.80 V with respect to a silver/silver chloride Ag/AgCl reference electrode. This is the generally accepted figure although values from -0.78 to -0.91 V (wrt Ag/AgCl) are found in the literature, the most negative being in polluted water.

According to DNV(Det Norske Veritas)-Recommended practice DNV-RP-8401, a potential of -0.8V relative to Ag/AgCl reference electrode is generally accepted as a design protective potential for carbon and alloy steels.

In addition, Lloyd's Register mentions that the cathodic protection system must be able of polarising the steel structure within the range of -0.8 to -1.2 V for open seawater conditions wih respect to Ag/AgCl reference electrode. Potential more negative than -1.2V should be avoided due to the disbonding of the coatings.

Material selection

There are three types of anodes that are used in ICCP: consumable,semi-consumable and non-consumable. While metal used as anodes dissolves its electrical resistance increases as oxidized metal is deposited to the surface. That is the major reason why consumable anodes must be replaced. Anodes used in ICCP: platinized titanium, lead-platinum lead silver.

Protective current requirements

According to Deny A Jones for moving seawater environment, the estimated current density requirement for Cathodic Protection, ranges from 0.03mA/m^2 to 0.15mA/m^2{11}.

In seawater, for example, an initial current in the region of 200 mA/m^2 for bare steel might well be required in the North Sea.{13}

A recent review on the field of cathodic protection of a container Ship using Boundary element method (BEM) identified the need for modern ship protection parameters. A recent review in the field of cathodic protection of a container ship using the Boundary Element Method (BEM) identified the need for modern ship protection parameters. According to the report, the water surface of the hull, which was estimated at 35,000m2 , was supplied with a total current of 2520A. The calculation of the required current density gave an approximate 72mA/m2. It is noteworthy that the current density demand for bare unprotected steel is estimated at 180mA/m2, whereas for coated structures the mitigation of current requirements ranges from 3.5% (6.3mA/m2) to 15% (27.2mA). In addition, as mentioned above, increased damage to the surfaces of the rudders and thrusters due to a high degree of turbulence is considered. Consequently, anodes have been installed near corrosion prone areas to minimize corrosion potential and corrosion rate. {16}

Factors Affecting Cathodic Protection

The major factors that must be considered in protecting a hull from corrosion are:

1. The nominal wetted surface area which requires protection.

2. The material characteristics of metallic components exposed to the seawater.

3. The chemical aspects of the bulk electrolyte (seawater) under operational
conditions, such as, seawater conductivity, pH, dissolved oxygen and surface reactions.

Care must be exercised in the use of dissimilar metals in contact or in close proximity in order to prevent galvanic corrosion taking place. These metals should be placed so far as is practicable or they must be separated by a middle piece with a suitable potential to deter the creation of a galvanic cell.

ICCP Failures

Cathodic protection does not come without problems. The main problem of ICCP is the geometric complex of the ship hull. Different points on the surface have also different potential due to their distance from the nearest anode.

Most of the time, failure of ICCP tools, appears when steel potential indicator and rectifier indicator does not calculate the desirable numerical value of the potential. Due to incorrect measurement the potential will be set to a new value, different from the actual needed for cathodic protection. For the reason that the problem of ICCP provoke erroneous, should be overcome, in order to control the corrosion, even in cases where DC currents attack the ship's hull.{17}

The power source is usually a rectifier which converts A.C to D.C. The typical values of the transformer output range from 15-100V and 5-100A.{13}.

Problem solutions

To minimize this fundamental error, it has become customary to conduct so-called instant OFF potential readings, mainly in the case of impressed current cathodic protection systems. On the practical level, in systems involving numerous buried sacrificial anodes such readings are usually not possible. In this approach, the impressed CP current is interrupted briefly to theoretically provide a "true" pipe-to-soil potential reading. This momentary interruption of current theoretically produces a reading free from undesirable IR drop effects.

Sacrificial Anode Passive System (SACP)

The sacrificial anode technique uses the natural potential difference that exists between the structure and a second metal which is exploited as an anode in the same environment to provide the driving voltage. As a matter of course, sacrificial anodes must be naturally more active than the protected metal surface. That means, their potential is more negative as measured by reference electrode. Also, anodes should be inexpensive and durable. Furthermore, over its lifetime, an anode must consistently have a high capacity to deliver electric current per unit mass of material consumed.

Material Selection

Marine industries mainly use magnesium, aluminum, or zinc as sacrificial anodes. Bow and stern coating problems have been empirically proved. Galvanic couples such as propeller, shaft, and hull corrosion. These locations are usually filled with small anodes in order to overcome this problem. Hydrogen embrittlement of steel due to cathodic protection is sometimes a concern. {18}

TABLE 5 :TYPICAL DESIGN CURRENT DENSITIES

Situation m/s (knots)	*Design Current Densities for Bare Steel mA/m² (mA/ft²)*	*Design Current Densities for Coated Steel mA/m² (mA/ft²)*
$V \leq 1$ (2 knots)	100-200 (9.3-18.6) without tidal influence 150-250 (13.9-23.2) with tidal influence	5-15 (0.5-1.4) 7-20 (0.7-1.9)
$1 < V < 10$ (20 knots)	220-350 (20.4-32.5)	11-28 (1.0-2.6)
$V \geq 10$ (20 knots)	350-500 (32.5-46.5)	18-40 (1.7-3.7)
Vessels in ice	500-750 (46.5-69.7)	35-90 (3.3-8.4)
Propeller surface	≥ 500 (46.5)	

ICCP vs SACP

The main advantages of Sacrificial anode method are its low cost, less supervision required, unlikely cathodic interference in other structures, simple installation and no overprotection occur. On the other hand, large structures like ships need many anodes due to their exposed surface. The total weight has increased. In addition, the driving voltages that are supplied from sacrificial are up to 1V while power source in ICCP can produce 100V.

Coatings

Ships have protective coatings as their primary means of corrosion control. The basic concept is not usually electrochemical in nature, it is simply to insulate the arrow from the corrosive environment. Different types of pf coatings are available, the most common of which are paints although metal coatings, plastics, waxes and greases. Factors such as, the total environmental conditions, the quality of the initial protection on new structures, the design and purpose of the structure should be taken into account for proper maintenance of protect over a period of time.

There is an overall benefit in using a good coating reinforced by cathodic protection. Actually, coating provides a major part of protection whereas ICCP remedies the coating defects. The joint exploitation of these technologies would minimize the cost of protecting a structure.

Design considerations should be made for high performance of marine coating. Coatings should be applied to surfaces under the optimal possible environmental conditions where humidity and other application circumstances can be monitored. Furthermore, coatings should only be applied when the vessel hull or the protected surface is fully and correctly prepared.

Delamination of a Coating from a Ship's Hull

The underwater hull is protected by cathodic protection fitted to ships in conjunction with a high-quality compatible paint system. Locations where painting coatings have been disponed are attacked by corrosion which spreads quickly. In addition, Hull fouling reduces vessels speed, increases fuel costs and imposes time and costs for hull maintenance. The use of biocide based antifouling paints are the most economical technique to control hull fouling.

Classification of corrosion protection methods

Among three methods of protection against corrosion, cathodic protection is the most eligible. ICCP system is a dynamic procedure, during which it is taken feedback through seawater environment and respond to modifications at potential of the surface. With this in mind this method is highly direct and effective. While a ship is in motion, increased oxygen concentration leads to higher amount of current density demand. According to Lucas, the dynamic state may increase the current demand by 3-5 times with respect to the static state. {19}. In particular, at the report of 'T. Bellezze, R. Fratesi, G. Roventi', the functionality of ICCP, in conditions of sine wave of potential and stray current due to floating water, has been proved.{20}.

CHAPTER 4

IV. Battery vessels – corrosion- protection issues

DC Stray Current

The aim is to investigate the localized places of the hull which have low resistance and the circuit paths through which leakage stray currents returns to the negative pole of the hull. The detection of these specific paths, and the installation of anodes and reference electrodes close to them, will yield the mitigation of corrosion, because using reliable measurements, ICCP system could modify the protection potential.

Stray currents are caused by sources of current flowing through unintended paths. At the point where the current enters the immersed structure the potential will be lowered, and electrical protection will occur. At points where the stray current leaves the path creating an electrical circuit, it can cause accelerated corrosion in the local area. The corrosion rate is increasing rapidly as a result of reduction in the value of the electrical potential nearby the affected structure.

Anodic current attack leads to pitting corrosion development, and hydrogen embrittlement of these steels is probable under cathodic protection – especially in zones of welded seams and thermal influence. At the stage of design of the cathodic protection it is necessary to consider data about the presence of stray currents.

Leakage current can be defined as the current lost at its source and penetrating a low resistance parallel circuit.

Effects of DC stray currents

It is known that stray currents affect infrastructures by accelerating the rate of corrosion. More specifically, corrosion rate of X80 Steel in a Near-Neutral Environment is more than ten times higher when there is a current iDC=0.25 mA/cm2. Due to the DC stray current the potential E of the Steel increases. This fact causes the anodic reaction of steel to take place at greater frequency. Also, as DC stray currents apply to the hull the resistance value sharply decreases. The corrosion rate of steel with applied DC currents is much greater than that occurred by AC currents. Moreover, stray currents produced by DC electrical source cause pitting corrosion to the surface which is exposed.{21}

Attack of external anodic current on actively corroding metal surface

When DC stray current of the anodic direction is impressed on the hull, the stream of electrons is directed from the metal surface to an external circuit. Taking into concern Faraday's law, positively charged metal ions produced by ion dissolving are equal to the strength of the anodic current. As anodic current rises, positive polarization of metal takes place, so the oxidation reaction (1) is moving to right. The potential of the metal surface can be measured by the following equation . It should be noted that, in a DC system, the current loss is by direct leakage.

$$E = E_{cor_r} + (a + b\log \mathrm{i}).$$

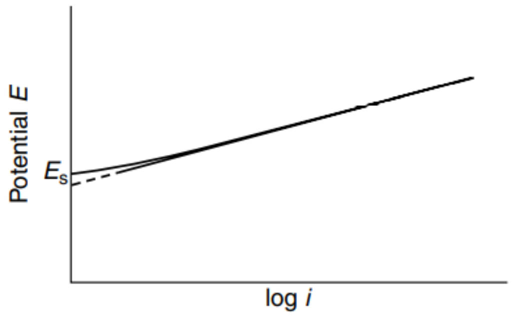


FIGURE 21: TAFEL PLOT OF ANODIC POLARIZATION DUE TO DC STRAY CURRENTS

Other occasions of DC stray current

Common sources of stray currents are cathodic protection on other lines, DC transit systems and telluric activity. A vessel can undergo corrosion by stray currents also during welding work when the positive pole is connected to the vessel and its negative pole to the welding rod. The corrosion rate of underground and underwater constructions in the areas of alternating current (a.c.) attack is usually lower than that in the areas of direct current (d.c.). Additionally, shaft voltages and resulting bearing currents must also be observed as the corrosion which is increased by these stray currents may damage the propulsion system of the ship. {22}

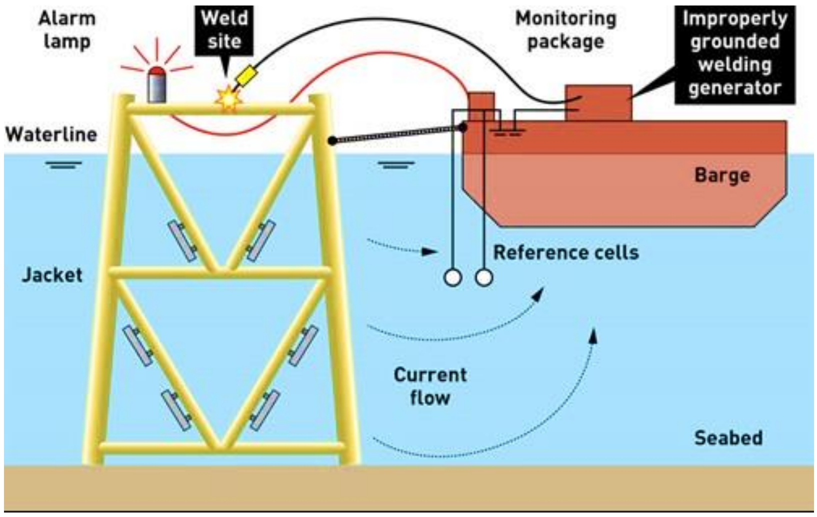


FIGURE 22: STRAY CURRENT CORROSION DURING MARINE WELDING OPERATIONS

The effects of anode distance and on current and potential distribution for ICCP systems

One underlying factor that affects the current distribution is the distance between the cathode and anode. The realistic problem that confronts mechanics is overprotection of places nearby anodes while at the same time surfaces of hull are under hazard due to low potential. High current density concentrates on paths of low resistivity that are usually the closest to the anodes. This stems from the fact that longer distance increases resistance to current flow. Research has proven that potential is increasing while current is lessening according to distance by the factor of exp. Furthermore, attention should be paid to the presence of defects in the protective coating.

$$Ex = E_0 \cdot \exp(-ax)$$

$$Ix = I_0 \cdot \exp(-ax)$$

$$\alpha = \frac{R_s}{Rx}$$

$$R_A = \sqrt{R_S R_L}$$

where RS is the ohmic resistance of the structure per unit length.

RL is known as the leakage resistance and refers to the total resistance of the structure-electrolyte interface, including the ohmic resistance of any applied surface coating. . The higher the integrity of the coating, the higher RL will be.

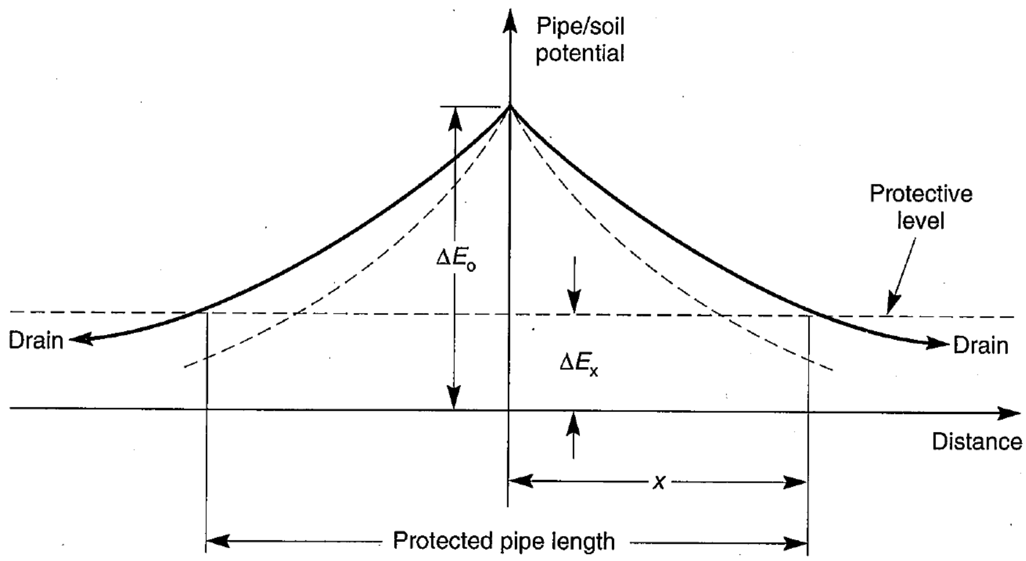


FIGURE 23: RANGE OF CORROSION PROTECTION

What Affects Problem Solving

The major factors that must be determined to provide a solution to DC stray current corrosion are as follows:

1. The source of the DC stray current affecting the structure. In the scope of this thesis, it is apparent that stray currents are supplied by the batteries propulsion system, ICCP power supplies and solar panels which may be installed on the upper deck of the vessel.

2. The localized place where the stray currents leave the hull-structure. These places are susceptible to attack by pitting corrosion.

3. The voltage and amount of current at the exit point.

Stray Current Detection

ICCP test

A common method used, in order to determine current requirements in existing systems, is current drain testing. In these tests, a CP current is injected into the structure with a temporary dc power source which supplies up to 10 A of current. Potential loggers that have been installed at selected test locations are used to monitor the potential response to the injected current. The recorded relationship between potential and current specifies the exact value of the current which is essential for hull protection. These tests usually only require a few minutes of time.

Stray Current due to Cathodic Protection

Stray currents can come from both manmade and natural sources and can produce static or dynamic stray currents. Static stray currents from foreign cathodic protection sources can be detected by interrupting the cathodic protection source and performing CIPS on the affected area. It is important to detect the area and magnitude of the stray currents and identify the source. Stationary loggers are used to detect any fluctuations in pipe to soil potential over time. One way to detect stray currents is to place stationary data logger at multiple points of the structure.

Considering IR Drop

Close Interval Potential Surveys (CIPS) are widely used to monitor the level of cathodic protection. The aim of the survey is to measure the instant off potential, which minimizes any effect from the other resistances in the circuit. The potential difference between the on-mode and the instant off is called the IR drop. The measured dynamic stray currents appear on both on and off modes.

CIPS is accomplished with two types of survey gear, current interrupters, and a specialized mobile data logger. Global Positioning System (GPS) is essential for synchronization between the current interrupter,CIPS survey instrument and stationary logger. Through using the GPS synchronized data from CIPS and the logger, the CIPS data can be corrected by removing the dynamic stray current effects. This gives a more accurate potential reading as it removes the influence by external interference.

Electrochemical Impedance Spectroscopy method

The electrochemical impedance spectroscopy, EIS, is a technique for the analysis of the response of corroding electrodes to small amplitude alternating potential signals of widely varying frequency. The EIS technique uses a typical three-electrode cell system controlled by a potentiostat with a Frequency Response Analyzer (FRA). In the EIS approach, by applying a small varying perturbation over a range of frequencies, it is possible to investigate the full response of the electrochemical system.

When a sinusoidal AC signal V(t) is applied to an electrode surface, the time-dependent current response I(t) is expressed by an angularly dependent impedance Z(ω) in accordance with Ohm's law.

$$Z(\omega) = \frac{V(t)}{I(t)}$$

Where t is measured is seconds and θ is the phase angle between V and I.

$$V(t) = V_0 \cdot \sin(\omega t)$$

$$I(t) = I_0 \cdot \sin(\omega t + \theta)$$

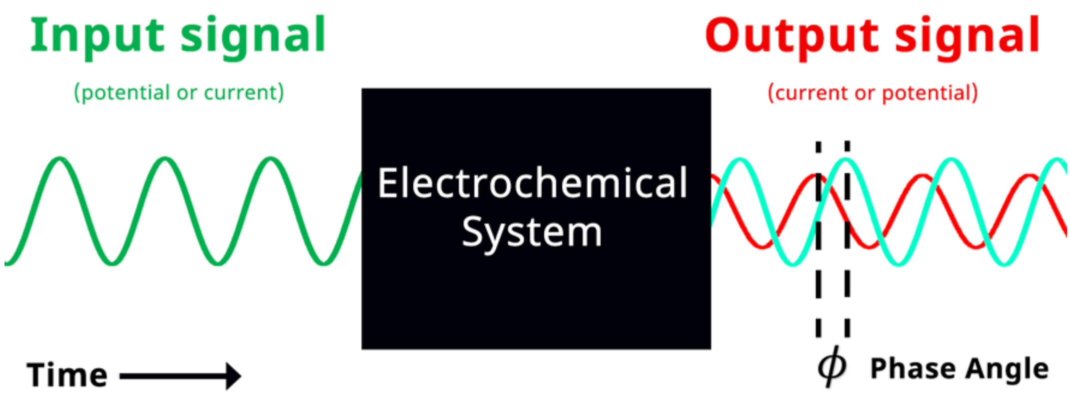


FIGURE 24: COMPARING THE APPLIED VOLTAGE (TIME) AND THE RESULTANT CURRENT (TIME) FUNCTIONS TO DETERMINE THE PHASE SHIFT (Θ) AND ABSOLUTE IMPEDANCE ([Z]) OF THE SYSTEM

The impedance Z(ω) may be expressed in terms of real and imaginary components and by obviating the dependency on the frequency, ω, that is:

$$Z = Re(Z) + Im(Z)$$

where Re(Z) and Im(Z) are the real and the imaginary components, respectively, of the impedance Z, expressed in Ohm.

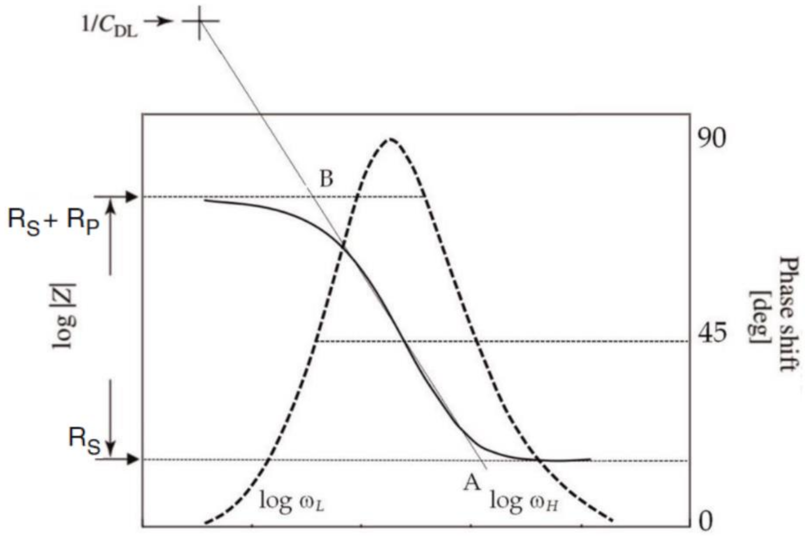


FIGURE 25: BODE PLOTS, WHICH CAN COMPARE THE ABSOLUTE IMPEDANCE OR THE PHASE SHIFT VERSUS FREQUENCY

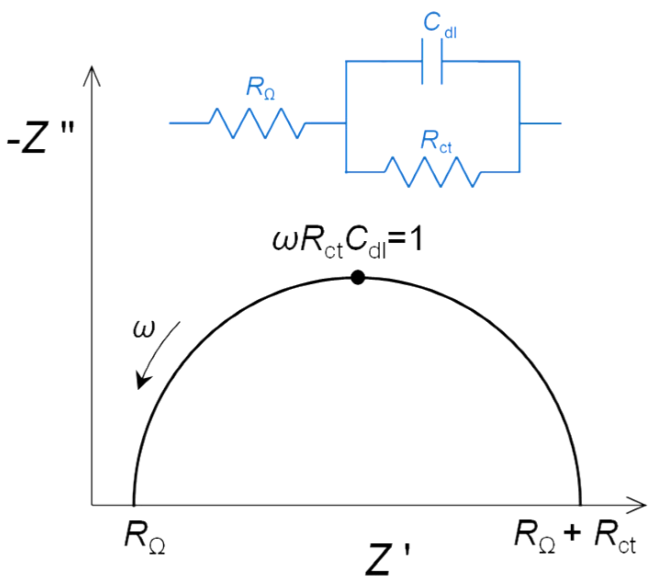


FIGURE 26: NYQUIST PLOTS, WHICH COMPARE THE REAL (ZRE) AND IMAGINARY (ZIM) COMPONENTS OF THE RESULTING IMPEDANCE.

Cathodic Protection Interaction

Cathodic protection might also have serious consequences that aggravate corrosion problem. Stray currents can be supplied from the rectifier into the electrolyte and traverse nearby immersed structures that are not being cathodically protected. Onto the field of vessel ICCP system, secondary structures subjected to interaction may be hulls of adjacent ships, unbonded parts of ship’s hull like propeller blades, pipes or cables laid close to the primary structure or to the cathodic protection anode system or ground bend.

The amount of interaction caused by a protection scheme using galvanic anodes will be much less than that involved in the case of impressed-current protection, because of the low current output obtained from each anode. The severity of corrosion interaction will depend on the density of the stray current discharged at any point on the secondary structure. Potential tests should be concentrated on the parts of the stern, such as the propeller and shaft, which are close to the structure to be cathodically protected, where the potential change is likely to be more positive.

Interaction tests shall be carried out on all unprotected structures around a proposed cathodic protection installation and shall be repeated annually or at some other appropriate interval to ensure that changes in the layout of the installation or electrical conditions are considered. It is most convenient if tests on all unprotected conduits or cables are carried out simultaneously, with the potential measurements being synchronized by GPS with the regular switching on and off the protective current. Then it is appropriate to continue further testing to confirm that any corrective measures applied to one installation do not adversely affect other installations.

Studies on DC Stray Current

The study shows that in conditions simulating the corrosion of mild steel buried in soil the logarithm of the anode current density is related approximately rectilinearly to anode potential. As an example, for a ten-fold increase of current density in the range lo-’ to 10^{-4}A/cm^2 , the increase of potential is between 40 and 65 mV in most conditions. Thus, a positive potential change of 20mV produces a two- to three-fold increase in corrosion rate in the various electrolyte and soil solutions used for the experiments. The adoption of a maximum permissible positive potential change of 20mV is based on theoretical and laboratory studies.

Problem Solving and Process Improvement

In the UK the most common method of reducing interaction is to connect the protected and unprotected structures together by means of metallic bonds. This method is more successful if care has been taken to ensure that the unprotected structure is electrically continuous. Furthermore, if the positive potential changes are very small and confined to a few points on a small, unprotected structure, it may be practicable to reduce the potential at these points by installing reactive anodes. Sacrificial anodes can be installed at the current discharged areas where risk of corrosion is high. Anodes have been used so that the current is being discharged from them rather than from the interfering structure.

DC stray currents due to operation of Batteries

High levels of electrical power are required, during the recharging of batteries via the shore supply system, and throughout maneuvering of the vessel, at the time of departing the port. DC Current reaches high values of approximately 10^3 A. Research on DC stray current corrosion measures the leakage current to be 10^{-6} times lower than the current source. The impact of leakage current value of 10^{-3} A, begets transitions to the electrical potential, capable of increasing the rate of ship's hull corrosion. To our knowledge, no study has considered the problem of corrosion, due to DC stray currents on battery ships. This lack of knowledge, as a consequence of the short time of investment on battery vessels, generated some difficulties with the specification of the real-time parameters of the problem.

ICCP system on battery vessels

To rectify the problem of the hull corrosion, battery ships have been produced, thus far, encompassing the ICCP system. As a first step, reference electrodes that have been already installed for Cathodic protection, may be capitalized for measurements of the potential of the surface. More particularly, the measurements must be carried out in the absence of supplied current by the rectifier, in order to determine the existence and impact of leakage currents from the battery source. Utilization of this knowledge aims at two major objectives. Firstly, we should be able to predict the rate of the corrosion taking into consideration the potential of the hull. Secondly, this must be an extremely useful concept to determine current requirements in existing systems. Once the extent of the stray currents has been identified, mitigation strategies may be necessary to protect the pipeline.

In recent years there has been growing interest in the use of ICCP system also on smaller vessels. To our knowledge Delivery of cathodic protection systems for three identical hybrid plug-in roll-on / roll-off (RoPax) passenger ferries to be built at Sembcorp Marine in Singapore. A well-known green ferry called Sembcorp, which has a 82.4-metre long multi-deck service speed of 10 knots is provided by cathodic protection.

TABLE 6: MF DRAGSVIK GENERAL CHARACTERISTICS

Name	MF Dragsvik
Segment	Cruise and Ferry
Vessel size	84,2 m
Passenger capacity	300
Car capacity	80
Gross tonnage	2476
Deadweight tonnage	441
Ship system	All-electric
ESS capacity	1582 kWh

FIGURE 27: MF DRAGSVIK-ONE OF THREE IDENTICAL ALL-ELECTRIC FERRIES OPERATED AND OWNED BY NORLED.

Marine environment

There are three main vessel-structural corrosion design zones in the marine environment: immersed, splash and atmosphere. The most dangerous environment is splash zone. This is due to the high oxygen and chloride content of the recurrent splashing of seawater, which destroys any protective film that might be formed on the steel surface. Splash zone affects areas over the water line.

TABLE 7: AREAS OF CORROSION IN A MARINE ENVIRONMENT

Environment Zones	*Corrosion Rate (mm/year)*
Buried zone	*0.1*
Underwater zone	*0.2*
Intermediate zone	*0.25*
Splash Zone	*0.4*

Solar Panels on-board and Corrosion

Solar Marine Power

Marine solar power systems can be installed on large ships such as car carriers, bulkers, passenger ferries and oil tankers plus on smaller ships such as commuter ferries, river boats and recreational vessels. Solar power is one of the great solutions to reduce the fuel cost and has less impact on environmental health. The on-board solar system plays an important role in reducing energy waste and maximizing energy production. This can be done with the system working with some devices that can monitor the intensity of ambient light for maximum solar energy harvesting process. The solar energy is collected through the solar collector and then stored in a battery that can occupy a large capacity of electricity for a long period of use and perhaps to replace or work with the diesel engine.

Factors Affecting Marine PV

Solar Panels installed over the vessel's deck are exposed to the ocean atmoshphere which with high salinity and humidity. These enviroment occurs high level of corrosion as salt spray and seawater are attached to the solar panel surface. {23, 24}. In addition, the salt water that covers the surface evaporates, thus minimizing radiation while salt settles on the surface similar to dust. A recent review of the literature on this topic found that a power reduction of 10% may affect the PV module due to parameters of the seawater enviroment.

FIGURE 28: MS TÛRANOR PLANETSOLAR, THE LARGEST SOLAR-POWERED BOAT IN THE WORLD

Great attention should be paid to the existence of stray current corrosion blind spots inherent in the grounding of PV systems and the associated DC ground fault detection mechanisms. The leakage current can cause accelerated corrosion in the PV support metal structures as well as in third party steel utilities that may exist near the PV installations. Leakage currents in solar panel systems arise as a result of fault or from the systematic and unavoidable flow of direct current (DC) through non-ideal materials of cables and poor insulation, PV modules and other array components. Two accidents of fire due to certain escape currents PV istallations have raised awareness of existed "blind spots" where stray currents leave the electrical wiring installation to enter low wiring installation to enter low resisstivity paths.

The PV system is a DC current source and the level of PV current and associated leakage current are thus dependent on external factors such as solar irradiance and other environmental conditions which include ambient temperature, hull resistivity. According to a related research in the field of ground PV system corrosion it was calculated that the leakage currents are reported to be about 56mA in 500-kWp array operating at 600Volts. However, it should be considered that DC leakage currents inevitably increase with the size of the PV system, as the system ages or in the case of unrecognized DC ground faults.

In this aqueous environment, there are very small amounts of current leaking from the cells to module frames and may increase significantly due to degradation of the sealing materials and water ingress. In fact, stray current flow is aggravated when moisture penetrates the glass of the module and as a consequence the resistance, between the active circuit of the module and the frame, is reduced.

Either a pipe or a hatch that is not well insulated can be an alternative route for the leakage current. Thus, severe damage can occur on the metallic structures at the location where the current discharges back for its return to the energy source. This point needs attention, as the construction process must take into account the effect of corrosion by a permanent current. These leakage current blind spots arise as existing limits for DC leakage currents have been based on other considerations, such as fire or personnel safety, which are affected by larger amounts of current. At this point, it should be noted that the point where the current first leaves the electrical circuit path will most likely be the frame of the PV module or the buried wiring where the insulation has been damaged.

To visualize and better understand the problem, the following diagram was created. As shown, the photovoltaic panels are mounted on the deck of the ship and connected via cables to the batteries located on the lower decks. A conductor for ballast or tank can be placed either parallel to the cables (as shown in the diagram) or vertically. The normal current path through the electrical circuit of the panels is shown in green. However, due to poor insulation, current is allowed to follow one of the red paths either through the pipeline or through a plate or other metal support. Therefore, it is more likely that any low resistance metallic paths (e.g. pipelines) present in the nearby area will be used, thus increasing the risk of corrosion of these metallic paths by stray currents at the location where the current will be discharged to flow to the grounded neutral of the substation. Figure 24 shows the identified locations where stray DC current strikes and increases the corrosion rate due to increased potential.

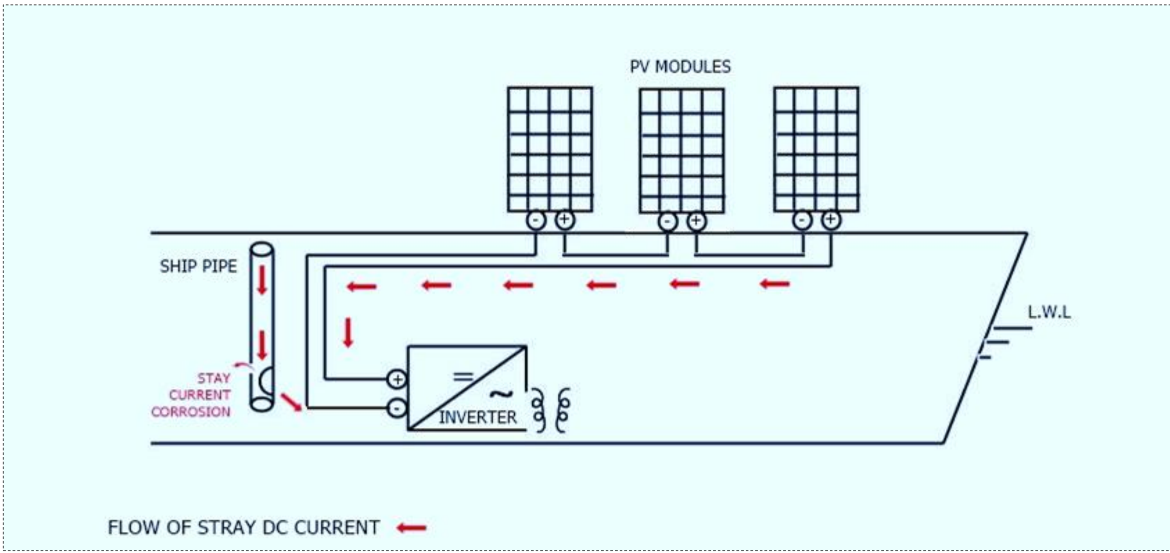


FIGURE 29: GRAPHICAL ILLUSTRATOR FOR DC STRAY CORROSION ON BATTERY SHIPS

CHAPTER 5

V)Simulation Of Corrosion From DC Stray Currents And Application Of ICCP

Comsol Multiphysics

Comsol Multiphysics 6.1

COMSOL Multiphysics® is a general-purpose software, ideal for applications for simulation of physical, chemical and mechanical effects. The program uses the Finite Element Method (FEM) for solving Partial Differential Equations (PDEs) with the corresponding initial and boundary conditions for such phenomena. It can be used alone or its functionality can be extended with any combination of complementary modules for simulation of designs and processes from various disciplines of physics and chemistry, such as electromagnetism, structural mechanics, acoustics, fluid mechanics and heat transfer.

The basic steps to create the model using the program

Comsol Multiphysics are the following:

1. Select an appropriate type of Comsol add-on.
2. Define constants and data to be entered into the program.
3. Generation of Geometry.
4. Definition of the physics of the system and its boundary conditions.
5. Definition of the problem.
6. Solving the problem and evaluating the results.

Ship Model Characteristics

The vessel used as a model to the simulation, is a fully electrified car ferry. The principal dimensions of the vessel are outlined in the following table. The designed fully electrified car ferry can transport approximately 100 passengers and more than 20 passenger cars, has a power capacity exceeding 1.6 MWh, and can operate for approximately 2 hr at the standard speed of 10 kn (5.144 m/s). The vessel is equipped with a removable power supply system is designed as a self-moving system equipped with various safety systems; battery management system (BMS), cell anomaly detection system, thermal management system through air-conditioning, and battery thermal runaway limit system. Two removable power supply systems are located on the deck of the vessel, at the same length as the shaft and the propeller. This is the section of the ship that existence and effects of direct current will be analyzed.
The hull of the model vessel is made of steel.. The shaft is made of while main propeler is nickel-aluminum-bronze(NAB) alloy. NAB minimizes corrosion rates to 0.015-0.05 mmy^{-1}. The general characteristics of the vessel are presented below.

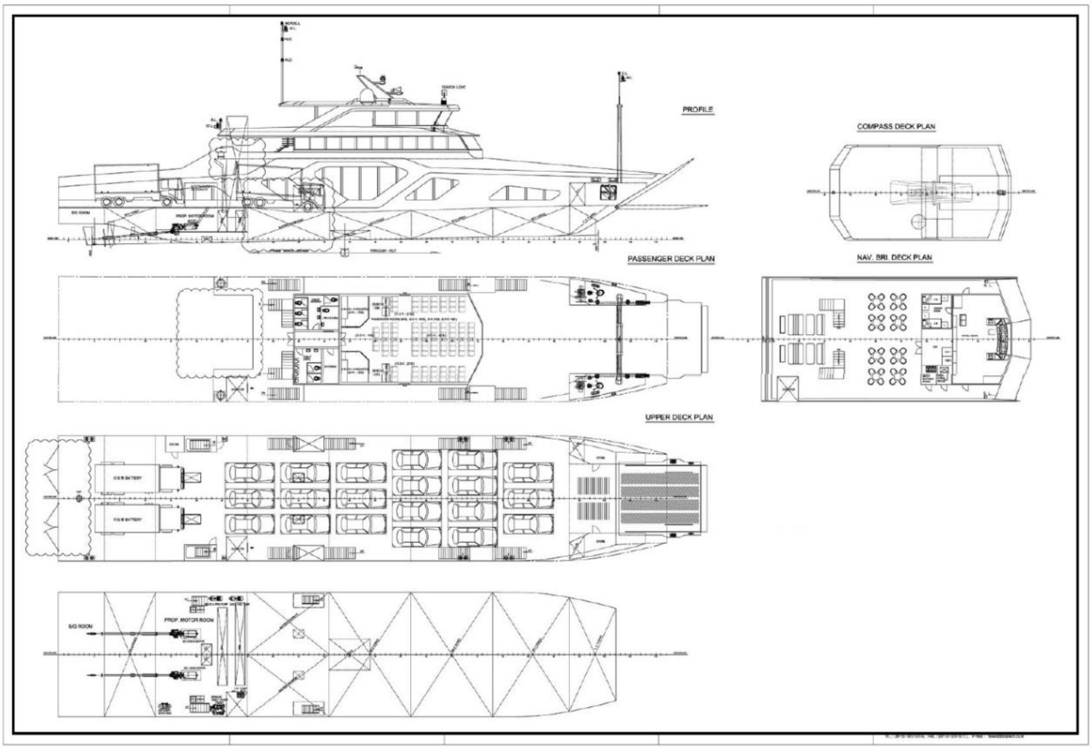


FIGURE 30: GENERAL ARRANGEMENT PLAN OF THE MODEL FULLY ELECTRIFIED CAR FERRY

TABLE 8: PRINCIPAL DIMENSIONS OF A FULLY ELECTRIFIED CAR FERRY

Length overall (LOA)	**58.6 m**
Length between perpendiculars (LBP)	49 m
Beam	13 m
Depth	2.5 m
Draught	1.65 m
Design speed km/h	29 km/h
Passengers persons	120
Cars units	20

TABLE 9: DESIGN VARIABLES FOR REMOVABLE POWER SUPPLY SYSTEM

Number	2
Size	6.1m
Weight	<12
Power Capacity	800 kWh
Output reference voltage	780 Vdc
Output voltage range	650-900 Vdc
Reference/maximum voltage	350/450 A

Description of the experiment

To illustrate the simulation of DC stray currents and cathodic protection by applying electric current ICCP, the following steps were followed:

i. Creation of metal structure geometry and the marine corrosive surroundings in the graphical environment of the program Autocad Inventror 2023. In this point, the anode and the Ag/AgCl reference electrode were placed on the protected structure. At the end of this process the dwg file was imported into the Comsol program.
ii. Definition of the system physics and quantitative physics characteristics of the materials of the metal structure and the propeller
iii. Creation of a mesh (Mesh) to carry out the calculations through Finite Elements Method (FEM).
iv. Execution of the program and calculation of the potential difference and current density in the structure and at the anode.
v. Create relevant diagrams

The simulation consists of two different part. Firstly, DC stray Current attack nearby the shaft of the vessel is repressented. To our hypothesis leakage of DC currents supplied by battery system leads to increased potential where the electric current was leaving the surface of the ship. In fact, the constant current converts a part of the ship's hull into an anode. The second part presents the stray DC currents near the stern and the ICCP system that works to address the problem.

Geometry of the Vessel

First of all, geometry of the ship had been designed on Autocad Inventor. The plan included the hull of the ship as well as the shaft and the propeller used for propulsion. All the surfaces of the ship were merged in order to create a single geometry. The model geometry is created by adding rectangular block outside the hull geometry to represent the ocean. Afterwards, autocad file had been imported to Comsol Multiphysics. The following figures represent the geometry of the model in three dimensional space of Cartesian coordinate system.

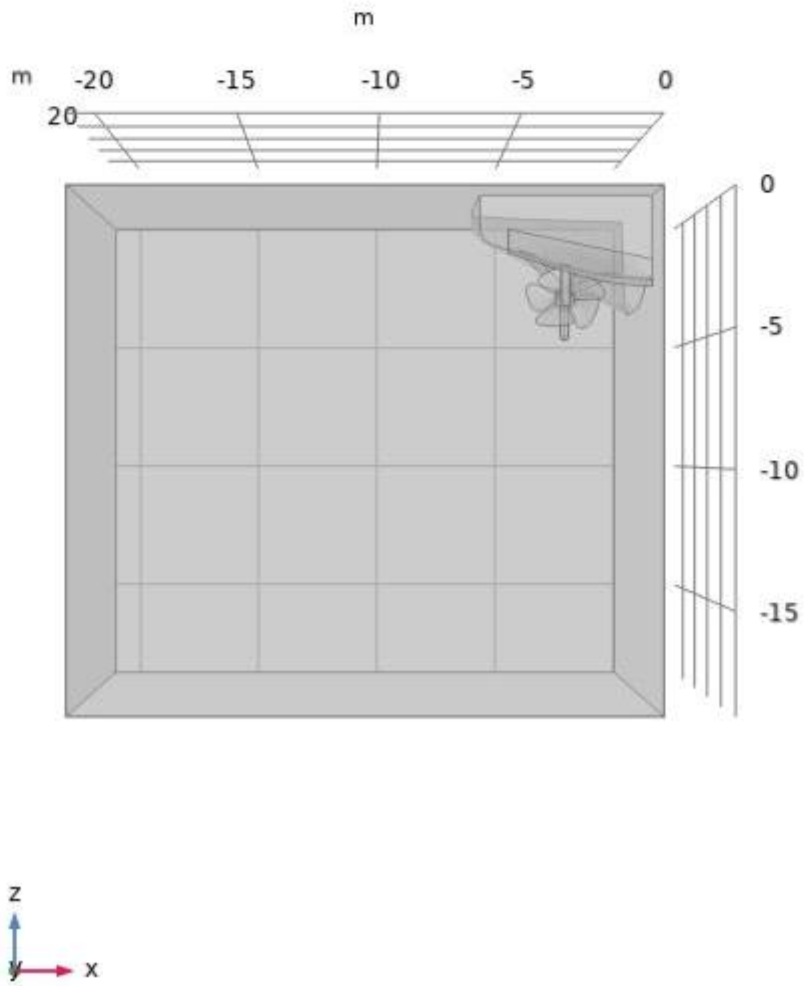


FIGURE 31: SIDE VIEW OF THE MODEL'S GEOMETRY

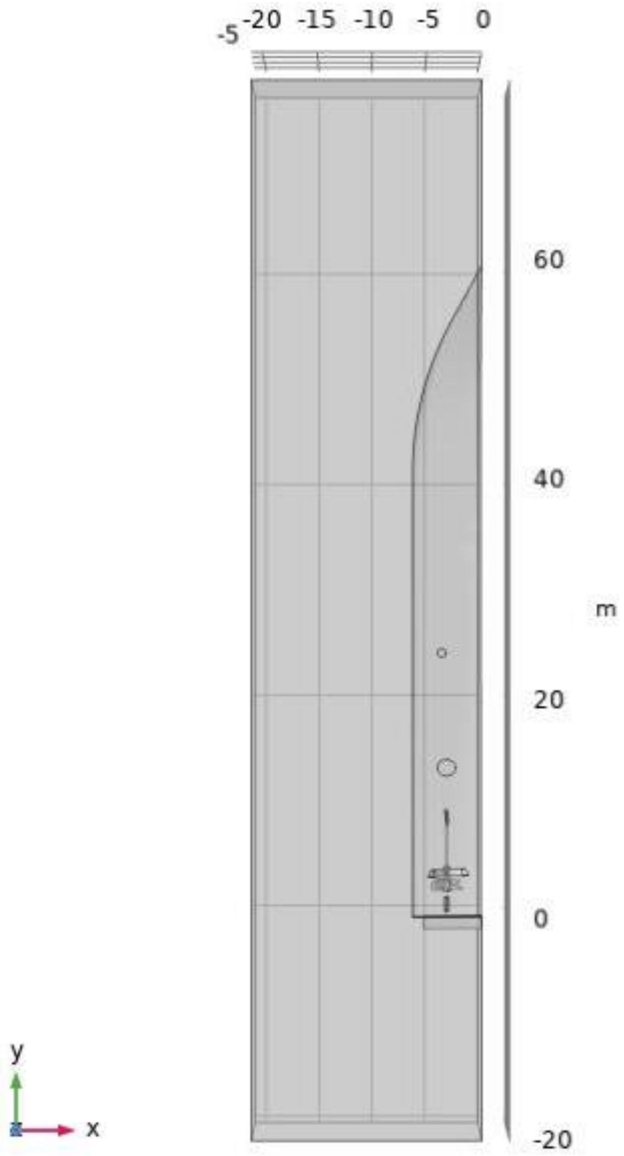


FIGURE 32: TOP VIEW OF THE MODEL'S GEOMETRY

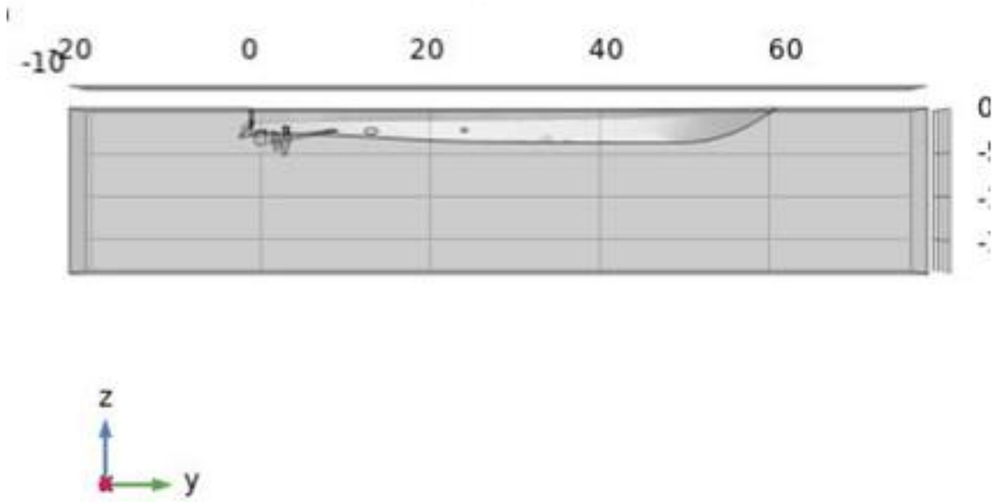


FIGURE 33: FRONT VIEW OF THE MODEL'S GEOMETRY

The coordinates of the point selected as the place of high risk due to its low potential, are (x,y,z) = (-3.15, 9.74, -2.5). In this area, the propeller shaft intersects with the hull of the ship.

- Axis x: axis of the width of the ship
- Axis y: axis of the length of the ship
- Axis z: axis of the height of the ship

The model is fitted with an Portable Silver-Silver chloride(Ag/AgCl) seawater reference electrode located at the following coordinates

- (x,y,z) = (3.595, 24.14, 2.42).

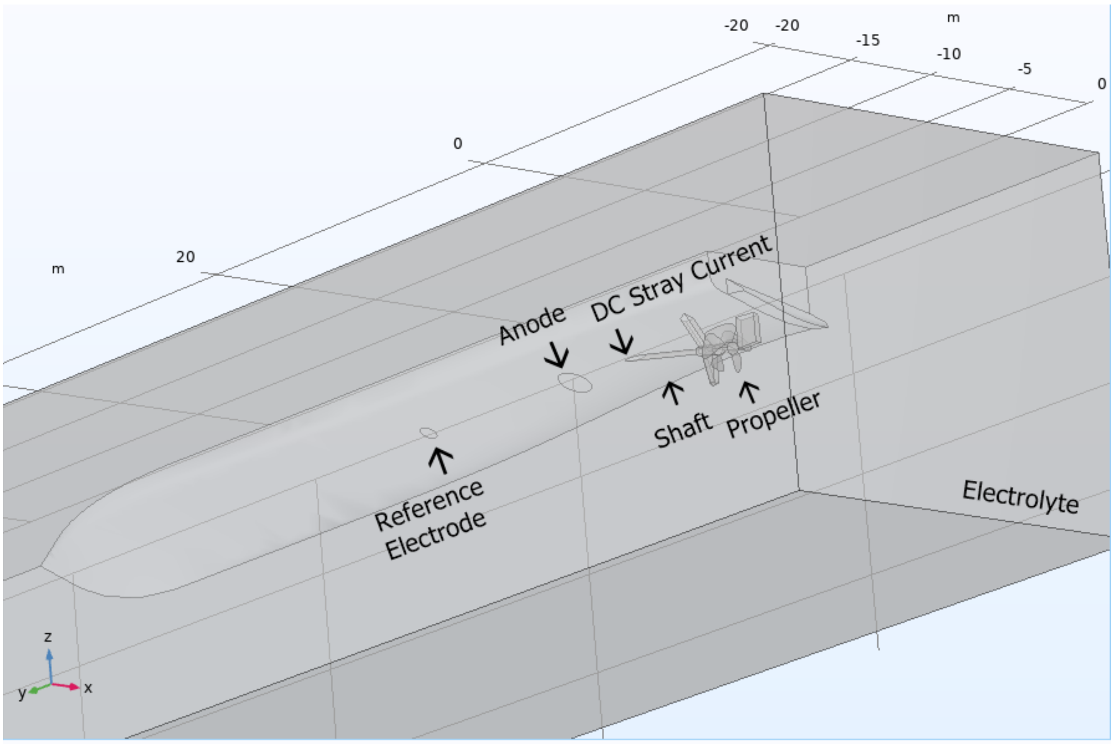


FIGURE 34: REPRESENTATION OF THE MAIN ELEMENTS OF GEOMETRIC CONSTRUCTION

Modelling of physical parameters

The present model example demonstartes stray current corrosion of ship using battery propulsion system. For this purpose, functions provided by Comsol Multiphysics had been used to simulate electrochemical reactions nearby vessel's stern. The function called 'the Current Distribution, Boundary Elements interface' was preferred due to flexibility in the definition of the initial parameters of the problem. These parameters are discussed in next chapter.

The Current Distribution, Boundary Elements interface is used to solve for the electrolyte potential, (SI unit: V), over the edge domains according to:

$$i_l = -\sigma_l \cdot \nabla_{\phi_l}$$

$$\nabla_{i_l} = 0$$

Where:

1. il (SI unit: A/m2) is the electrolyte current density vector
2. σl (SI unit: S/m) is

the electrolyte conductivity which is 0.005 S/m for the soil domain.

At the anode edge, the applied current density is prescribed using the Electrolyte Current Density node as:

$$n \cdot i_l = i_{\alpha pp}$$

where n is the normal vector, pointing out of the domain. This mode is used for the Second Study when Cathodic Protection is in operation.

At the protected and interference ship hull, kinetics of electrochemical reactions is
prescribed using the Edge Electrode node as:

$$n \cdot \mathrm{i}_l = f(\phi_l)$$

Where:

1. $f(\phi_l)$ is an interpolation function obtained form the experimental polarization data available in corrosion material library that was discussed in previous chapter.

Noteworthy is that in real operating conditions, phenomena occur which are not taken into account in the following simulation because they are outside the scope of this thesis. Nevertheless, it is worth pointing out that the rotational movement of the propeller affects the corrosion that develops in the area. Pitting corrosion occurs under special conditions, involving sodium chloride (salt) in sea water and greatly exacerbated by the elevated temperatures found in tropical ocean environments. Small pits continue to grow in a self sustainingcycle increasing the possibility of material failure. Corrosion due to relative movement of corrosion is not addressed in this simulation.

Material selection

Corrosion Material Library, provided by Comsol Multiphysics, had been used to set up the material properties for the electrode kinetics at the shaft and propeller electrode surfaces.

The hull of the model vessel is made of steel. The shaft is made of while main propeler is nickel-aluminum-bronze(NAB) alloy. NAB minimizes corrosion rates to 0.015-0.05 mmy^{-1}. The polarization curves of coated steel surface in seawater are given by the non-linear relation:

$$i(\varphi, fc) = f_d f_c [i_{corr} e^{\frac{\varphi-\varphi corr}{ba}} - i_{corr} e^{-\frac{\varphi-\varphi corr}{bc}}]$$

Where φ is the potential in V (vs Ag/AgCl/seawater reference electrode RE), i is the current density A/m. Also φ_{corr}=-0.656 V (vs Ag/AgCl/seawater reference electrode RE) and also icor=1.63mA/m^2. In static conditions b_a=0.0434V/dec and b_b=0.0434V/dec.

The following figure represents Tafel Curves for steel as a function of the coating percentage:

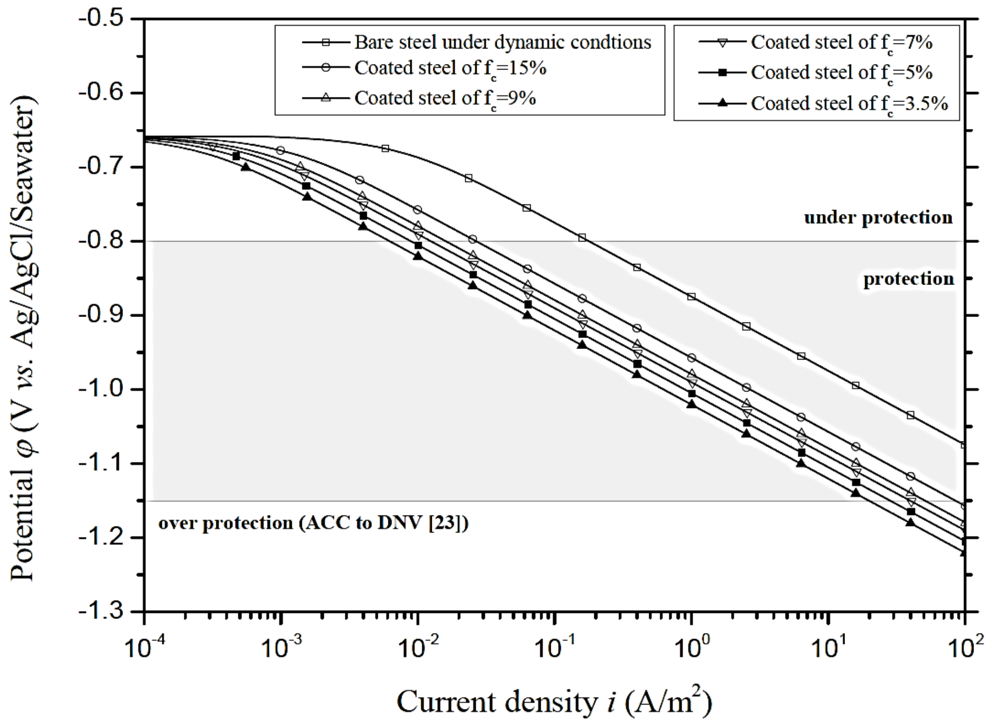


FIGURE 35:TAFEL PLOTS OF UNCOATED AND COATED STEEL SAMPLES IMMERSED IN SEAWATER SOLUTION.

The polarization curves of the bare NAB alloy at the rotation speed of 800RPM:

$$i(\varphi, fc) = [i_{corr} e^{\frac{\varphi - \varphi corr}{ba}} - i_{corr} e^{-\frac{\varphi - \varphi corr}{bc}}]$$

Where φ is the potential in V (vs Ag/AgCl/seawater reference electrode RE), i is the current density A/m. Also φ_{corr}=-0.33 V (vs Ag/AgCl/seawater reference electrode RE) and also icor=0.1mA/m^2. In static conditions b_a=0.0651V/dec and b_b=0.0651V/dec.

In the Model Builder window, there is a function used to plot polarazation curve for NAB alloy.

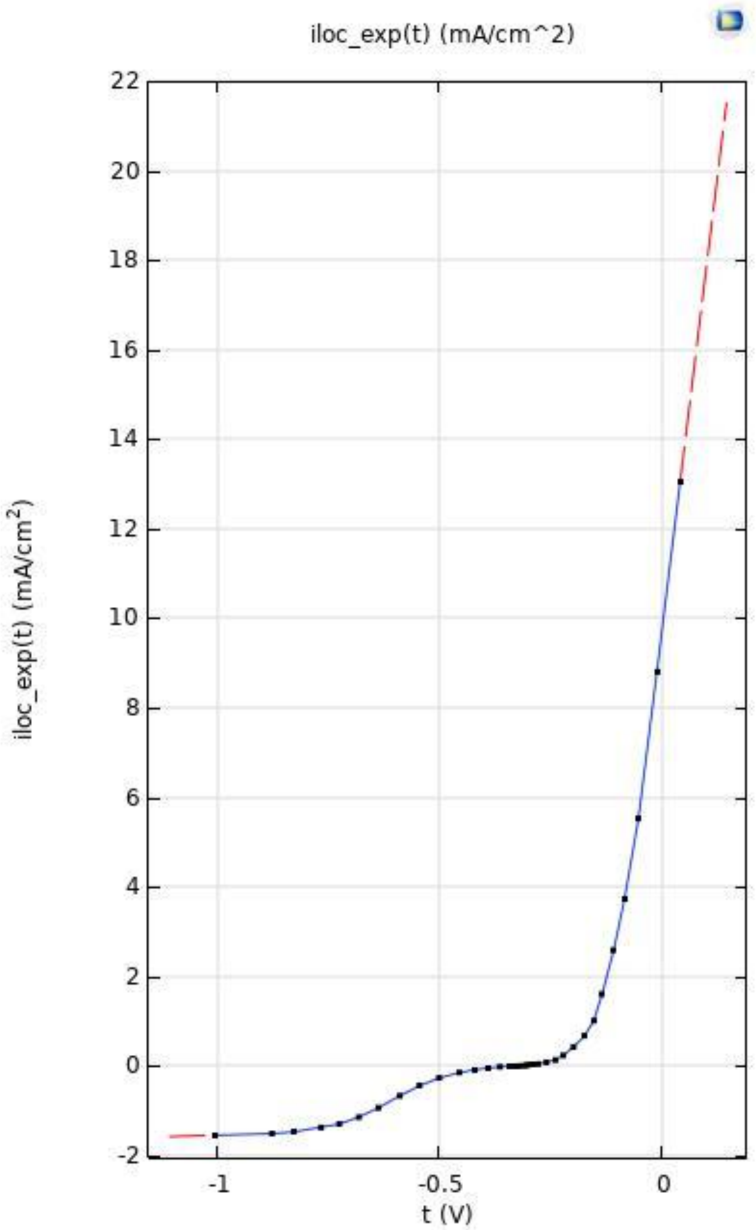


FIGURE 36: TAFEL PLOTS OF NAB STEEL IMMERSED IN SEAWATER SOLUTION.

A problem-solving approach

To illuminate this uncharted area of DC stray corrosion on vessels, we illustrated a model to simulate these phenomenon. For our first goal, we focus on the problem of DC stray currents. As indicated in a previous chapter DC stray currents supplied by the main power source- battery, are leaking from the power supply ducts. Thus, current drives through a part of vessel's hull to another making a new electrical path. There is no previous research in this field. A number of hypotheses were therefore proposed which will lead to further work and research on the subject.

In an attempt to evaluate the impact of stray currents, we have made the following assumption that the leaking current is located at the stern of the ship. It is know, that the propulsion system consisting of batteries is installed nearby stern side of vessel. As an example, on the vessel under study, the batteries have been placed at 13 m forward to AP. Taking into consideration the location of stray currents, it is clear that shaft and propeller undergo the risk of extreme corrosive potential. A significant parameter of mitigating the range of corrosion is the choice of material as well as the coatings of these two surfaces. In particular, the propeller matterial must be more noble than hull steel, in such a manner that positive polarazition does not overcome the equilibrium potential. Furthermore, the total current demand amounts to higher in the case of the uncoated propeller compared to the case of the coated propeller,could be attributed to the larger cathodic surface in the case of the uncoated propeller.

It is presumably that cathodic protection system which is installed near these parts of hull overcomes the problem of stray currents. ICCP accomplish to restore potential to the desired values of protected zone. As the rectifier responds to dynamic conditions the supplied current density should be regulated to values higher than the stray current. An example is provided to understand how cathodic protection mitigates the problem. If the stray ***icur*** current comes out from a point near the anode of the ICCP, then the rectifier will provide more current ***iapp*** to eliminate the leakage current and further maintain the surface area in the protected zone.

It is written in mathematical formulas

$$iapp > icur$$

$$Iapp = icur + Icor$$

Where Icor is the current density demand while the ship is not under stray current attack.

"Analogies with fluid flow can be a big help in developing intuition about electric current and circuits. For example, in the making of wine or maple syrup, the product is sometimes filtered to remove sediments. A pump forces the fluid through the filter under pressure; if the flow rate (analogous to) is proportional to the pressure difference between the upstream and downstream sides (analogous to E), the behavior is analogous to Ohm's law."

"The problem is analogous to an ornamental water fountain that recycles its water. The water pours out of openings at the top, cascades down over the terraces and spouts (moving in the direction of decreasing gravitational potential energy), and collects in a basin in the bottom. A pump then lifts it back to the top (increasing the potential energy) for another trip. Without the pump, the water would just fall to the bottom and stay there."

University Physics with Modern Physics

Young and Freedman

Using the same mechanical analogy of the movement of an electric current with the movement of a fluid in a pipe proposed by Young and Freedman, we can easily understand that a decrease in the pressure of the water pump (in relation to the potential of the current) causes a decrease in its flow (respectively the electric current flowing through it - the ohm law). The optimal solution in case of water leakage would be to steal the flow completely i.e. to zero the pressure difference of the pump. In our problem this is achieved by the optimum insulation of the mechanical installations and, secondly, the hull of the ship. However, because a leakage of dc current is always possible we choose to vary the potential difference in order to reduce the leakage current. In the pump example this is done either by closing the tap minimally or by increasing the fluid pressure in the direction of the source

Study 1 DC stray Current attack nearby the shaft of the vessel

The first simulation provides a first approach to the problem of stray currents in Battery vessels. As shown in figures below, the potential decreases in absolute value nearby the area of stray current. In particular, electrical potential takes values up to -0.3 V fairly close to the circular path of the current. If we assume that we make a circle over the surface of the hull with a radius of 1m and centered at the center of the shaft-ship interface, the potential gradually stabilizes near the value -0.61V. This particular potential is located in the corrosion zone of the shipbuilding steel. It demonstrates the acceleration of corrosion due to stray currents and the consequent deterioration of structural strength. Remarkably, this potential difference accelerates the corrosion rates radically since the chemical reaction of decomposition of the structure is intensified.

The results of the project for the surface potential are presented below.

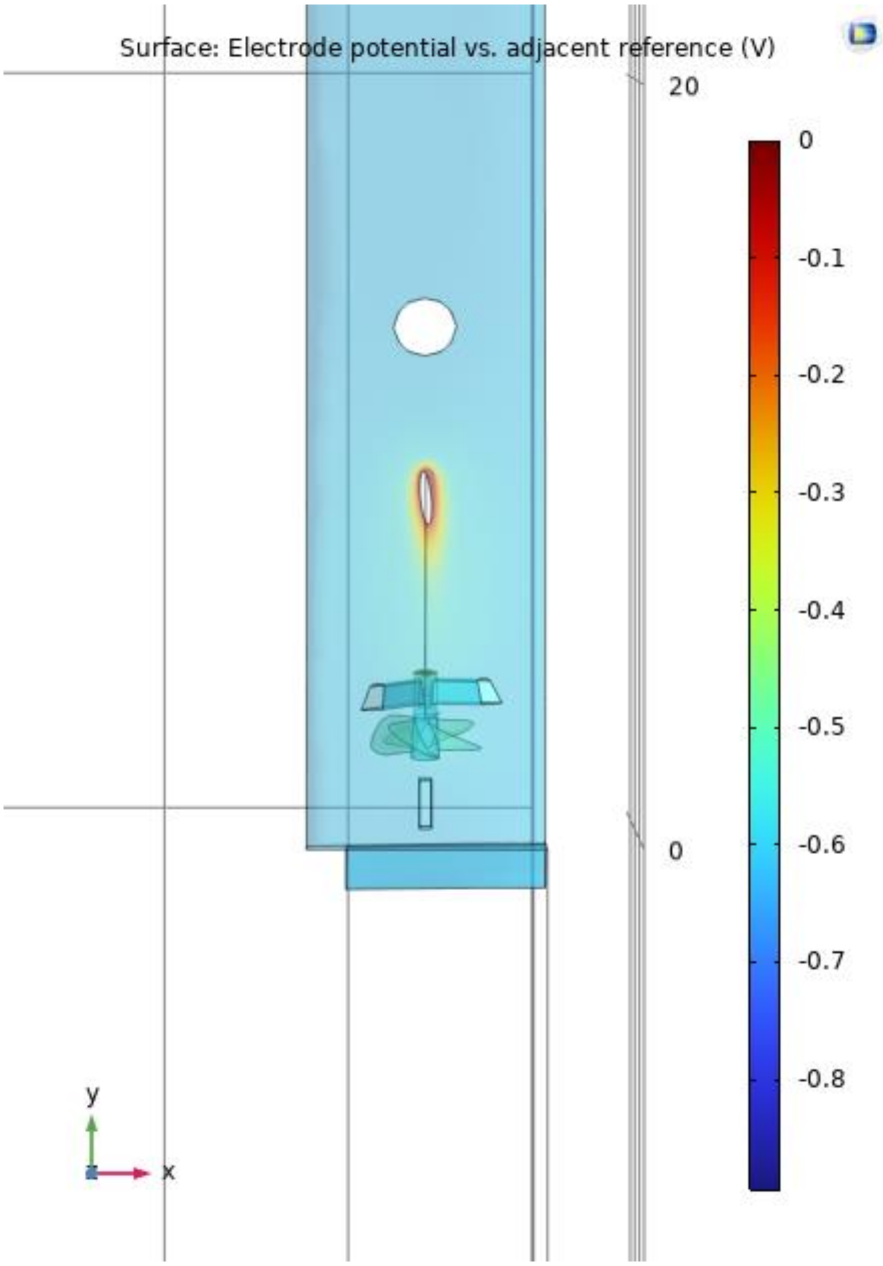


Figure 37: Top View of Corrosion Due to DC Stray Current

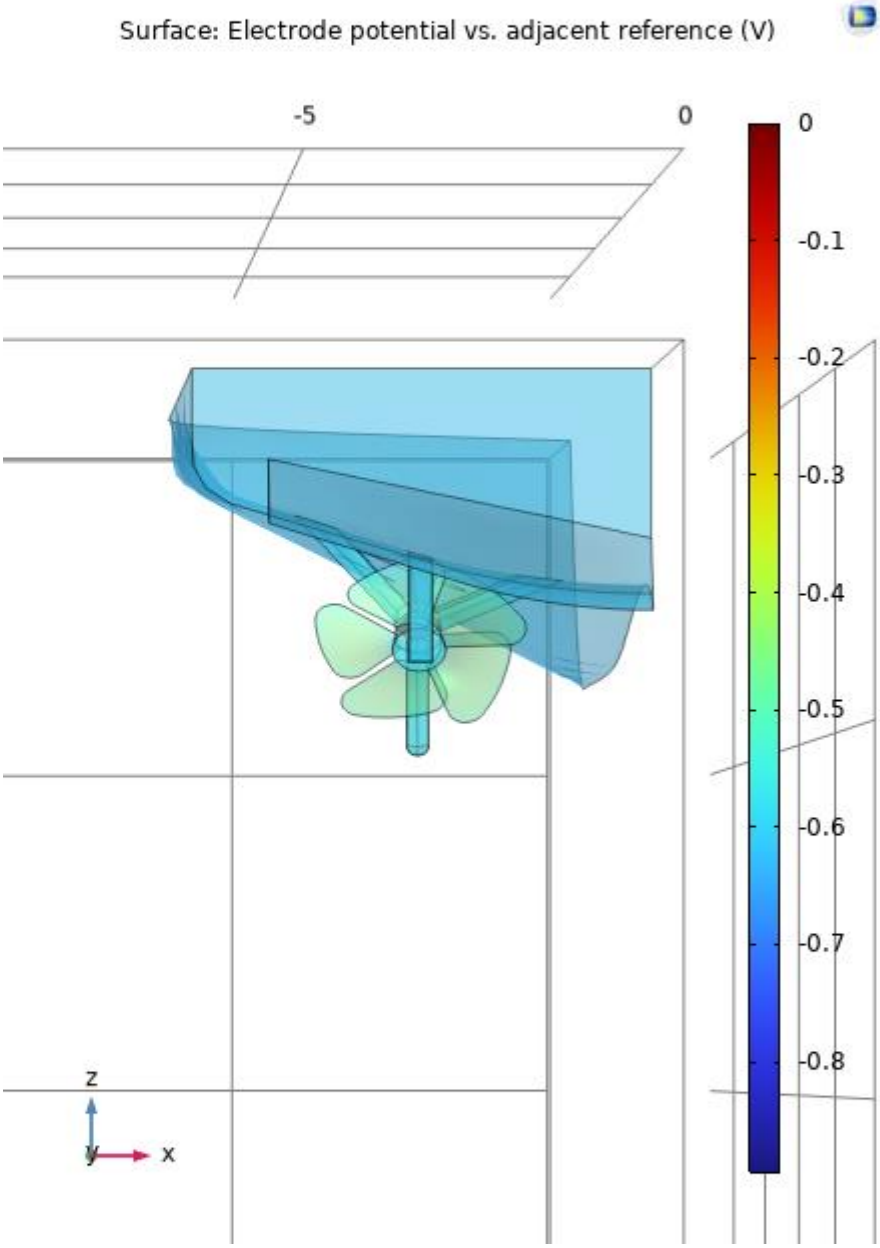


FIGURE 38: SIDE VIEW OF CORROSION DUE TO DC STRAY CURRENT

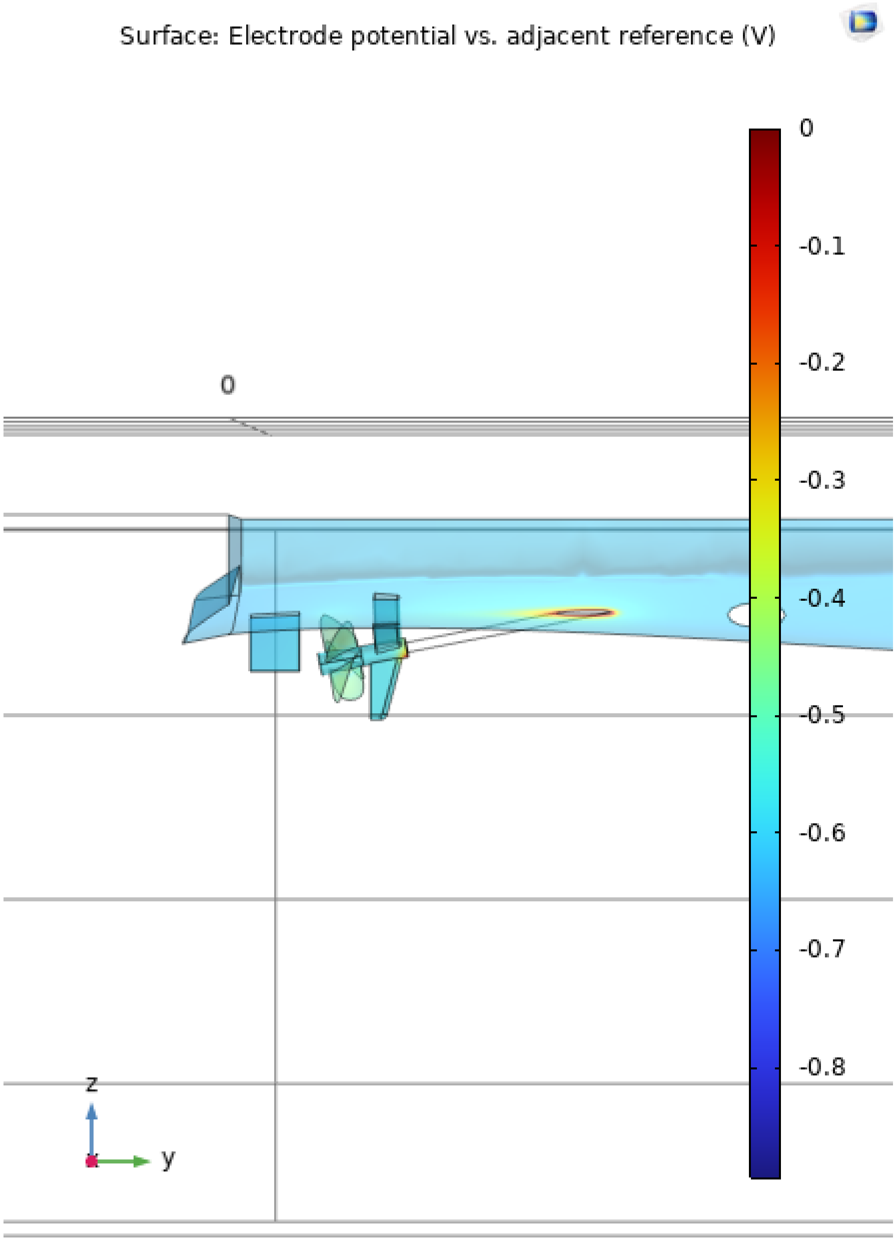


FIGURE 39: PROFILE VIEW OF CORROSION DUE TO DC STRAY CURRENT

Study 2 ICCP protection and DC stray Current Attack nearby the shaft of the vessel

Likewhise the previous simulation, a stray current supplied by the source is driven in a circular path exiting from a point near the intersection of the shaft with the vessel's hull. At this point and around this particular region the loss of equilibrium potential is detected. The following pictures identify the parts of the hull where the problem of rapid corosion due to DC current is found. The areas in red and yellow have a very low potential that ranges from -0.4V to -0.68V . Consequently the occurs tha anodic reaction of steel takes place at greater frequency.

ICCP system tends to mitagate corrosion rates ICCP system tends to mitagate corrosion rates. As illustrated in figures below, the values of potential ranges from -2V to 0.85V within a circular region near the anode. Outside the specified zone, the vessel's surface is protected as well. It should be noted that in the cyclic area surrounding the anode used for the ICCP system, potentials exceeding -1.5V are generated compared to Ag/AgCl reference electrode. The values under -1.53 V exhibited at the hull is more negative than the overprotection limit of -1.15 Vintroduced by DNV and less negative, than the corresponding one of -2 V adopted by Lee and Lim {25}. As it is known, a circular area nearby anodes is perfect electrically insulated. In conclusion,no overprotection occurred due to the used marine epoxy coating by the proposed ICCP system.

In propeller potential values range from -0.35v to -0.5. From these data the one comprehend that we are in the protected area. On closer inspection at the diagram on the page48 an enginner conclude experimental values of propeller potential are beneath equilibrium potential. Beneath.In absolute terms proppeler potential is lower than potential of hull. This is to be expected since a specific material was chosen to protect the helix from corrosion.

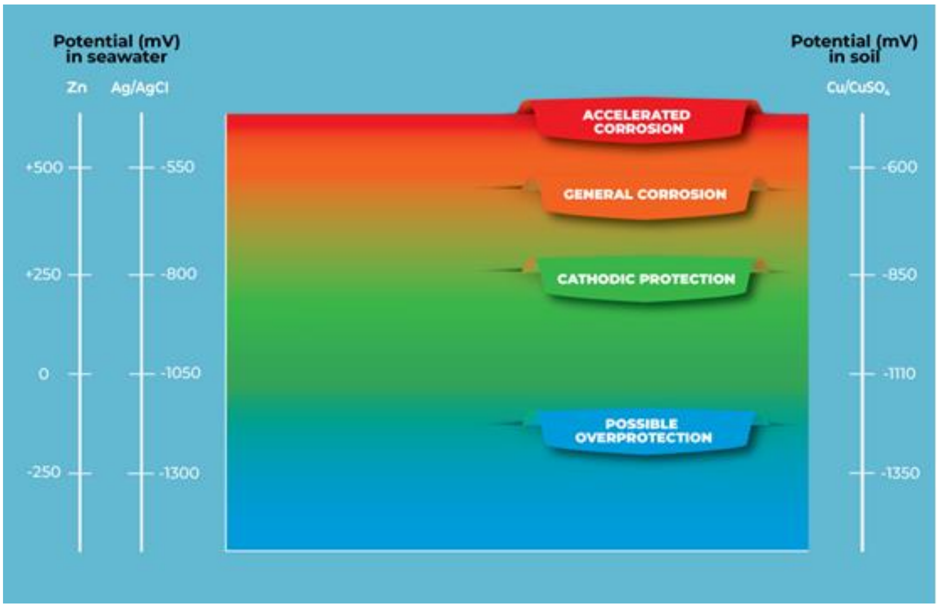


FIGURE 40: CATHODIC PROTECTION LEVEL VERSUS DIFFERENT REFERENCE ELECTRODES

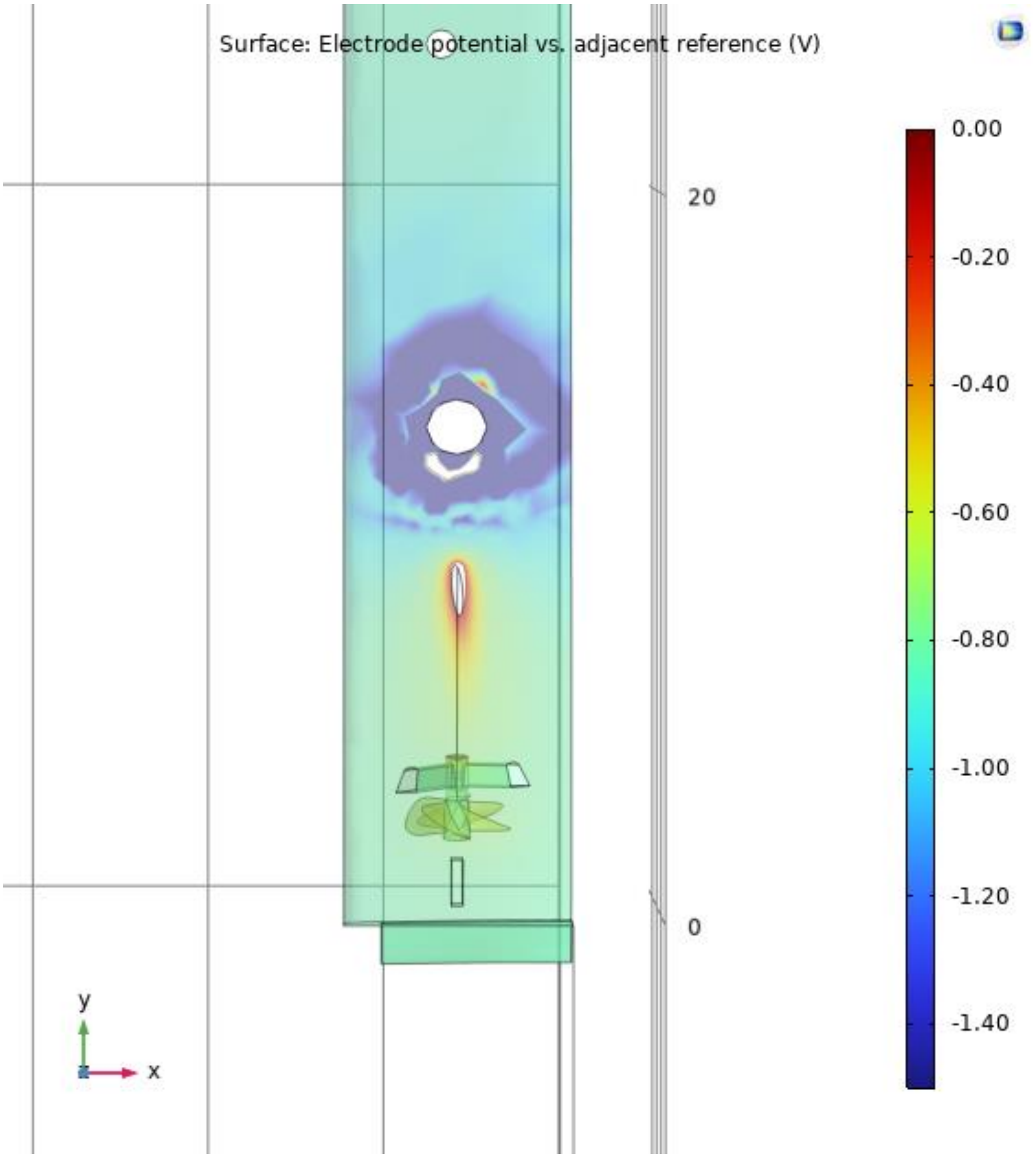


FIGURE 41: TOP VIEW OF CATHODIC PROTECTION USED TO MITIGATE CORROSION DUE TO DC STRAY CURRENT

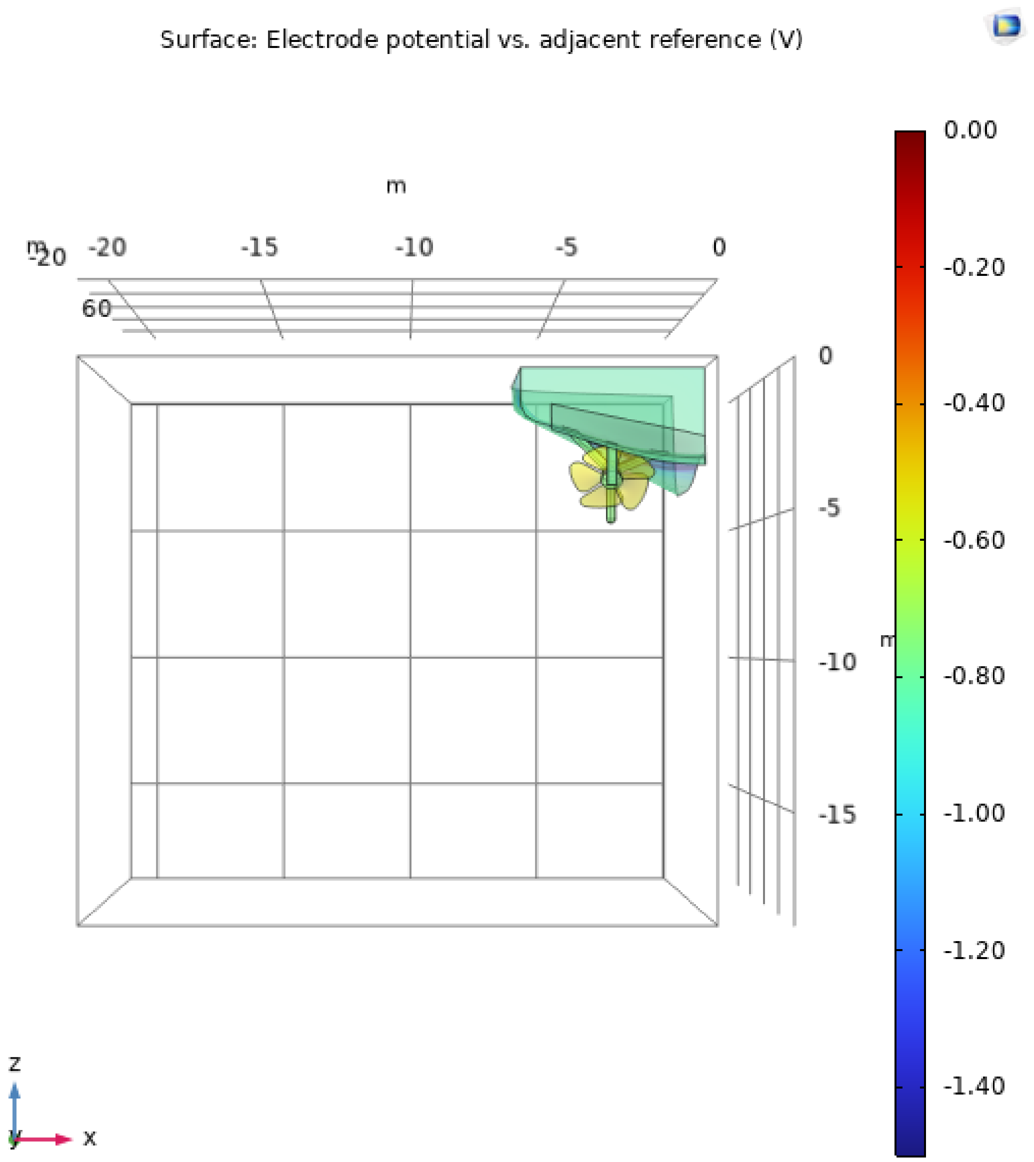


FIGURE 42: SIDE VIEW OF CATHODIC PROTECTION USED TO MITIGATE CORROSION DUE TO DC STRAY CURRENT

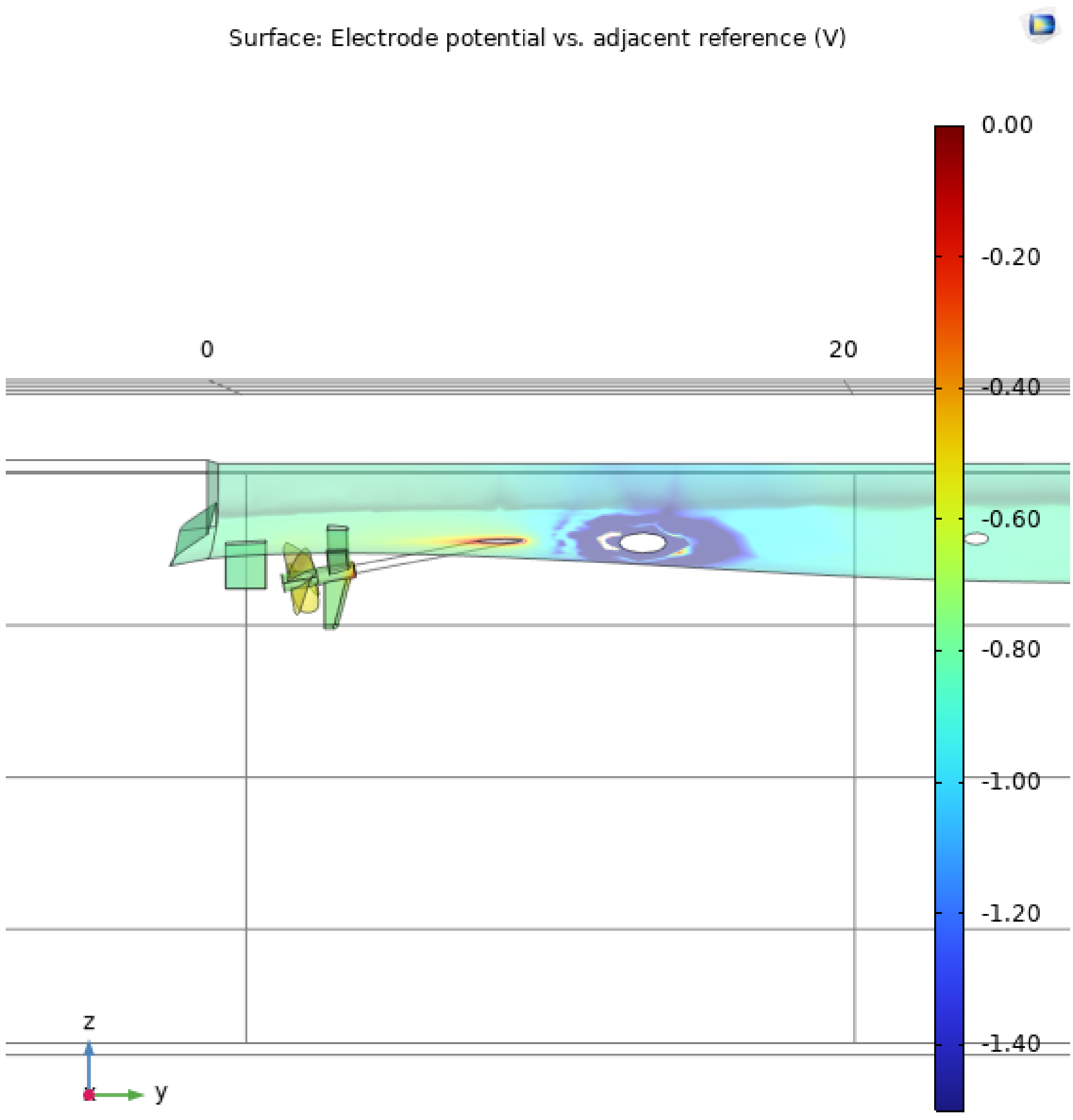


Figure 43: Profile View View of Cathodic Protection Used to Mitigate Corrosion Due to DC Stray Current

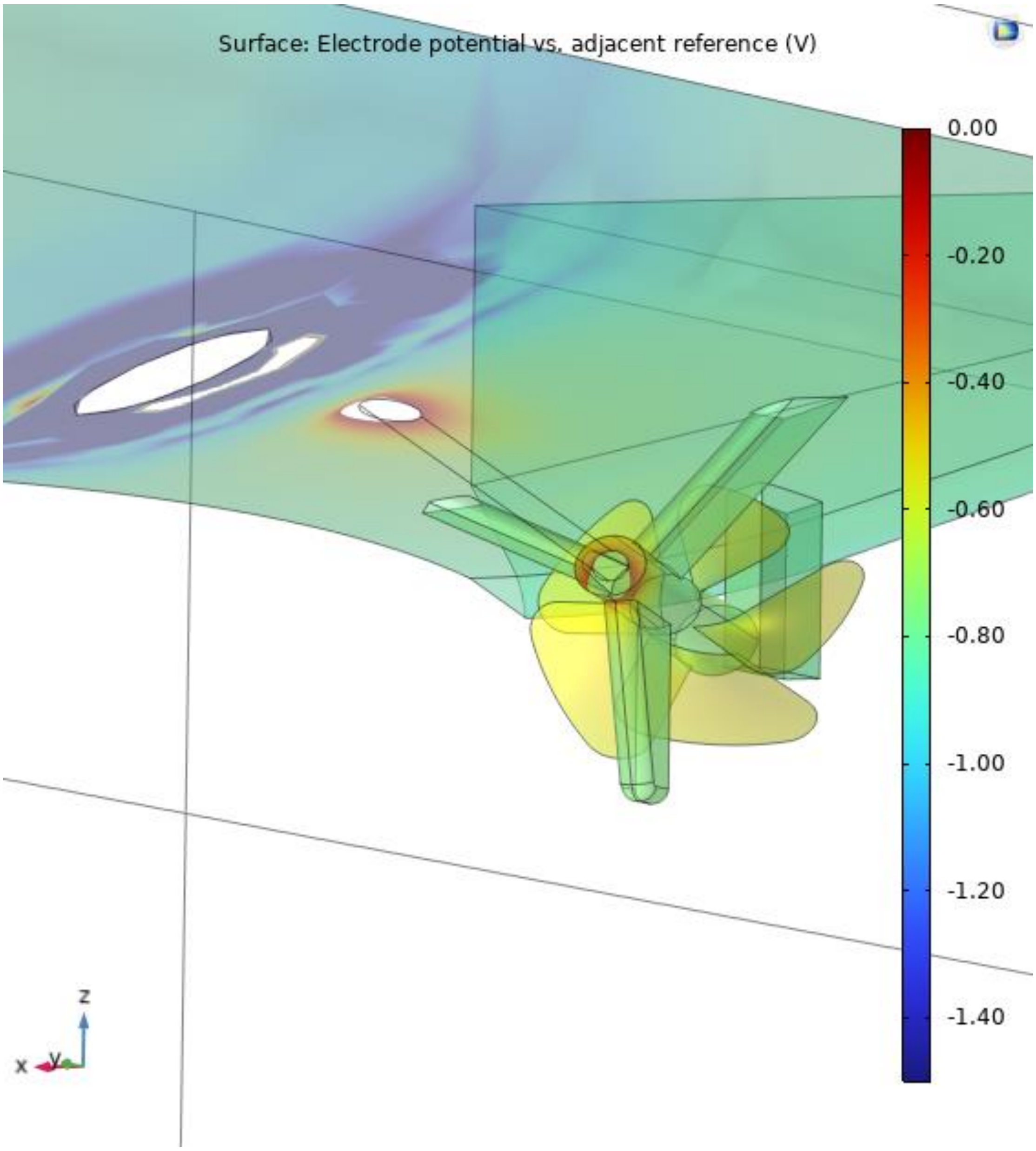


FIGURE 44: 3D VIEW OF CATHODIC PROTECTION USED TO MITIGATE CORROSION DUE TO DC STRAY CURRENT

Discussion and Conclusion

It is fundamental to note that the area between the anode of ICCP and the place that stray current drives out, is protected during the cathodic protection oparation. Table 10 shows a significant difference in the potential values between the two different states of protection or not. The following table sets the values of the potential for two different points which are separated by a distance of 300mm. The large increase in potential due to cathodic protection is undeniable.

TABLE 10: POTENTIAL NEARBY CORROSION ATTACK

Axis x {m}	Axis y {m}	Axis z {m}	Potential {V}
3.595	10.01	-2.42	-0.54
3.595	10.30	-2.42	-0.84

Weakness of the ICCP system

Nevetheless, ICCP protection of this simulation fails to protect the area between AP and the shaft. Contrary to ours expactations we did not find a significant difference to potentials between the situations under examination. Despite the fact that ICCP system wasexpected to ovecome the problem, the results revealed some of the disadvantages of ICCP.

First of all, vessels under 100 metres in length are usually equipped with 1 or 2 anodes. The installation of more than this number of anodes tends to be economically unsustainable. This is the reason why a problem is detected in the control of the potential at points with a strong measured potential rise. Therefore, it can be suggested that the installation of sacrificial anodes near the stern zone can overcome the problem of high potential rise.

Taken together, these findings implicate a role for cathodic protection on vessels with electric propulsion system.

Conclusions and recommendations

The aim is to investigate the points of the hull that have a higher potential and the routes outside the circuit through which parasitic leakage currents return to the negative pole of the source. Mitigation of the problem may be achieved by the parallel placement of sinks near the area where parasitic currents are expected to occur. Furthermore, proper placement of reference electrodes and application of the IR drop method will improve knowledge about the existence and influence of circulating currents.

The applicable knowledge on battery systems on ships is being continuously developed. A search of the international literature indicates that the study of their interaction with the rest of the structure is at an early stage. Further research in the field of protection from circulating continuous currents is considered beneficial and necessary in order to draw firm conclusions that will reduce the risks and optimise the benefits of the new alternative energy source.

Appendix 1-Modeling Instructions

NEW

1. From the File menu, choose New.
2. In the New window, click Model Wizard.

MODELWIZARD

1. In the Model Wizard window, click 3D.
2. In the Select Physics tree, select **Electrochemistry>Primary and Secondary Current Distrubution>Cureent Distribution, Boundary Elements(cdbem)**
3. Click Add.
4. Click Study.
5. In the Select Study tree, select General Studies>Stationary.
6. Click Done.

GEOMETRY 1

Then, the geometry of the ship hull import is carried out from a geometry file.

Import Geometry

1. In the Home toolbar, click Import.
2. In the Settings window for Import, locate the Import section.
3. Click Brows
4. Browse to the model's geometry from the autocad file.
5. Click Import.
6. In the Geometry toolbar, click Build All.

The geometry lookS like FigureX.

MATERIALS

Corrosion Material Library was used to set up the material properties for the electrode

kinetics at the propeller electrode surfaces. Also,

ADD MATERIAL

NAB in seawater at 30 C

1. Go to the Add Material window.
2. In the tree, select Corrosion>Copper Alloys (Bronzes)>NAB in seawater at 30 C.
3. Click Add to Component in the window toolbar.
4. In the Settings window for Material, locate the Geometric Entity Selection section.
5. From the Geometric entity level list, choose Boundary.
6. From the Selection list, choose Propeller.

Hull Steel

1. Go to the Add Material window.
2. In the tree, select Corrosion>Copper Alloys (Steel)> AISI 4140 steel
3. Click Add to Component in the window toolbar.
4. In the Settings window for Material, locate the Geometric Entity Selection section.
5. From the Geometric entity level list, choose Boundary.
6. From the Selection list, choose Hull Surface.

CURRENT DISTRIBUTION, BOUNDARY ELEMENTS (CDBEM)

Afterwards, the physics of the model were set up. We Started with selecting the reference electrode. Then, the electrolyte conductivity, the potential of the shaft due to stray current and electrochemical reaction kinetics were set up. At the second study, we set the potential supplied by ICCP.

1. In the Model Builder window, under Component 1 (comp1) click Current Distribution,Boundary Elements (cdbem).
2. In the Settings window for Current Distribution, Boundary Elements, click to expand the Physics vs. Materials Reference Electrode Potential section.
3. From the list, choose 0.197 V (Sat .Ag/AgCl vs. SHE).

Electrolyte 1

1. In the Model Builder window, under Component 1 (comp1)>Current Distribution,
2. Boundary Elements (cdbem) click Electrolyte 1.
3. In the Settings window for Electrolyte, locate the Electrolyte section.
4. In the σl text field, type sigma.

Electrolyte Potential 1(DC stray current)

1. In the Physics toolbar, click Edges and choose Electrolyte Potential.
2. In the Settings window for Electrolyte Current Potential, locate the Edge Selection section.
3. From the Selection list, choose point 84.
4. Locate the boundary electrolyte potential section. In the text field, type Edc.

Electrolyte Current Density 1(ICCP)

1. In the Physics toolbar, click Edges and choose Electrolyte Current Density.
2. In the Settings window for Electrolyte Current Density, locate the Edge Selection section.
3. From the Selection list, choose Anode.
4. Locate the Electrolyte Current Density section. In the text field, type iapp.

Edge Surface 1

1. In the Physics toolbar, click Edges and choose Edge Surface.
2. In the Settings window for Edge Surface, locate the Edge Selection section.
3. From the Selection list, choose Hull Surface.

Electrode Reaction 1

1. In the Model Builder window, click Electrode Reaction 1.
2. In the Settings window for Electrode Reaction, locate the Equilibrium Potential.
3. From the Eeq choose User defined. In the text field type Eeq.
4. In the Settings window for Electrode Reaction, locate the Electrode Kinetics section.
5. From the iloc,expr list, choose From material.

Edge Surface 2

1. In the Physics toolbar, click Edges and choose Edge Surface.
2. In the Settings window for Edge Surface, locate the Edge Selection section.
3. From the Selection list, choose Propeller.

Electrode Reaction 1

1. In the Model Builder window, click Electrode Reaction 1.

2.In the Settings window for Electrode Reaction, locate the Equilibrium Potential.

3.From the Eeq choose From material

4.In the Settings window for Electrode Reaction, locate the Electrode Kinetics section.

5.From the iloc,expr list, choose From material.

MESH 1

Set the fine mesh at all line segments.

1. In the Model Builder window, under Component 1 (comp1) click Mesh 1.
2. In the Settings window for Mesh, locate the Sequence Type section.
3. From the list, choose User-controlled mesh.

Size 1

1. In the Model Builder window, right-click Edge 1 and choose Size.
2. In the Settings window for Size, locate the Element Size section.
3. Click the Predefined>Normal button.
4. Click Build All

STUDY: DC_STRAY_CURRENT_ATTACK

For the first study the Electrolyte Current Density was disabled in order to examine the impact of the leakage current to unprotected hull and propeller. A second study was carried out, to solve the model for the coexistence of current and cathodic protection

Step 1: Stationary

1. In the Model Builder window, under Study : DC_STRAY_CURRENT_ATTACK 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 tree, select Component 1 (comp1)> Current Distribution, Boundary Element> Electrolyte Current Density 1
5. Right-click and choose Disable.

RESULTS

1. In the Model Builder window, click Study 1.
2. In the Home toolbar, click Compute

Electrode Potential vs. Adjacent Reference (cp) 1

1. In the Model Builder window, under Results click
2. Electrode Potential vs. Adjacent Reference (cp) 1.
3. In the Settings window for 3D Plot Group, locate the Plot Settings section.
4. Clear the Plot dataset edges check box.
5. Locate the Color Legend section. From the Position list, choose Left.
6. Click the Zoom Extents button in the Graphics toolbar.
7. In the Electrode Potential vs. Adjacent Reference (cp) 1 toolbar, click Plot

STUDY: DC_STRAY_CURRENT_ATTACK+ICCP

For the first study the Electrolyte Current Density was disabled in order to examine the impact of the leakage current to unprotected hull and propeller. A second study was carried out, to solve the model for the coexistence of current and cathodic protection

Step 1: Stationary

1. In the Model Builder window, under Study : DC_STRAY_CURRENT_ATTACK 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 tree, select Component 1 (comp1)> Current Distribution, Boundary Element> Electrolyte Current Density 1
5. Right-click and choose Enable.

6. ***RESULTS***

1. In the Model Builder window, click Study 1.
2. In the Home toolbar, click Compute

Electrode Potential vs. Adjacent Reference (cp) 1

1. In the Model Builder window, under Results click Electrode Potential vs. Adjacent Reference (cp) 1.
2. In the Settings window for 3D Plot Group, locate the Plot Settings section.
3. Clear the Plot dataset edges check box.
4. Locate the Color Legend section. From the Position list, choose Left.
5. Click the Zoom Extents button in the Graphics toolbar.
6. In the Electrode Potential vs. Adjacent Reference (cp) 1 toolbar, click Plot

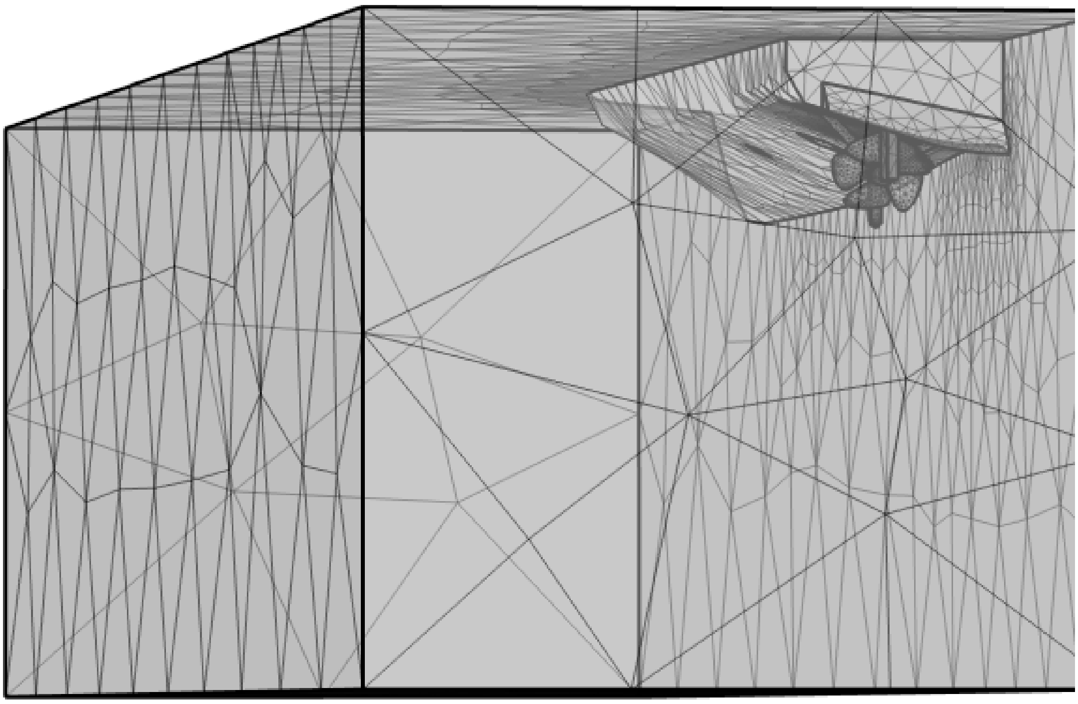


FIGURE 45: 3D VIEW OF MESH PLOT NODES

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