DEVELOPMENT OF GREEN CORROSION INHIBITORS FOR PROTECTION FROM INTERNAL CORROSION OF BURIED CROSS COUNTRY PIPELINES

A thesis submitted to the
University of Petroleum And Energy Studies Dehradun

For the Award of
Doctor of Philosophy
in
Chemical Engineering

BY
Anand Kumar Tewari

May 2019

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School of Engineering
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Dehradun – 248007: Uttarakhand

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DECLARATION

I declare that the thesis entitled "*Development of green corrosion inhibitors for protection from internal corrosion of buried cross country pipelines*" has been prepared by me under the guidance of Dr R P Badoni, Professor of Department of Chemical Engineering, University Of Petroleum and Energy Studies, Dehradun & Dr Kannan Chandrasekaran, Pipeline & Corrosion Research, Indian Oil Corporation Limited, Faridabad. No part of this thesis has formed the basis for the award of any degree or fellowship previously.

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THESIS COMPLETION CERTIFICATE

This is to certify that the thesis "Development of Green Corrosion Inhibitors for Protection from Internal Corrosion of buried cross country pipelines" by Anand Kumar Tewari, in partial completion of the requirements of award of Degree of Doctor of Philosophy (Engineering) is an original work carried by him under our joint supervision and guidance .

It is certified that work has not been submitted anywhere else for the award of any other diploma or degree of this or any other University

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ABSTRACT

Pipelines are important mode of transportation of liquid and Gas petroleum. There are cost effective, energy efficient environment friendly and reliable means of transportation, compared to other surface transportation mode. While there are many advantages of the pipeline system but the pipelines are buried underground so it faces corrosion challenge both from hostile surrounding soil as means of external corrosion and as well as internal corrosion due to corrosive nature of flowing fluid.

The suitable anticorrosion coating is applied on the external surface of pipeline in the factory before pipeline is welded and laid into underground trenches. In the factory while coating, both ends of pipe, are left uncoated for facilitating the girth weld for pipeline construction. After field welding, the joints are coated to have uniformity and monolith protection against corrosion when laid underground. In addition to the coating of the pipeline which saves pipeline from hostile soil attack, the impressed current based cathodic protection system, is also applied to the underground pipeline. The above two protections are meant for preventing external corrosion of the pipeline.

However, corrosion due to flowing fluid and associated water, sulphur, carbon dioxide and other impurities etc., causes the internal corrosion of the pipeline. For prevention of the pipeline from internal corrosion, a chemical known as corrosion inhibitor (CI) is injected in small doses normally at originating pump station of cross country pipeline. The corrosion inhibitor forms a protective layer on inner surface of the pipeline, so as to nullify the effect of corrosive nature of water and other corrosive elements entrapped in hydrocarbon. The use of corrosion inhibitors constitutes, most economical ways to mitigate the internal

corrosion, protect metal surfaces against corrosion and prolong the life of pipeline.

Basically there are two types of corrosion inhibitors, used for prevention of internal corrosion.

1. Inorganic compounds
2. Organic compounds

There are inorganic anions providing passivation / protection of metal surfaces through their incorporation into the oxide layer. The most widely used of these are: Chromate (CrO_4), Nitrate (NO_2), Molybdate (MoO_3), Phosphate (H_2PO_3) and Silicates etc.

However, conventional corrosion inhibitor makes use of chemical substances consisting of heavy metals and inorganic chemical substances such as chromates and phosphates that are harmful to the human health. Inorganic corrosion inhibitors containing arsenic etc. are harmful in nature and known to induce multiple organ damage at low concentration. High concentration of chromium can lead to DNA damage. In addition, presently there are many organic inhibitors belonging to different chemical families like Fatty Amides, Pyridines, Imidazole and other azoles. While many organic and inorganic compounds have shown good performance as Corrosion Inhibitors for different metals and alloys but many of these compounds are toxic and do not fulfill the emerging requirements of environment standard. Considering the limitations of the present. The present research work mainly focusses on various types of the plant products, which have been studied under actual laboratory condition, for their corrosion inhibition properties. The plants extracts are excellent and viable alternatives for chemical corrosion inhibitors, because of their availability, ease of handling and bio degradability. These extracts are obtained in simple way with minimum purification requirement.

These plant extracts are generally obtained through extraction process using high selectivity, low cost & low toxicity solvents that are widely available.

The extracts contain variety of natural oils, tannins, pigments, steroids, terpenes and flavones as known to have as potential corrosion inhibition properties. These products are generally the basic building blocks suitable as Green Corrosion Inhibitors (GCI). The extensive literature search was made in the domain of GCIs for their corrosion inhibiting properties on various metal and alloys used in various industries and process plants, the focus of the study has been synthesis, characterization, and development of select GCIs for petroleum pipeline applications. Accordingly, laboratory scale study of the plant extracts of Neem, Karanjia, Jatropha, Hibiscus and Eucalyptus, has been carried out. The characterization of these plant produce Neem, Jatropha, Karanjia, has been undertaken, in detail according to the industry codes, testing protocols and practices. In addition, limited study has also been undertaken on Hibiscus flowers and Eucalyptus leaves. The study was also supplemented to understand the impact of small doses of antioxidant along with plant produced corrosion inhibitors, for further enhancing their corrosion mitigating properties. The study also included impact of the optimum doses of these green corrosion inhibitors on the petroleum product characteristics.

The extracts of Neem, Karanjia and Jatropha were prepared after drying and de-coating manually. The kernels of seeds were crushed into small pieces for better extraction of oil and filled in soxhlet apparatus. The hexane which is most favorable commercial medium for oil extraction has been used. The hexane is refluxed at 65-70 $^{\circ}$C for 8-10 hrs and distilled under Rota evaporator to recover hexane and oil extracts. In general yield of 30-40 % is obtained.

The characterization has been done to understand chemical / molecular structure and correlate their performance as corrosion inhibitors. The physical study indicates that green corrosion inhibitors are soluble in hydrocarbon and insoluble and non-dispersible in water phase. From the density and viscosity values, the inference on the flow-ability and pump-ability is drawn. The density and viscosity indicates that these green corrosion inhibitors are comparable with hydrocarbons and can be easily pumped though dosing pump.

The characterization of the above extracts was done to understand the molecular structure of green corrosion inhibitors. It was undertaken using Infrared (IR) spectrometer, Nuclear Magnetic Resonance (NMR) spectrometer as well as using Raman Spectroscopy.

The physical characterization of extracts indicates that

- Extracts are denser than hydrocarbon. The viscosities indicate that diluted solutions of extracts are pumpable into pipeline transportation system
- The Neem and Karanjia extracts are slightly less acidic than Jatropha extracts.

The chemical analysis of the extract, indicates that

- Extracts are triglycerides of fatty acids with average acid chain of 17.5-18. The fatty acids can be saturated, mono unsaturated, di-unsaturated or poly unsaturated.
- The Jatropha extracts mainly consist of Oleic acid (unsaturated) with other saturated acids in small quantities. It is odorless and colorless oil.
- Karenjia and Neem extracts were observed to have more saturated acids.
- Karenjia extracts is seen to have significant poly unsaturated linoleic acids along with phenolic and naphthenic components.
- The IR spectra show a sharp band at 3000cm^{-1} which indicates presence of Olefinic C-H mainly due to presence of oleate moieties in all extract samples
- From the Raman spectroscopy, the presence of unsaturated long hydro carbon chain (1655cm^{-1}) and weak signal for Ester (1740cm^{-1}) could be inferred in all the samples. The Karenjia extracts shows the presence of aromatics which are not seen in Jatropha and Neem Extracts.
- The Oleate Ester Moieties can help in formation of thin films on metal surface as polar compounds

- The Carbonyl Group C=O, presence of free fatty acids especially the saturated type and Aromatic compounds can enable the film-formation by reacting with metal surface.

In the present study, performance evaluation of identified green corrosion inhibitors was undertaken at Indian Oil Corporation, Research & Development Division Laboratory at Faridabad. The laboratory is modern and equipped with all necessary latest equipment and supporting infrastructure. All the tests right from simplest testing, like ASTM immersion test, which is a static test, was conducted to study impact of corrosion on doped samples. The weight loss of immersed coupon determines the effectiveness of corrosion inhibitor film. In addition, using appropriate medium of petroleum fuel, the corrosion rating as per spindle test ASTM D 665 modified as per NACE TM 0172, provides the industry acceptable procedure for corrosion mitigation property of corrosion inhibitor. This test being static doesn't represent the pipeline flow condition. Further, a wheel test which simulates the dynamic flow condition of pipeline is also carried out. The efficacy of corrosion inhibitor is assessed in terms of percentage inhibition efficiency for a given doses rate.

$I_{Eff} = (R_0-R_i)/ R_0 \times 100$ where R_0 is the corrosion rate without inhibitor and R_i is corrosion rate with inhibitor.

In this work both quantitative and qualitative assessment of selected green corrosion inhibitor is undertaken. The quantitative evaluation included spindle test, rotating disc, rotary wheel test, rotating cage type electrode test besides static immersion test in the laboratory in the simulated condition. In the qualitative testing the focus area is electrochemical characterization which included Electrochemical Impedance Spectroscopy (EIS) and Liner Polarization Resistance (LPR) studies.

In this research work Aviation Turbine Fuel (ATF) has been considered as hydro carbon medium for the entire study. The test coupons of required carbon steel material were selected as per standardized testing protocol. In addition, impact of required doses of Green Corrosion Inhibitor doses on the fuel characteristics, was also studied for MS, SKO and HSD and results are observed to be favorable.

The doses rates of the selected green corrosion i.e. Hibiscus, Eucalyptus, Neem, Jatropha and Karanjia were studied using above mentioned g spindle test method protocol. The range of doses included for Hibiscus from 200-8000ppm, Eucalyptus 1500-8000ppm, Neem 200-2500ppm, Jatropha 100-8000ppm, Karanjia 100-8000ppm. The wheel test was also carried with addition of 2 % and 10 % volume of 3.5 % of Sodium Chloride (NaCl) as representative of the pipeline condition to make assessment of percentage of inhibition of coupon under different scenario. The performance rating of the inhibitors at different concentration was thoroughly studied. The inhibition efficiency of Green Corrosion Inhibitors was evaluated for various combination and doses of the GCIs with 10 % volume of 3.5% NaCl and 7 % NaCl solutions also.

The tests included the short term, medium term and long term tests. The testing duration was right from few hours to long duration tests of more than 25 days also. The static test was typically for 550- 600hours whereas coupons in long duration tests were evaluated after 1150hours. Apart from these physical laboratories based studies in representative condition of the pipelines, the evaluation of these identified green corrosion inhibitors were also carried out in another laboratory based on Electro Chemical Examination. The electro chemical evaluation of corrosion susceptibility of a given medium can quickly indicate the propensity of medium to cause corrosion at its natural potential as well range of potentials right from anodic to cathodic levels. The electrochemical examination is non-transient steady state experimentation. It may not give quantitative but certainly gives directional performance of GCIs. The test conducted in the process included Electro Chemical Impedance Spectroscopy (EIS) and Linear Polarization Resistance (LPR). The corrosion current density and inhibition efficiency can be worked out using these techniques. The corrosion current density values obtained from Galvanic cells and polarization measurement using Tafel extrapolations. The Linear Polarization resistance is a quick, non-destructive testing technique commonly used for evaluation of corrosion rates. LPR requires the medium to be conductive. The test is conducted as per ASTM G 59 and ASTM G 102. To overcome the challenge of ensuring conductivity for studies, inhibitor film on coupon was made and retained by dipping in inhibited hydrocarbon and dried at 60 °C. Thereafter coupons were dipped in 3.5 % brine solution for better electrochemical response. However, due to discontinuation inhibitor film on the coupon, mainly on account of porosity and surface tension, the studies were impaired. In order to have conductive aqueous medium with dispersed inhibitor to facilitate electro chemical examination, a micro emulsion with commercial surfactant (Titron-X) was selected. Initially 5ml surfactant with 5ml neat GCI in 50ml demineralized water used for sonication for 10 minutes. The stable solution could be made with good dispersion of GCI in water medium. The content of surfactant was further optimized and stable emulsions were formed with 0.5ml of surfactant for 5ml inhibitor and 50ml DM water. The LPR studies were carried out on aqueous micro emulsion for one of the GCI Jatropha at three different temperatures 30 °C, 50 °C and 70 °C.

The results and discussion of the above experiments are summarized as under:

Under the Laboratory performance evaluation, Spindle tests were under taken with Un-doped ATF. It was observed to have worst rating of grade ‘E’ with extensive corrosion pits on spindle. Hibiscus and Eucalyptus compositions were observed to have limited corrosion inhibition potential. The Neem, Karanjia and Jatropha composition have shown good corrosion inhibition potential. These GCIs were evaluated at 1600ppm, 1400ppm and 1200ppm respectively for meeting minimum specified rating of B^{++} as per industry norms. This result obtain through the tests, corroborates effectiveness of green corrosion inhibitors.

The oxidant was added in small doses for doses optimization study of Green Corrosion Inhibitors. It was observed that both phenolic and amine based oxidants, supplement corrosion inhibition tendency of Neem as corrosion inhibitor. An addition of 3000ppm of antioxidant was effective to the extent that Neem extract doses reduced to 100ppm for B^{++} criteria.

From the spindle test, it is deduced that surfactant has synergistic effect on the performance of all the three green corrosion inhibitors. A 50ppm addition of surfactant is enough to reduce the doses of Neem by 200ppm, however for the same reduction of optimum doses of Karenjia and Jatropha, an addition of surfactant doses to the extent of 200ppm and 100ppm respectively, is required.

The static test indicates no weight loss even after 550hours of exposure to ‘E’ rated ATF with or without inhibitor. This implies that corrosion does not occur in neat hydro carbon solution.

In the rotary wheel test ATF with 2 % vol. of aqueous 3.5 % of NaCl in presence of all three inhibitors at their respective optimum doses were used, the corrosion rates decreased by more than order of magnitude. Among the three Neem and Karanjia provided lower corrosion rate compared to Jatropha.

Percentage inhibition efficiency of all three green corrosion inhibitors indicated higher value more than 90% in the wheel test. However, Neem and Karanjia indicated more than 95 % efficiency. The corrosion efficiency of Neem is further validated by very low Fe component observed to have been separated in the brine phase towards the end of wheel test. The similar results obtained when tested with 10 % Vol. of 3.5 % brine solution. In case of 10 % Vol. of 7 % brine solution, corrosion rates are seen to increase and inhibition efficiency got decreased. The test clearly validates the fact that corrosion inhibition efficiency of all three green corrosions inhibitors Neem, Karanjia and Jatropha, under turbulent and dynamic flow condition is much better and which is also a representative of actual pipeline conditions.

The Electro Chemical Characterization was done under Linear Polarization Resistance (LPR) studies conducted on various concentrations of the potential green corrosion inhibitors both at room temperature and at varying temperatures the following are inferred:

The Tafel response of all the inhibitors indicate that the E_{corr} values representing the equilibrium corrosion potential of the steel coupon in the aqueous micro emulsion of the inhibitor shifts more towards anodic values with the increase in concentration. This aspect signifies the potential for all the inhibitors to form more stable films with the increase in concentration.

The corrosion current (I_{corr}) values for all the inhibitors show a decreasing trend in general with the increase in concentration. However, the rate of decrease in corrosion current falls sharply at concentrations above the optimum concentration as established by the subsequent spindle test.

Equivalent concentration of Neem and Karenjia oil as corrosion inhibitors clearly indicates much lesser corrosion current compared to Jatropha.

The Corrosion Inhibition Efficiency increases in general with the increase in concentration. However, Inhibitor efficiency saturates at optimum concentration level, as established by the subsequent spindle test. The Neem and Karenjia oil, as corrosion inhibitors exhibit higher inhibition efficiency of around 60% as compared to around 50% efficiency of Jatropha oil under electrochemical examination.

The high temperature LPR studies on Jatropha oil, has indicated that an increase in corrosion current with the increase in temperature. This is attributed to the thermal activation of the electrochemical process in which the mobility of the ions in general increases causing the instability of the inhibitor film and its passivation. The Inhibition efficiency is also seen to decrease with the increase in temperature.

The potential Neem extract studied in this work as a green corrosion inhibitor is expected to provide the inhibition of metal surfaces that are covered by the adsorbed water molecules. The inhibitor recat with replacing water molecules with organic molecules

Establishment of the adsorption isotherm can describe the adsorption mechanism of the corrosion inhibitor and also information on the nature of metal inhibitor interaction. Adsorption depends on the charge and nature of the metal surface, adsorption of solvent and other ionic species, electrochemical potential at solution interface and the temperature of the corrosion reaction. The adsorption isotherms can be Langmuir, Frendluich, Temkin, Flory-Huggins, Dhar–Flory-Huggins, Bockris-Swinkles etc.

The studies on adsorption isotherm for Neem extract as a corrosion inhibitor indicate a linear relationship of C/Θ values with C values for each of the test temperatures. It is therefore, inferred that Neem extract obeys Langmuir adsorption isotherm at all the temperatures at which tests have been carried out.

The thermodynamic properties of the adsorption process of Neem extract as corrosion inhibitor have been calculated for the various temperatures at which tests have been conducted. A negative value of ΔG^{o}_{ads} indicates a spontaneous adsorption, strong interaction between the inhibitor molecules and the metal surface. Generally, values of ΔG^{o}_{ads} upto -20kJ/mol are consistent with electrostatic interactions between charged molecules and charged metal surface indicating physical adsorption. A very small value of K_{ads} further confirms that the inhibitor molecules are physically adsorbed on the steel surface.

An exothermic process (negative ΔH^{o}_{ads}) indicates adsorption to be physisorption or chemisorption while in an endothermic process (positive ΔH^{o}_{ads}) the adsorption is necessarily chemisorption. In case of Neem extract, the negative values of ΔH^{o}_{ads} clearly supports the physical adsorption phenomenon and further supports the observations made from ΔG^{o}_{ads} and K_{ads}. Negative values of ΔS^{o}_{ads} further implies that the rate determining step in the corrosion inhibition step involves association rather than dissociation step reducing the disorder in the system as the metal tends to corrode to form activated complex.

The potential green corrosion inhibitors derive their inhibitive characteristics from the ability of their molecules to adsorb with a polar group acting as the nodal centre for adsorption process. The adsorbed film provides a barrier between the metal and the corrodent. The efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers. The resultant inhibitive properties are a reflection of their performance under static and dynamic flow conditions encountered in pipeline applications.

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TABLE OF CONTENTS

1 CHAPTER 1: INTRODUCTION 1

1.1 INTRODUCTION.. 2
1.2 INDIA'S ENERGY SCENARIO 3
1.3 OIL REFINING IN INDIA.. 5
1.4 MODES OF TRANSPORTATION AND DISTRIBUTION OF PETROLEUM PRODUCTS 7
1.5 EXPANSION PLANS OF CROSS COUNTRY PIPELINE NETWORK IN INDIA.. 9
1.6 PIPELINE – MATERIALS OF CONSTRUCTION 15
1.7 CORROSION PHENOMENON 18
1.8 TYPES OF CORROSION.. 19
1.9 CORROSION IN THE PETROLEUM PIPELINES 23
1.10 MONITORING AND MEASUREMENT OF INTERNAL CORROSION IN THE PIPELINES.. 27
1.11 CORROSION INHIBITOR FOR CORROSION CONTROL 32
1.12 PROBLEM STATEMENT 37
1.13 ORGANIZATION OF THE THESIS.. 40

2 CHAPTER 2: LITERATURE SURVEY, GAP AREAS & RESEARCH OBJECTIVE 42

2.1 INTRODUCTION.. 43
2.2 LITERATURE REVIEW... 43
2.3 INFERENCES FROM THE ABOVE SURVEY.................................... 65
2.4 GAP AREAS AND RESEARCH OBJECTIVES 66

3 CHAPTER 3: RESEARCH METHODOLOGY 68

3.1 REASEARCH OBJECTIVE.. 69
3.2 RESEARCH PROCESS... 70
3.3 DESCRIPTION OF RESEARCH METHODOLOGY 71
3.4 SELECTION OF TEST MEDIA.. 71
3.5 SELECTION OF PLANTS GREEN CORROSION INHIBITOR 72

3.6 EXTRACT PREPARATION & CHARACTERIZATION 72
3.7 SELECTION OF TESTING PROCESS & TEST PROCEDURE 73
3.8 ORGANIZATION OF THE STUDY 75
3.9 SIGNIFICANCE OF THE STUDY 75

4 CHAPTER 4: EXTRACTION AND PHYISICO- CHEMICAL CHARECTERISATION OF GREEN CORROSION INHIBITOR............. 77

4.1 INTRODUCTION.. 78
4.2 EXTRACTION OF GREEN CORROSION INHIBITOR FROM PLANT PRODUCES 79
4.3 PHYSICO - CHEMICAL CHARACTERIZATION OF GREEN CORROSION INHIBITORS 80
4.4 PHYSICAL PROPERTIES 80
4.5 CHEMICAL CHARACTERIZATION 82
4.6 RESULTS AND DISCUSSIONS: 88

5 CHAPTER 5: PERFORMANCE EVALUATION OF GREEN CORROSION INHIBITORS *PART ONE (PHYSICAL)*.............................. 90

5.1 INTRODUCTION.. 91
5.2 ROTATING SPINDLE TEST - ASTM D669 (NACE TM 0172) 92
5.3 STATIC IMMERSION TEST 95
5.4 ROTATING WHEEL TEST 96
5.5 COMPATIBILITY OF THE POTENTIAL GREEN CORROSION INHIBITORS WITH TRANSPORTATION FUELS 98
5.6 RESULTS AND DISCUSSION:... 99

6 **CHAPTER 6: PERFORMANCE EVALUTAION OF GREEN CORROSION INHIBITORS –*PART TWO (ELECTRO CHEMICAL)* 132**

6.1 INTRODUCTION.. 133
6.2 ELECTROCHEMICAL MEASUREMENT OF CORROSION RATES 133
6.3 MICRO EMULSION OF GCI FOR ELECTROCHEMICAL STUDIES 138
6.4 ELECTROCHEMICAL TEST SETUP.. 138
6.5 ELECTROCHEMICAL IMPEDANCE STUDIES.............................. 140
6.6 LINEAR POLARIZATION RESISTANCE STUDIES....................... 142
6.7 CORROSION INHIBITION MECHANISM OF NEEM EXTRACT . 156

7 CHAPTER 7: CONCLUSIONS AND FUTURE RESEARCH............ 163

7.1 CONCLUSION & SUMMARY OF WORK.. 164
7.2 FUTURE RESEARCH.. 170
7.3 BRIEF BIO DATA OF AUTHOR.. 171

8 REFERENCES 174

LIST OF ABBREVIATIONS

LPG:	Liquefied Petroleum gas
CI:	Corrosion Inhibitor
PPAC:	Petroleum Planning & Analysis Cell
LNG:	Liquefied Natural gas
MFL:	Magnetic Flux leakage
IR Spectroscopy:	Infrared Spectroscopy
NMR:	Nuclear Magnetic Resonance
NACE:	National Association of Corrosion Engineers
TAN:	Total Acid Number
LPR:	Linear Polarization Resistance
HDI:	Human Development Index
MMT:	Million Metric Tonnes
BCM:	Billion Cubic Meter
MMTPA:	Million Metric Tonnes per Annum
GW:	Gigawatt
HPCL:	Hindustan Petroleum Corporation Limited
BPCL:	Bharat Petroleum Corporation Limited
MoPNG:	Ministry of Petroleum and Natural Gas
PMUY:	Prime Ministers Ujwala Yojana
IOCL:	Indian Oil Corporation Limited
CTF:	Central Tank Farm
ONGC:	Oil & Natural Gas Corporation
CPF:	Central Processing Facility
CPCL:	Chennai Petroleum Corporation Limited
OIL:	Oil India Limited

HMEL:	HPCL Mittal
BORL:	Bharat Oman Refineries Limited
ATF:	Aviation Turbine Fuel
GAIL:	Gas Authority of India Limited
MMSCMD:	Million Metric Standard Cubic Meter per Day
RGTIL:	Reliance Gas Transportation Industry Limited
RGPL:	Reliance Gas Pipeline Limited
AGCL:	Assam Gas Company Ltd
DNPL:	Duliajan Numaligarh Pipeline Limited
ASME:	American Society of Mechanical Engineers
GDP:	Gross Domestic Product
SCC:	Stress Corrosion Cracking
MIC:	Microbiologically Influenced Corrosion
SRB:	Sulfate Reducing Bacteria
IOB:	Iron Oxidizing Bacteria
HBB:	Heterotrophic Biofilm forming Bacteria
CP:	Cathodic Protection
OISD:	Oil Industry Safety Directorate
KL:	Kiloliter (equivalent to cubic meter)
PSP:	Pipe to Soil Potential
DCVG:	Direct Current Voltage Gradient
CAT:	Current Attenuation Test
ER:	Electrical Resistance
PIG:	Pipeline Inspection gauge
IPS:	Instrumented Pig Survey
ILI:	In Line Inspection
NDT:	Non Destructive Testing
POD:	Probability of Detection
HAZ:	Heat Affected Zone
EIS:	Electrochemical Impedance Spectroscopy

ASTM: American Standard of Testing Material
DNA: Deoxyribonucleic acid
GCI: Green Corrosion Inhibitors
SEM: Scanning Electrode Microscope
ANOVA: Analysis of Variance
CSIR: Council of Scientific and Industrial Research
ISO: International Organization for Standardization
EFM: Electrochemical Frequency Modulation
EDX: Energy Dispersive X-Ray
DFT: Density Functional Theory
MD: Molecular Dynamics
MS: Mild Steel
XSL: Xanthanium Strumarium Leaves
FTIR: Fourier transform Infrared
GCMS: Gas Chromatography Mass Spectroscopy
BP: British Petroleum
CAPEX: Capital Expenditure
GLV: Green Leafy Vegetable
CR: Corrosion rate
IE: Inhibitor Efficiency
FESEM: Field Emission Scanning Electron Microscopy
AEG: Aqueous extract of Ginger
OCP: Open Circuit Potential
EDAX: Energy dispersive X-ray spectroscopy
QS: Q235 steel
TO: Turbinaria Ornata
MBB: Marine Biofiliming Bacteria
HPB: Human Pathogenic Bacteria
AISI: American Iron & Steel Institute
SVET: Scanning Vibrating Electrode Technique

AFM:	Atomic Force Microscopy
JC:	Jatropha Curcas
BS:	Bharat Stage
HSD:	High Speed Diesel
DRA:	Drag Reducer Additive
CCD:	Charged Coupled Device
UNS:	Unified Numbering System
API:	American Petroleum Institute
RPM:	Rotation per Minute
PPMA:	Poly Methyl Methacrylate
DM water:	Demineralized water

LIST OF FIGURES

Figure 1.1: Global Primary Energy Consumption by Source 2
Figure 1.2: India Energy consumption 2017 (Source Ready Reckoner PPAC India) 3
Figure 1.3: Comparison of domestic production and import of LNG in India 5
Figure 1.4: Types of fuel to meet energy demand & projections 5
Figure 1.5: Major refineries of India... 7
Figure 1.6: Petroleum pipeline network across the country (PPAC, 2018).......... 10
Figure 1.7: Expenditure in various activities for corrosion assessment & mitigation 18
Figure 1.8 Pitting Corrosion on the External Pipeline surface 20
Figure 1.9: Seam failure of Crude Oil Pipeline due to corrosion/ micro cracks in Northern India causing crude oil spillage 24
Figure 1.10: Crude Oil Spillage in irrigated field on account of corrosion leakage. Seam opening of pipeline on account of corrosion... 25
Figure 1.11: Schematic of Axial MFL Based Inline Inspection 30
Figure 1.12 Schematic of Axial MFL Based Inline Inspection 31
Figure 3.1: Research Process Flow Diagram.. 70
Figure 3.2: Characterization of the Green Corrosio Inhibitor............................. 73
Figure 4.1 Seeds of Jatropha, Neem and Karenjia, Hibiscus flower and Eucalyptus leaves.. 78
Figure 4.2: Schematic of Extraction of Oil from Jatropha, Karenjia and Neem seeds 79
Figure 4.3: M/s Anton Paar make DMA 4100 M Density meter......................... 81
Figure 4.4: M/s TA make AR 2000Ex model Rheometer 81
Figure 4.5: M/s Shimadzu make IR spectrometer 83
Figure 4.6: IR spectrum of extract from Jatropha(J), Karenjia(K) &Neem (N) ... 83
Figure 4.7: M/s Brucker make 1H Proton Nuclear Magnetic Resonance (NMR) Spectrometer 84
Figure 4.8: ^{1}H Proton NMR spectrum of extract of Jatropha (J), Karenjia (K) and Neem (N) 85
Figure 4.9: M/s Horiba make Raman Confocal Microscope 86
Figure 4.10: Raman microscope output of extract of Jatropha............................ 86
Figure 4.11: Raman microscope output of extract of Karenjia............................ 87
Figure 4.12: Raman microscope output of extract of Neem 87
Figure 5.1: NACE TM0172 Spindle test setup... 110
Figure 5.2: Dimensional details and construction of beakers as per NACE TM0172.. 110

Figure 5.3: Dimensional details of carbon steel spindles as per NACE TM0172 111
Figure 5.4: Grinding and polishing equipment 111
Figure 5.5: Microstructure of Carbon steel coupon showing equiaxed Ferrite and Pearlite (X500) 111
Figure 5.6: Rotating Wheel Test setup 112
Figure 5.7: Worst rating of grade 'E' with very extensive corrosion pits on the spindle 112
Figure 5.8: Ratings of spindle with Hibiscus at 8000ppm 113
Figure 5.9: Ratings of spindle with Eucalyptus at 5000ppm 114
Figure 5.10: Ratings of spindle with Spindles for optimization of dosages for Neem at 1600ppm 115
Figure 5.11: Spindles for optimization of dosages for Karenjia at 1400ppm 116
Figure 5.12: Spindles for optimization of dosages for Jatropha at 1200ppm 117
Figure 5.13: Spindles for optimized dosages for Neem at 1600ppm 118
Figure 5.14: Spindle for optimized dosages for Karenjia at 1400ppm 118
Figure 5.15: Spindle for optimized dosages for Jatropha at 1200ppm 118
Figure 5.16: Performance ratings of the inhibitors at different concentrations 119
Figure 5.17: Performance rating of combination of Neem with Aminic antioxidants at different concentrations 120
Figure 5.18: Spindles showing the effect of Antioxidant on Neem extract 120
Figure 5.19: Spindles showing the effect of Phenolic antioxidant on Neem extract 121
Figure 5.20: Spindles showing the effect of Aminic antioxidant on Neem extract 121
Figure 5.21: Performance rating of combination of Neem with Antioxidants at different concentrations 122
Figure 5.22: Performance rating of combination of Neem with surfactant at different concentrations 122
Figure 5.23: Performance rating of combination of Jathopha with surfactant at different concentrations 123
Figure 5.24: Performance rating of combination of Karenjia with surfactant different concentrations 123
Figure 5.25: Performance rating of combination of Green Corrosion Inhibitors with Surfactants at different concentrations 124
Figure 5.26: Test bottles containing coupons at the end of 550hours of static tests for 1200ppm of Jatropha 125
Figure 5.27: Test bottles containing coupons at the end of 550hours of static tests for 1600ppm of Neem 125

Figure 5.28: Test bottles containing coupons at the end of 550hours of static tests for 1400ppm of Karenjia 126
Figure 5.29: Static test bottles of reference ATF with coupons at the end of 550hours of exposure 126
Figure 5.30: Corrosion rates of Green Corrosion Inhibitors with 2% volume of 3.5% NaCl 127
Figure 5.31: Inhibition Efficiency of Green Corrosion Inhibitors with 2% volume of 3.5% NaCl 127
Figure 5.32: Wheel test bottles after 1150hours of test 128
Figure 5.33: Coupons after testing with 2% volume of 3.5% NaCl after 1150hours 128
Figure 5.34: Corrosion rates of Green Corrosion Inhibitors with 10% volume of 3.5% NaCl 129
Figure 5.35: Inhibition Efficiency of Green Corrosion Inhibitors with 10% volume of 3.5% NaCl 129
Figure 5.36: Coupons after testing with 10% volume of 3.5% NaCl after 600hours 130
Figure 5.37: Corrosion rates of Green Corrosion Inhibitors with 10% volume of 7.0% NaCl 130
Figure 5.38: Inhibition Efficiency of Green Corrosion Inhibitors with 10% volume of 7.0% NaCl 131
Figure 5.39: Coupons after testing with 10% volume of 7.0% NaCl after 430hours 131
Figure 6.1: Typical Nyquist and Bode plots for different electrochemical equivalent circuits 137
Figure 6.2: M/s AUTOLAB make Electrochemical Test set up 139
Figure 6.3: Surface and sectional microstructure of Carbon steel coupon showing normal Ferrite and Pearlite (X500) 139
Figure 6.4: Nyquist plot of solution without Inhibitor 140
Figure 6.5: Nyquist plot of solution with 1200ppm of Jatropha Extract 141
Figure 6.6: Nyquist plot of solution with 1400ppm of Karenjia Extract 141
Figure 6.8: Nyquist Plot of solution with 1600ppm of Neem Extract 141
Figure 6.9: Open Circuit Potential vs. Time for the aqueous 3.5% NaCl solutions doped with potential green corrosion inhibitors at their optimized dosage rates 147
Figure 6.10: Tafel plots of solutions with different concentrations of Jatropha extract 147
Figure 6.11: Tafel plots of solutions with different concentrations of Karenjia extract 148

Figure 6.12: Tafel plots of solutions with different concentrations of Neem extract 148
Figure 6.13 Typical Tafel slopes for optimized concentration of (a) Neem, (b) Karenjia and (c) Jatropha extracts........ 149
Figure 6.14: Typical Tafel curves without inhibitor studied at different temperatures........ 149
Figure 6.15: Typical Tafel curves of 600ppm Jatropha extract as studied at different temperatures........ 150
Figure 6.16: Typical Tafel curves of 1200ppm Jatropha extract as studied at different temperatures........ 150
Figure 6.17: Tafel plots of solutions with Neem 600ppm inhibitor at different temperatures........ 151
Figure 6.18: Tafel plots of solutions with Neem 1200ppm inhibitor at different temperatures........ 151
Figure 6.19: Tafel plots of solutions with Neem 1600ppm inhibitor at different temperatures........ 152
Figure 6.20: Langmuir Adsorption plots for steel in aqueous NaCl medium with different concentrations of emulsified Neem oil extract at three different temperatures........ 152
Figure 6.21: Arrhenius plots of the corrosion rate for steel in aqueous medium in absence and presence of Neem oil extract........ 153
Figure 6.22: Plot of corrosion current with concentration of the potential green corrosion inhibitors........ 153
Figure 6.23: Plot of Percentage Inhibition efficiency with concentration........ 154
Figure 6.24: Plot of corrosion current with temperature for various concentrations of Jatropha Inhibitor........ 154
Figure 6.25: Plot of Percentage Inhibition efficiency with temperature for various concentrations of Jatropha Inhibitor........ 155
Figure 6.26: Plot of corrosion current with temperature for various concentrations of Neem Inhibitor........ 155
Figure 6.27: Plot of Percentage Inhibition efficiency with temperature for various concentrations of Neem Inhibitor........ 156

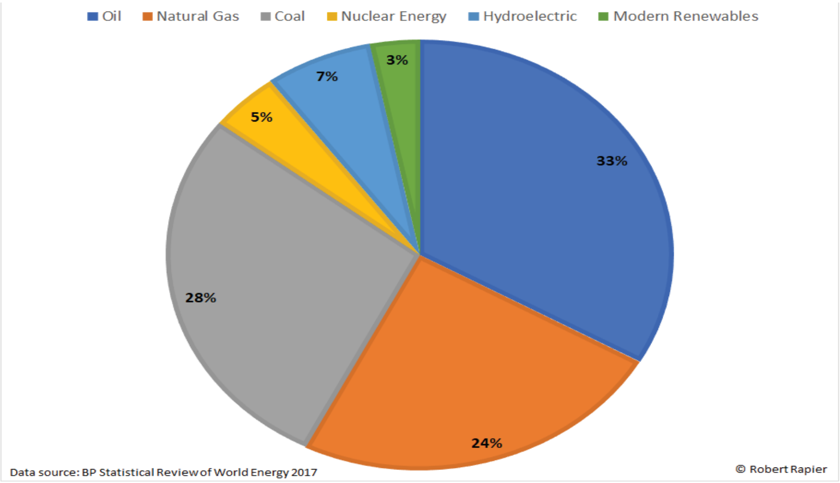
LIST OF TABLES

Table 1-1: LNG terminal in India (PPAC, 2018) 4
Table 1-2: Proposed refining expansion plan of India... 6
Table 1-3: Major Crude Oil Pipeline network in India (PPAC, 2018) 11
Table 1-4: Major Petroleum Product Pipelines in India (PPAC, 2018)............... 12
Table 1-5: Major LPG pipelines in India (PPAC, 2018) 14
Table 1-6: Major Natural Gas Pipelines in India (PPAC, 2018) 14
Table 4-1: Summary of Plant extracts studied... 89
Table 4-2: Physical properties and TAN values of extracts 89
Table 5-1: Qualitative Ratings of NACE TM0172 Spindle test......................... 102
Table 5-2: Dosage rates of Green Corrosion Inhibitors studied 102
Table 5-3: Composition of coupons.. 102
Table 5-4: Static Test results... 103
Table 5-5: Wheel test results for 2% volume of 3.5%NaCl 104
Table 5-6: Wheel test results for 10% volume of 3.5 %NaCl 105
Table 5-7: Wheel test results for 10% volume of 7.0%NaCl 106
Table 5-8: Analysis of separated Brine phase for ‘Fe’ content 106
Table 5-9: Comparative characteristics of Kerosene fuel doped with optimized dosages of potential Green Corrosion Inhibitors 107
Table 5-10: Comparative characteristics of Motor Gasoline fuel doped with optimized dosages of potential Green Corrosion Inhibitors 108
Table 5-11: Comparative characteristics of Diesel fuel doped with optimized dosages of potential Green Corrosion Inhibitors 109
Table 6-1: Composition of LPR coupons 139
Table 6-2: Computed Resistance of the passivating film from EIS studies 140
Table 6-3: Summary of Room temperature LPR results of the green corrosion inhibitor extracts 144
Table 6-4: Summary of the high temperature LPR test on Jatropha.................. 145
Table 6-5: Summary of the high temperature LPR test on Neem...................... 146
Table 6-6: Thermodynamic functions for adsorption of emulsified Neem oil Extract in 3.5 % NaCl aqueous medium at different temperatures.................... 159
Table 6-7: Activation energies for adsorption of Neem extract on steel in emulsified aqueous 3.5 % NaCl solutions 159

Chapter 1: INTRODUCTION

1.1 INTRODUCTION

Energy is key indicator of standard of living of citizens of any country. It has direct correlation with per capita consumption of energy and Human Development Index (HDI). Global energy market is going through the transition phase. Rapid growth and prosperity of a nation is closely associated with growth in energy demand. Now the demand drivers are Asia and developing countries. The energy mix world over is showing trend towards cleaner and lower carbon fuels driven by environmental considerations. The global trends clearly indicate that share of coal and oil in the primary energy mix would be substantially reduced and replaced by cleaner fuels like gas and renewable (Fig.1.1).



Data source: BP Statistical Review of World Energy 2017

Figure 1.1: Global Primary Energy Consumption by Source

The present primary energy mix of the world as per British Petroleum statistical review of world energy 2017 (British Petroleum, 2017), shows that the oil dominate the scenario, followed by coal and natural gas which has a share of 24%.

As per this report the Indian energy consumption is projected to grow by more than 4.2 % per annum which is faster than all the major economies in the world. It is also projected that by 2020 Indian will overshoot China in terms of the energy consumption.

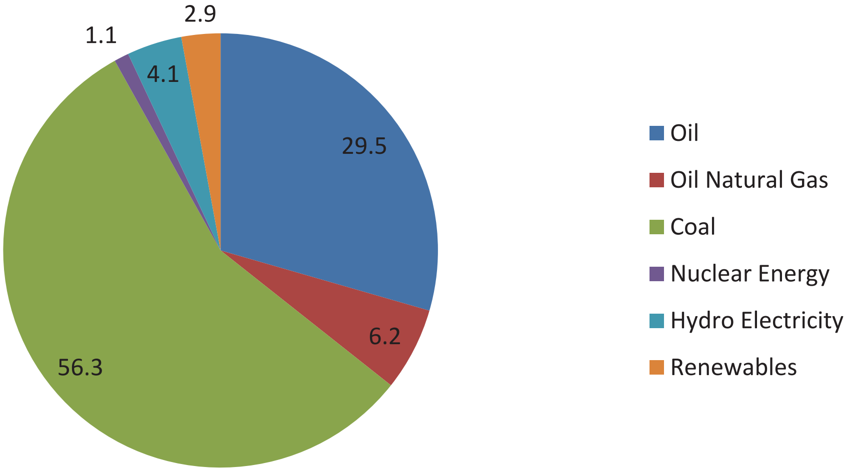


Figure 1.2: India Energy consumption 2017 (Source Ready Reckoner PPAC India)

1.2 INDIA'S ENERGY SCENARIO

India's share of the global energy is set to rise from the current 5% to 11% by 2040 emphasizing the rapid transformation and unprecedented growth in the energy sector. India is meeting its larger requirement of fuel through import of crude oil (Fig.1.2) with the import dependency in the range of 82%. In the year 2017-18, India produced nearly 36 MMT of crude Oil, whereas the petroleum product consumption was close to 205 MMT, the production of petroleum product was more than 254 MMT thus leaving the margin for export. India is fourth in the world in terms of the Refining capacity after USA, China and Russian Federation. In terms of value, crude oil as well as petroleum product import in 2017-18 for India was billon US$101. The petroleum product export was nearly Billon US$35. In general, the petroleum import is nearly 22 % of the total import in India.

As far as natural gas is concerned, India is at twenty seventh position among the world's top natural gas producing countries and fourteenth among the world's largest gas consumers with a 54.2 Billion Cubic Meter (BCM) consumption ((PPAC, 2018). India is largely dependent on import which is close to 45% with a projected widening of this gap in the coming years. This calls for a large scale facility creation for import of gas in LNG (Liquefied Natural Gas) form. Accordingly, utilizing the vast coastal line of the country, apart from the crude oil import the LNG import facilities are operational as well as under development. The largest import terminal of 15 MMTPA LNG import facility at Dahej is already operational. The details of the present LNG import terminals are indicated in Table 1-1.

Table 1-1: LNG terminal in India (PPAC, 2018)

Name	**Promoters**	**Capacity [MMTPA]**	**Capacity Utilization [%]**
Dahej	Petronet LNG Ltd.	15	105.3
Hazira	Hazira LNG Pvt. Ltd.	5	58.9
Dabhol	Ratnagiri Gas & Power Pvt. Ltd	1.69	64.9
Kochi	Petronet LNG Ltd.	5	12.2

The India is poised for growth with focus on cleaner fuel with an ambitious target for gas as 15% of energy mix by 2030, which is at present barely 6% of the primary energy mix. Further, the Govt. of India's focus is on renewable energy with emphasis to produce 175 GW of electricity through renewable sources by 2022 with a contribution of 100 GW from solar energy. The primary energy mix is depicted in Fig.1.4.

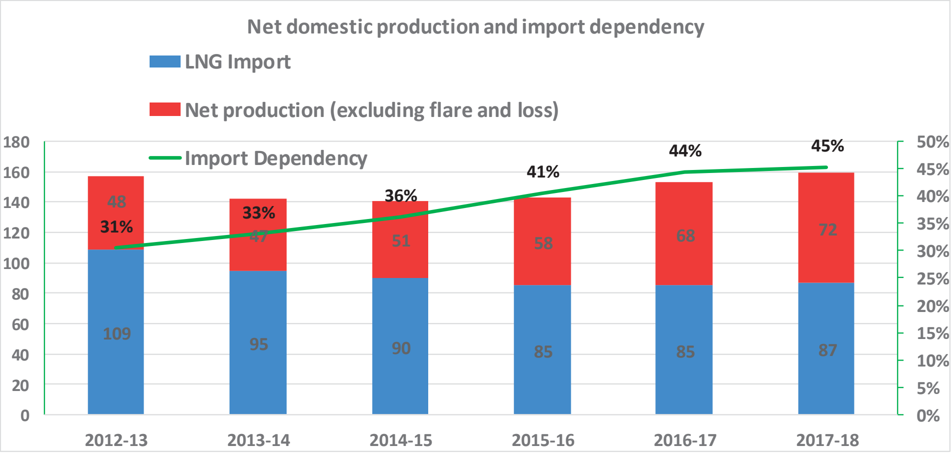


Figure 1.3: Comparison of domestic production and import of LNG in India

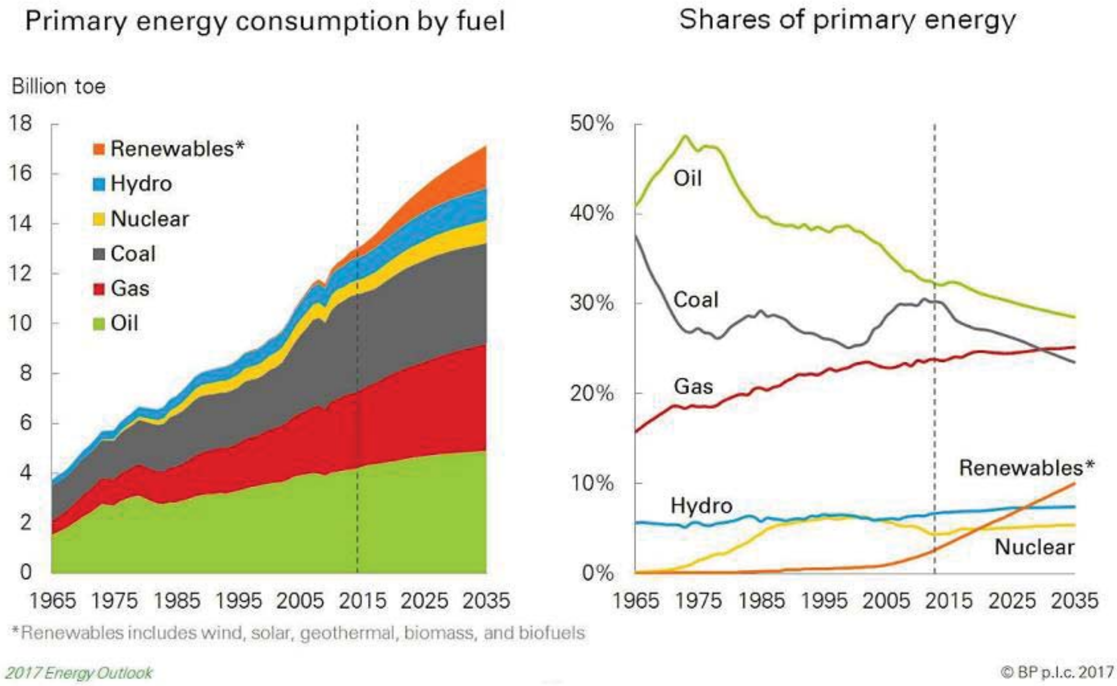


Figure 1.4: Types of fuel to meet energy demand & projections

1.3 OIL REFINING IN INDIA

The refinery industry has been growing progressively since the past seven decades and has witnessed an increase in number of refineries from one to the present twenty-three numbers. This resulted in significant growth in refining capacity from 5 MMTPA to 247.6 MMTPA. Indian Oil Corporation and subsidiaries operate eleven refineries with a combined capacity of 80.7 MMTPA followed by Reliance with two refiners of combined capacity of 67.2 MMTPA, HPCL with three refineries has 24.8 MMPA capacity followed by BPCL with three refineries of capacity 30.4 MMPTA. Fig.1.5 shows a map of Indian refineries, their location and capacity. In line with the Government of India's vision of energy access, energy efficiency, energy sustainability and energy security, the working group of Ministry of Oil & Natural Gas (MOPNG) has submitted its report in Jan 2018 on enhancing refinery capacity by 2040. The report considers the plan of domestic refining capacity augmentation to meet the demand supply gap arising out of expected rapid urbanization and improving living standard of common Indian citizen. In addition to the brown field expansion of refineries a gross root refinery of 60 MMTPA is also planned on the western coast of the country. Table 1-2 indicates the current refinery capacity at present as well as proposed expansion plan.

Table 1-2: Proposed refining expansion plan of India

Companies	**Design Capacities in MMTPA**			
	Existing	2020	2025	2030
IOC & Group	80.7	81.85	114.75	116.55
HPCL & ONGC	42.2	50.9	62.9	62.9
BPCL	36.5	38.3	56	56
ESSAR	20	20	45	45
RIL DTA	33	33	40.5	63
RIL SEZ	35.2	35.2	35.2	35.2
RRPCL	0	0	60	60
Total	**247.6**	**259.15**	**414.35**	**438.65**

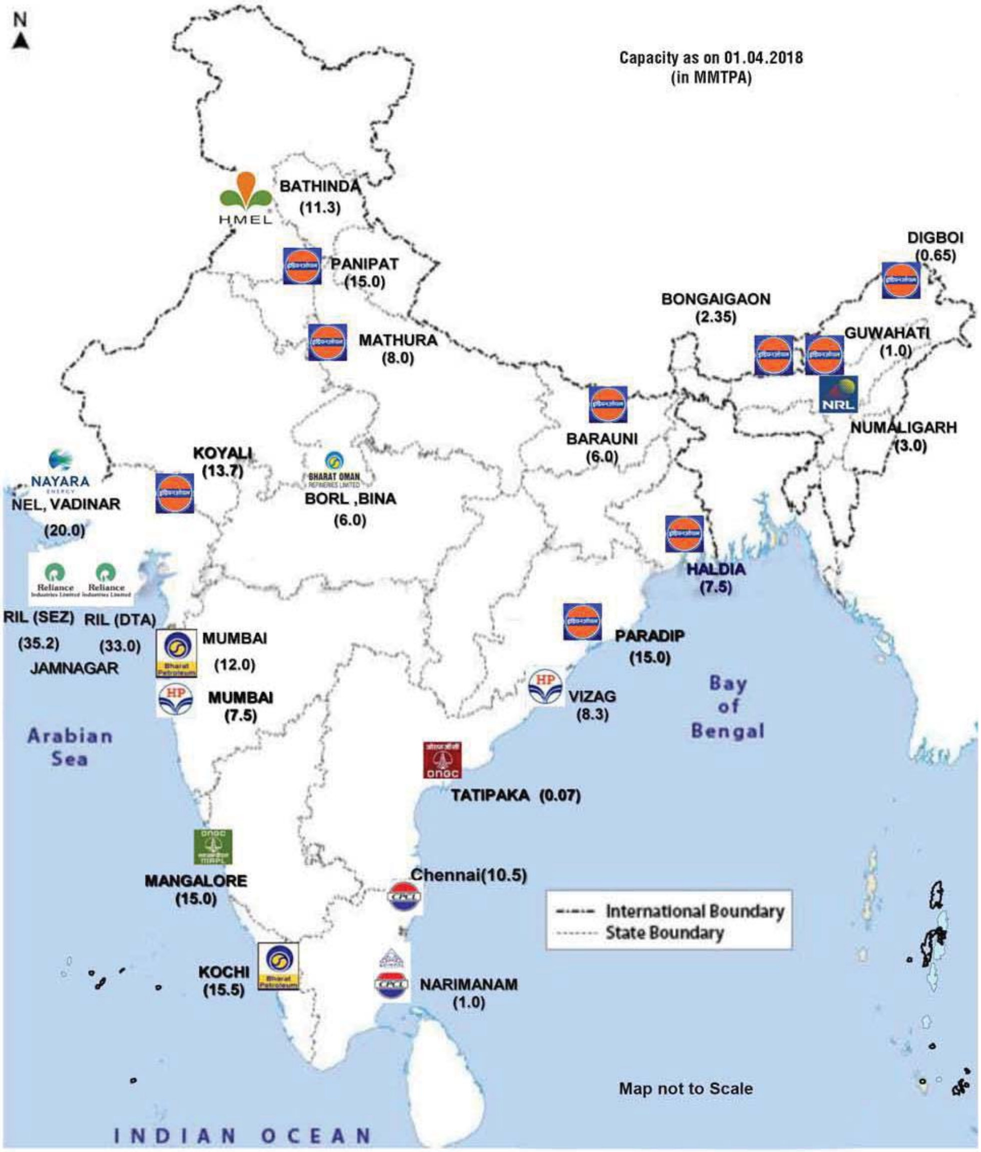


Figure 1.5: Major refineries of India

1.4 MODES OF TRANSPORTATION AND DISTRIBUTION OF PETROLEUM PRODUCTS

As elucidated above, India is largely import dependent both in case of crude oil as well as natural gas. The port infrastructure supports the oil and LNG unloading. The crude oil requirement of oil refineries located at coastal locations is met through smaller subsea pipelines whereas the land locked refineries are fed through cross country pipelines, which carry crude oil from the ports.

Similarly, for the petroleum products, the production center and consumption centers are different. This necessitates the requirement of cross country network of the petroleum pipelines for transportation of the petroleum product from production center to every nook and corner of the country where requirements exit or likely. A map of the refineries locations in India is shown in Figure 1.5.

There are various modes of the transportation of petroleum products in the country

- Coastal movement
- Pipelines
- Railways
- Road tankers
- Upcoming water ways

Each mode of transport has its distinct advantages but the pipelines are preferred, mode of transportation. World over the pipelines are preferred mode of transportation of petroleum products like liquid petroleum, natural gas, crude oil and LPG etc. It is preferred compared to other modes like rail and road primarily on account of cost effectiveness, energy efficiency, and uninterrupted supplies free from surface disturbance, environment friendly and reliable means of transportation. The accident and unwanted spillages and losses are minimal through pipeline mode. Presently India has around 45000Km of the oil and gas Pipeline for distribution of energy across the country. The demand of the energy is growing at rapid pace in India. Accordingly, requirement of distribution infrastructure like pipeline for supplementing the supplies of gas and petroleum products is likely to come up with the same pace. The pipeline infrastructure in our country is likely to increase manifold. At present, only gas pipeline to extent of nearly 15000Km are under execution, besides natural gas, petroleum product and LPG Pipeline to the extent of another 15000Km are under construction. Within couple of years, India would be reaching to the extent of nearly 80000Km of cross country oil & gas pipelines. Though the network of the pipeline in our country is smaller compared to developed nation like US, Canada etc, but it has potential for sustained growth and development. The major pipeline network is shown in Fig.1.6. Table 1-3 to Table 1-6 provides the list of pipeline network of crude oil, petroleum products, LPG and natural gas respectively.

1.5 EXPANSION PLANS OF CROSS COUNTRY PIPELINE NETWORK IN INDIA

The expansion of refineries is linked with the product evacuation plan, while the coastal refineries have coastal movement though ship tankers for dispatches of petroleum product besides other modes, whereas land locked refineries depend largely on surface transport like railways and road as well as pipelines. The inherent advantages of the pipelines as described in the previous paragraph, is key driver for growth of the pipelines. Additionally, the emphasis of Government of India on large scale LPG distribution under the Prime Ministers Ujwala Yojana (PMUY) scheme calls for wide spread LPG pipeline network in the country for facilitating availability of LPG at demand centers. The country is importing LPG to the extent of nearly 50 % to meet its demand. Presently there are six major LPG transportation pipelines in the country approximately 3000Km length and a combined capacity of 8 MMTPA. The LPG Pipeline network is also under expansion and being targeted by individual oil company as well as the joint venture. IOCL, BPCL and HPCL have joined hands to lay the 2700Km long Kandla Gorakhpur Pipeline, the world’s largest LPG pipeline. In addition, pipelines from Paradip refinery and Haldia refinery to bottling plants in eastern region of country are now operational and under augmentation.

The Natural gas network is also under expansion as on date nearly 12000Km of the network is already under execution. Additionally, a gas grid is being developed in North Eastern region of the country. Indian Oil being the largest liquid pipeline operator in the country is executing new pipeline projects of Rs 20,000Crore which will add 7000Km of the liquid petroleum and gas pipelines to its existing pipeline strength.

Figure 1.6: Petroleum pipeline network across the country (PPAC, 2018)

Table 1-3: Major Crude Oil Pipeline network in India (PPAC, 2018)

Pipeline	Owner	Length [km]	Capacity [MMTPA]	Throughput [MMTPA]	Utilization [%]
CTF (Central Tank Farm) Kalol to CTF Nawagam - New (New line commissioned in August 2010)	ONGC	62.5	3.1`	0.959	30.6
Nawagam-Koyali (18" line) Old (1)		78.4	5.4	1.79	33.1
Nawagam-Koyali (18" line) New (2)		79.6	5.4	0.376	7
Nawagam-Koyali (14" line) (Old) (3)		78.4	3.3	1.32	40.2
MHN-NGM (Mehsana-Nawagam) trunk line - New (New crude oil trunk line commissioned. Under operation since December 2010)		77	2.3	2.061	91.0
CTF (Central Tank Farm), Ankleshwar to Koyali		94.8	2.2	0.92	41.8
CTF (Central Tank Farm), Ankleshwar to CPF (Central Processing Facility),		44.3	0.4	0	0
CPF (Central Processing Facility), Gandhar to Saraswani ‘T’ point		56.7	1.8	0.686	38
Akholjuni- Koyali oil pipe line (Commissioned in July 2010).		65.5	0.5	0.193	40.1
Lakwa-Moran oil line (New)		17.5	1.5	0.107	7.1
Lakwa-Moran oil line (Old)		14.6	1.5	0.305	20.3
Geleki-Jorhat oil line		48.5	1.5	0.417	27.8
Borholla- Jorhat oil line		42.8	0.6	0.154	25.6
NRM (Narimanam) to CPCL (Chennai Petroleum Corporation Limited		4.9	0.7	0.339	45.8
KSP-WGGS to TPK Refinery		13.5	0.1	0.031	37.7
GMAA EPT (Gopavaram Early Production Terminal) to S. Yanam Unloading Terminal		3.5	0.1	0.046	50.9
Mumbai High - Uran - Trunk (MUT) 30’’ pipeline		204	15.6	10.021	64.1

Heera - Uran - Trunk (HUT) 24’’ pipeline (6)		81	11.5	3.064	26.6
Bombay-Uran Trunk (BUT) 30’’ pipeline (7) 203.0 6.4		203	6.4	0	0
Salaya-Mathura pipeline (SMPL)	IOCL	2646	25	26.203	104.8
Paradip-Haldia-Barauni pipeline (PHBPL		1355	15.2	16.437	108.1
Mundra-Panipat pipeline		1194	8.4	8.437	100.4
Salaya Mathura Pipeline (Offshore segment		14	-	-	-
Paradip Haldia Barauni Pipeline (Offshore)		92	-	-	-
Duliajan-Digboi-Bongaigaon-Barauni pipeline	OIL	1193	8.4	6.631	78.9
Mangla-Bhogat pipeline	CAIRN	660	8.7	7.798	89.5
Bhogat Marine	CAIRN	28	0.4	2.12	573
Mundra- Bathinda pipeline	HMEL	1017	9.0	8.907	99
Vadinar-Bina pipeline	BORL	937	6.0	6.718	112.0
TOTAL		10406	145.0	106	73.1

Table 1-4: Major Petroleum Product Pipelines in India (PPAC, 2018)

Pipeline	Owner	Length [km]	Capacity [MMTPA]	Throughput [MMTPA]	Utilization [%]
Barauni - Kanpur pipeline (1)	IOCL	856	3.5	2.257	64.5
Guwahati -Siliguri pipeline		435	1.4	1.832	130.9
Haldia-Barauni pipeline		526	1.25	1.485	118.8
Haldia-Mourigram-Rajbandh pipeline		277	1.35	1.824	135.1
Koyali-Ahmedabad pipeline (5)		79	1.1	0.153	13.9
Koyali-Sanganer pipeline KSPL		1300	4.6	4.351	94.6
Koyali-Ratlam pipeline		265	2.0	1.452	72.6
Koyali-Dahej pipeline		197	2.6	0.938	36.1
Mathura-Tundla pipeline		56	1.2	0.426	49.3
Mathura-Bharatpur pipeline		21		0.165	
Mathura-Delhi pipeline		147	3.7	2.763	74.7

Panipat-Amabala-Jalandhar (Including Kurukshetra-Roorkee-Najibabad branch line)		434	3.5	3.060	87.4
Panipat-Delhi (Including Sonepat-Meerut branch line) pipeline		189	3.0	1.10	36.7
Panipat Bijwasan ATF pipeline		111			
Panipat-Bathinda pipeline		219	1.50	1.546	103.1
Panipat-Rewari pipeline		155	2.1	1.69	80.5
Chennai-Trichy-Madurai pipeline		683	2.3	2.841	123.5
Chennai - Meenambakkam ATF pipeline		95	0.810	0.23	127.8
Chennai-Bengaluru pipeline		290	2.45	1.715	70.0
Digboi - Tinsukia pipeline		75	1.0	0.528	52.8
Devangonthi - Devanhalli pipeline		36	0.660	0.424	64.2
Paradip Raipur Ranchi pipeline(PRRPL)		1073	5.0	3.619	63.4
Mumbai-Manmad-Bijwasan pipeline	BPCL	1389	6.0	7.015	116.9
Bina-Kota pipeline		259	4.4	3.388	77
ATF P/L Mumbai Refinery (MR)		15	1.4	0.933	66.6
ATF P/L Kochi Refinery (KR)-Kochi airport		34	0.6	0.38	63.3
Kota - Jobner branch pipeline(		211	1.7	0.579	34
Mumbai Refinery- Wadi lube pipeline		12	1.3	0.262	20.2
Cochin-Coimbatore-Karur (CCK) pipeline	Petronet	293	3.3	2.651	80.3
Mumbai-Pune-Solapur pipeline	HPCL	508	4.3	4.655	108.3
Vizag-Vijaywada-Secunderabad pipeline		572	5.38	5.752	106.9
Mundra-Delhi pipeline		1054	5.0	3.487	69.7
Ramanmandi-Bahadurgarh pipeline		243	4.71	4.34	92.1
Ramanmandi-Bathinda pipeline		30	2.1	0.852	40.6
Awa-Salawas pipeline		93	2.3	0.722	31.4
Bahadurgarh-Tikrikalan pipeline		14	0.750	0.528	70.4
Rewari- Kanpur Pipeline		443	7.98	2.672	33.5
ATF piepline from Mumbai Refinery to		20	1.1	0.667	61.6

Mumbai Airport					
Black Oil Pipeline (BOPL)		22	1.50	0.325	21.7
Lube Oil Pipeline : Trombay to Wadibundar		17	1.0	0.440	44
Mangalore-Hassan-Bengaluru (MHB)	Petronet	363	2.143	3.50	163.3
Numaligarh-Siliguri pipeline	OIL	654	1.72	1.86	108.7
Total		13764	103.1	79.0	76.6

Table 1-5: Major LPG pipelines in India (PPAC, 2018)

Pipeline	Owner	Length [km]	Capacity [MMTPA]	Throughput [MMTPA]	Utilization [%]
Panipat-Jalandhar pipeline	IOCL	274	0.7	0.599	85.6
Paradip Haldia Durgapur pipeline		157	0.503	0.05	9.3
Mumbai-Uran pipeline	BPCL	28	0.80	0.337	42,7
Jamnagar-Loni pipeline	GAIL	1414	2.50	2.673	106.9
Vizag-Secunderabad pipeline		618	1.330	1.040	78.2
Mangalore-Hassan-Mysore-Solur	HPCL	356	1.94	0.783	40.4
Total		2847	7.8	5.50	70.50

Table 1-6: Major Natural Gas Pipelines in India (PPAC, 2018)

Pipeline	Owner	Length [km]	Capacity [MMSCMD]	Average flow [MMSCMD]	Utilization [%]
Hazira-Vijaipur-Jagdishpur pipeline/Gas rehabilitation and expansion project pipeline/ Dahej-Vijaipur pipeline & spur/ Vijaipur-Dadri Pipeline	GAIL	4554	53.0	29.52	56
DVPL-GREP upgradation (DVPL-II & VDPL	GAIL	1385	54	35.92	67
*Chhainsa-Jhajjar-Hissar pipeline (CJPL)	GAIL	310	5	1.01	20

(Including spur lines) commisioned up to Sultanpur, Jhajjar-Hissar under hold (111Km)					
Dahej-Uran-Panvel pipeline (DUPL/ DPPL) including spur lines	GAIL	928	19.9	13.94	70
Dadri- Bawana-Nangal pipeline (DBPL), Dadri-Bawana: 106Km, Bawana-Nangal: 501 KM, spur line of BNPL: 196Km	GAIL	852	31	5.49	18
Dabhol-Bengaluru pipeline (including spur) Phase -1- 997Km, Phase 2 - 114.6Km	GAIL	1116	16	1.27	8
Kochi-Koottanad-Bengaluru-Mangalore (Phase-1)	GAIL	48	6.0	2.29	38
Tripura (Agartala)	GAIL	60	2.3	1.30	57
Gujarat	GAIL	685	8.3	4.37	53
Rajasthan (Focus Energy)	GAIL	151	2.4	1.35	57
Mumbai (Uran-Thal-Usar & Trombay-RCF)	GAIL	131	7.0	6.43	91
KG Basin (including RLNG+RIL)	GAIL	884	16	5.40	34
Cauvery Basin	GAIL	306	8.7	3.25	38
East- West pipeline (RGTIL)	RGTIL	1480	80	17	21
Shahdol-Phulpur pipeline (RGPL)	RGPL	304	3.5	0.53	15
GSPL network including spur lines		2618	43	25.33	59
Assam regional network	AGCL, DNPL	817	3.2	2.25	69
Dadri-Panipat	IOCL	140	9.5	4.34	46
Total		16770	369		

1.6 PIPELINE – MATERIALS OF CONSTRUCTION

The iron and steel are most versatile, least expensive and most widely used engineering materials. They have excellent mechanical properties and ease of fabrication. The main disadvantage is poor resistance to the corrosion. This happens even in mild service environment and thus requiring appropriate mitigation measures for corrosion protection. The low carbon steel is extensively used for structural, columns, pipelines, supports, trusses etc. The pipelines are made of a variety of grades of low carbon steel. The cross country pipelines are laid underground at an average depth of 1 meter with soil cover on top. These pipelines are designed as per international codes and standards such as ASME B31.4 and ASME B31.8 for liquid and Gas pipelines respectively. The other relevant national and international codes are followed for fabrication and laying through the operation and maintenance phase.

The pipelines being buried in soil as well as carrying corrosive constituents as impurities in hydrocarbon phase, experience corrosion challenge both from the hostile external soil side as well as internal liquid hydrocarbon or gas side.

According to World Corrosion Organization COORDIA, the annual losses due to the corrosion world over are US $ 2.2 Trillion which is 3% of the world GDP (COORDIA, 2018). In the United States alone, the loss due to corrosion was to the extent of $276 billion annually in 1998, which rose to $ 1.1 trillion in 2016 (G2MT Laboratories, 2016). In India loss due to corrosion is estimated to be in the range of 4-5 % of its GDP (NACE, USA, 2018). In Indian context it is roughly estimated as approx. Rs. 25000-30000 Crore per annum. Besides the cost of corrosion, the effect of corrosion on public safety and on environment is equally important. The potential saving estimated on account of corrosion monitoring, prevention & control is of the order of 25% of the cost of corrosion. Besides direct cost, Corrosion has a very serious effect on premature or in-service failure of infrastructure like bridges, water supply system, crude oil supply, petroleum pipeline, subsea pipelines, steel storage tanks, ships, pressure vessels, refinery columns, heat exchangers, reactors, boilers etc., Such huge loss and its direct impact on our developing economy necessitates adoption of concrete, cost effective and environment friendly measures for minimization of corrosion. Periodic corrosion protection measures are essential for corrosion mitigation. Accordingly, it is imperative that steps for corrosion protection are taken right from the conceptual / design stage of infrastructure and same is followed judiciously to construction stage and extended suitably to entire useful life of the infrastructure.

Comprehensive study has been carried out for evaluation of cost related to corrosion and its consequences for a major pipeline operator. Five years of data has been collected for major cost components associated to corrosion. Preliminary data was collected under the heads of corrosion inhibitor, replacement cost, in-line inspection, above ground surveys, corrosion monitoring & spares, coating repair, cleaning, cathodic protection, training, containment loss, Tariff loss, & other associated cost. The total expenditure on the above was further categorized according to the heads of monitoring, inspection, prevention, repair, replacement & loss.

The average cost of corrosion per Km per year for the India's leading pipeline operator, works out to be Rs.1,42,000 for per Km of onshore cross country pipelines. With these cost pipeline operators in India are estimated to be spending around Rs. 622.00 Crore per year. This amount is equivalent to 88.8 million USD per year. The distribution of cost analysis for corrosion is displayed in Fig.1.7.

Unlike the US Department of Transport or Canada National Safety Board, no elaborate data base on the pipeline failures is available in India. However, the details of some the failures are referenced in the Oil Industry Safety Directorate website (OISD, India, 2019). A gas pipeline operated by GAIL blasted in Southern Indian state of Andhra Pradesh in 2014, killing 22 people and injuring 37 people (PNGRB, 2015). The internal or external corrosion is one of the important cause of liquid or gas pipeline failure. The consequence of such failures is extremely high. From the above discussion we can infer the corrosion is rampant phenomenon for pipelines operators in India both for liquid hydro carbon and natural gas pipelines. Accordingly, the enough safeguard is taken by pipeline operators for prevention of corrosion

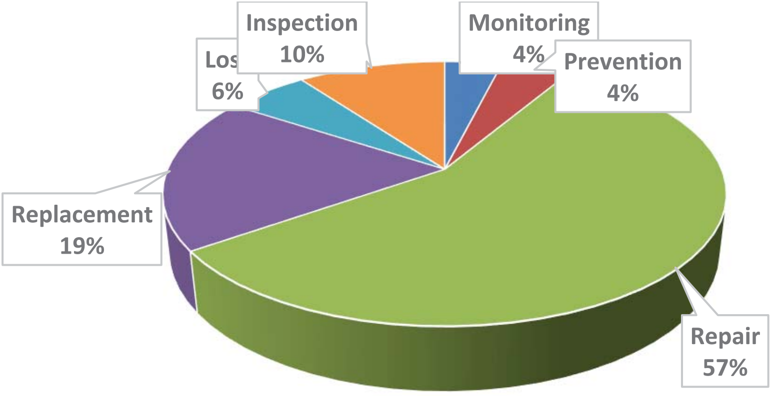


Figure 1.7: Expenditure in various activities for corrosion assessment & mitigation

1.7 CORROSION PHENOMENON

Corrosion is encountered in many forms which considerably affects refineries, petro chemical plants, oil and gas production facilities, chemical process industries, power plants, shipping industry, ports and cross country underground pipelines etc. The corrosion process is a natural phenomenon as metals tend to degrade and reach to their original form of the ore stage. The corrosion is defined as destruction or deterioration of materials because of its reaction with environment.

Corrosion is undesirable but serious and naturally occurring phenomenon. It is time dependent deterioration of material because of its reaction with environment. The destruction of the metal / alloy occurs by chemical or electro chemical reaction with the environment as elucidated by the most common phenomenon of rust formation in the iron oxygenated water system as follows:

At the anodic area Fe ionizes to form Fe^{++} ion in presence of moisture releasing two free electrons that can migrate to cathodic regions. Dissolved oxygen in the aqueous system forms hydroxyl ion (OH^-) at the cathode. In the process the free electrons are consumed at the cathode completing the electric circuit.

Anodic reaction: $Fe \rightarrow Fe^{++} + 2e$ ------ (1.1)

Cathodic Reaction: $1/2\ O_2 + 2\ H_2O + 2e \rightarrow 2\ OH^-$ ----- (1.2)

Fe^{++} and $2\ OH^-$, further react to form ferrous hydroxide

$Fe^{++} + 2\ OH^- \rightarrow Fe(OH)_2$ ------ (1.3)

$Fe(OH)_2$ is further oxidized to Ferric Oxide

$Fe(OH)_2 + 1/2\ O_2 \rightarrow 1/2\ H_2O + Fe(OH)_3$ (Green color) ----- (1.4)

If allowed to dry, then

$2\ Fe(OH)_3 \rightarrow Fe_2O_3 + 3\ H_2O$ (Rust brown color) ------ (1.5)

The above electrochemical reaction is driven spontaneously by the potential difference between anodic and cathodic regions which could be because of local heterogeneities in chemical composition, differential oxygen cell or differential concentration of corrosion products. However, for the corrosion to occur and sustain, a conductive path between the anodic and cathodic regions is essential.

1.8 TYPES OF CORROSION

In general, Corrosion manifests itself in various forms which are dependent on the combination of the metal and the corrosive environment. The following eight forms of corrosion are widely reported (Fontana, 2005).

1.8.1 GENERAL CORROSION

This is uniform loss of metal over the entire surface. Uniformly distributed chemical or electro chemical where reaction is uniformly distributed throughout the surface. This indicates general loss of thickness uniformly. Often it leaves behind scale of deposit. The oxidation and reduction reactions occur randomly over entire exposed surface. The silver metal turning into black in the environment due to reaction and oxide formation is one example of general corrosion.

1.8.2 PITTING CORROSION

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits. The pipelines often encounter pitting corrosion.

1.8.3 CREVICE CORROSION

Intensive localized corrosion usually occurs within crevices and other shielded areas on metal surface exposed to corrosive environment. Crevice Corrosion refers to the localized attack on a metal surface at, or immediately adjacent to, the gap or crevice between two joining surfaces. The gap or crevice can be formed between two metals or a metal and nonmetallic material. This type of attack usually occurs due to small volume of stagnant solution caused by holes, gaskets joint, lap joint, surface deposit, crevice under bolt etc.

Figure 1.8 Pitting Corrosion on the External Pipeline surface

1.8.4 GALVANIC CORROSION:

A potential difference occurs between two metals when they are immersed in corrosive or conductive environment. When two different materials are in electrical contact and immersed in the same corrosive environment then such corrosion takes place due to flow of electrons. The corrosion of less corrosion resistant metal usually increased and attack on more corrosion resistant metal is decreased. Less resistant metal becomes anodic and more resistant metal becomes cathodic. Because of presence of electric current flow in dissimilar metals, it is called galvanic corrosion.

1.8.5 EROSION CORROSION

It is combination of combined action of chemical attack and mechanical abrasion or wear as consequence of fluid motion. It is especially harmful for alloys which passivate by forming a protective surface film. The abrasive action may erode away the film leaving exposed a bare metal surface. Usually it can be identified by surface grooves and waves having contours that are characteristics of the flow of fluid. Increasing the fluid velocity normally enhances the rate of corrosion. Also fluid is more corrosive in presence of bubbles and suspended particulate matter. Erosion corrosion is generally occurring in process piping, especially at bends, elbows and reducers etc. where abrupt changes in pipe diameter and direction of flow takes place.

1.8.6 STRESS CORROSION CRACKING (SCC)

Stress corrosion cracking (SCC) is the cracking induced from the combined influence of tensile stress and a corrosive environment. The impact of SCC on a material usually falls between dry cracking and the fatigue threshold of that material. The required tensile stresses may be in the form of directly applied stresses or in the form of residual stresses. The problem itself can be quite complex. Usually, most of the surface remains unaffected but with fine cracks penetrating into the material are noticed. In the microstructure, these cracks can have intergranular or transgranular morphology. Macroscopically, SCC fractures have brittle appearance. SCC is classified as a catastrophic form of corrosion, as the detection of such fine cracks can be very difficult and the damage is not easily predicted. A disastrous failure may occur unexpectedly, with minimal overall material loss. Once a small pit is developed it acts as local stress raiser and pit yawns open and fresh electrolyte reaches anode tip of pit where further yawn and possible branching takes place.

1.8.7 MICRO BIOLOGICALLY INFLUENCED CORROSION (MIC)

The microbial influenced corrosion as also known as microbial corrosion or biological corrosion. It is deterioration of metal on account of metabolic activity of microorganism. There are more than a dozen bacteria which causes microbial corrosion in carbon steel, stainless, steel, aluminum and copper alloys in water and soils in pH range of 4-9 at the temperature ranging from 10 to 50 °C. These bacteria are classified as aerobic bacteria which require oxygen for their growth and activities. Other types of bacteria are called anaerobic bacteria which survive in absence of oxygen. Sulphate reducing bacteria is aerobic which causes accelerated corrosion to ships, other structures. It is a kind of corrosion which initiated or accelerated by activities of microorganism such as Sulphate Reducing Bacteria (SRB) Iron Oxidizing Bacteria (IOB) Heterotrophic biofilm forming Bacteria (HBB). There are many industries are affected by microbial influenced corrosions like chemical processing industries, onshore and offshore oil and gas industries, pipelines which are hydro tested, the residual river water may cause MIC. The MIC is common in water treatment industry, sewage treatment and also aviation industry. Microbial influenced corrosion is caused by specific genera of bacteria which feed on nutrients found in water and other elements found in soil. Sea water is primary source of sulphate reducing bacteria. The biological activities modify the local chemistry like acid producing and in turn render it more corrosive to the metals. The MIC causes corrosion at much faster rate than other forms of the corrosion, often sea water in the off shore crude oil handling pipelines, petroleum product pipelines hydro tested with river water without effective treatment etc. is major source of MIC for pipelines. Once MIC is detected a biocide is injected in the plug form to mitigate the action of these microbes.

1.8.8 HYDROGEN EMBRITTLEMENT

Various metal alloys especially some steels experience significant reduction in ductility and tensile strength when atomic hydrogen (H) penetrates into the material. The phenomenon is aptly referred as hydrogen embrittlement. The term hydrogen induced cracking and hydrogen stress cracking is the same phenomenon

1.8.9 INTERGRANULAR CORROSION

The microstructure of metals and alloys is made up of grains, separated by grain boundaries. Intergranular corrosion is localized attack along the grain boundaries, or immediately adjacent to grain boundaries, while the bulk of the grains remain largely unaffected. This form of corrosion is usually associated with chemical segregation effects (impurities have a tendency to be enriched at grain boundaries) or specific phases precipitated on the grain boundaries. Such precipitation can produce zones of reduced corrosion resistance in the immediate vicinity. The attack usually progresses on a narrow path along the grain boundary and, in a severe case of grain boundary corrosion; entire grains may be dislodged due to complete deterioration of their boundaries.

1.9 CORROSION IN THE PETROLEUM PIPELINES

The cross country petroleum or gas pipelines are buried at an average depth of one meter in the earth. Being buried in soil, carbon steel pipelines faces the corrosion attack from the surrounding soil, broadly following two types of the corrosion is generally encountered in underground cross country petroleum pipelines

- *External corrosion*
- *Internal corrosion*

The pipeline operators maintain their best efforts to avoid the pipeline failure due to corrosion. However, many pipeline failures take place due to corrosion, both due to internal and external corrosion. The underground pipeline is subjected to hostile soil environment, although anticorrosion coating is applied but any coating flaw or failure of CP system causes the serious corrosion problem. Hence regular monitoring of the cathodic protection system as well coating condition assessment is carried out. The consequence of such corrosion related failure are very high as spillage of the highly inflammable product release causes environment pollution, soil pollution, contamination in underground water sources besides disruptions in the supplies (Figs.1.9 & 1.10). In addition, the external factors such as high tension transmission lines crossing the pipeline may also induce corrosion and resultant failure.

In India as such the reporting of each incident of the pipeline failure takes place as per regulatory requirements. However, no structured data base is available in public domain. But in case of United State through length of their pipelines is much higher i.e. approx. 2.5 Million miles, they have a structured system of data reporting through a National Safety Board. Similar system exists for Canada and most of the European countries. In our country, the Oil Industry Safety Directorate (OISD) maintains case studies of major failure / accidents related with the cross country pipelines

Figure 1.9: Seam failure of Crude Oil Pipeline due to corrosion/ micro cracks in Northern India causing crude oil spillage

Figure 1.10: Crude Oil Spillage in irrigated field on account of corrosion leakage. Seam opening of pipeline on account of corrosion

Every spillage depending upon pipeline size and pressure the spillage quantity ranges between 20 to 100 KL and rectification time after removal of oil etc takes place nearly 24-48hour. Thus causing not only supply disruptions but also serious environmental consequences. In terms of cost it ranges between Rs. 50 Lakh to Rs. 2.50Crore in each case.

1.9.1 EXTERNAL CORROSION

The cross country petroleum pipelines are laid underground, generally on average depth of one meter inside the earth and thus face the hostile soil environment on external surface. Being cross country pipeline running over hundreds of kilometers of length, the pipelines encounter marshy soil, water inundation, and coastal offshore conditions at many locations. In addition, presence of rocks, tree roots tend to apply mechanical damages to the pipeline as well.

A stringent quality control during fabrication ensures a defect free pipe as well as longitudinal seam / spiral weld spools with practically no heterogeneities. In addition, the pipe to pipe field butt joints are carried out with an equal quality control and testing. In order to protect the pipeline from the in service external corrosion damages, a suitable anticorrosive coating is applied on the external surface during the mill fabrication as well as on the field at the joints, for joint coating. The efficacy and integrity of the external coating system is tested using holiday detector, before burying the pipeline. Periodic above ground coating surveys are undertaken to assess the coating condition of the pipeline, Stretches of poor / bad coating is identified and wherever required, the refurbishment of coating is carried out.

In addition to the coating the impressed current based cathodic protection system is installed for protection of the pipeline, which maintains the buried pipeline as cathode and prevent the further corrosion.

Regular Pipeline to Soil Potential (PSP) survey is conducted to ensure the effectiveness of cathodic protection system. Wherever the drop in either on or off potential condition is observed, the same is appropriately addressed.

Periodic coating surveys like Direct Current Voltage Gradient (DCVG) and Current attenuation (CAT) surveys are undertaken to assess the coating condition of the pipeline.

1.9.2 INTERNAL CORROSION

The internal surface of the hydrocarbon pipelines remains wetted with hydrocarbons. Hydrocarbons are generally non corrosive to steels. However, there is always some amount of water / moisture entrained within the hydrocarbon system. The source of water / moisture could be the produced water from the exploration sites in case of crude oil, process steam condensate in case of products. Though the hydrocarbons are pumped out from tankages after appropriate settling of water, however, some amount of water is unavoidable. Petroleum product and crude oil pipelines are subjected to general surface corrosion caused by the presence of corrosive organic / inorganic sulphur compounds, dissolved carbon dioxide, hydrogen sulphide, dissolved salts etc in the water.

In liquid pipeline like crude oil and petroleum product pipeline, the settlement of water at lower points is likely cause of internal corrosion at localized spots.

The internal corrosion in the pipelines can largely controlled by application of corrosion inhibitors. Corrosion Inhibitors (CI) are inorganic / organic amines & their derivatives. These are injected in very small doses on a continuous basis into the hydrocarbon stream to provide a stable protective surface film on the internal surface and thus preventing the pipe from corrosive attack.

1.10 MONITORING AND MEASUREMENT OF INTERNAL CORROSION IN THE PIPELINES

The monitoring of internal corrosion in the pipeline is essential to assess the integrity of the pipeline. In the petroleum pipeline industry, the corrosion is measured using the following methods:

1.10.1 CORROSION COUPONS

The coupon is cut from the same material as pipeline and installed inside pipeline with the help of suitable mounting device. The weight of the coupon is measured at the time of installation. After a period normally six months the coupon is removed, cleaned and washed as per procedure weighed again. The loss of weight is indicator of the metal loss through corrosion. Since the test coupon and pipe are of the same metal, it gives fair indication regarding general corrosion rate in the pipeline.

The expression for corrosion rate is mills per year (mpy). To covert corrosion rate from mpy to equivalent metric unit i.e. mm/yr using the following formula:

1 mpy= 0.0254 mm/yr.

To calculate the corrosion rate from metal loss

$$1 \text{ mm/y} = 87.6 \text{ W/DAT} \quad \text{--------} \quad (1.6)$$

where 'W' is weight loss in milligrams, 'D' is metal density in gm/cc^3, 'A' is area of sample in cm^2 and 'T' is the time of exposure of metal surface in hours

It is an in direct method, though it gives fair indication regarding general metal loss on account of the corrosiveness of the flowing liquid. However, it doesn’t give any idea regarding dominance of corrosion in particular point or section of the pipeline.

1.10.2 ELECTRICAL RESISTANCE PROBES (ER PROBES)

These are metallic probes having a wire of fixed diameter mounted in the flow regime with regular measurement of parameters like current, voltage, resistance of the probe. Due to corrosive properties of the flowing crude oil or petroleum product, the cross sectional area of the probe wire gets reduced and the resistance accordingly changes. The measurement of the change in resistance gives fair indication of the corrosion rate.

Generally, less than 1 mill per year is considered to be the acceptable limits of corrosion rate in pipelines. Other means of monitoring corrosion are hydrogen test probe, ultrasonic testing using angle beam or shear wave ultrasonic, acoustic emission testing etc.

1.10.3 PIG RESIDUE ANALYSIS

Pipeline Inspection Gauges (PIG) is normally used to clean the internal surfaces of the pipeline as well as to assess their internal integrity. In addition, above monitoring mechanism, cleaning PIGs (Pipeline Inspection Gauge) are launched in crude oil pipelines and petroleum product pipeline periodically and the pig residue/ muck received is analyzed for 'Fe' and other components. The component in the pig residue gives fairly good indication regarding the internal corrosion of the pipeline. Normally in the residue analysis the presence of microbes is also tested and action is taken, if Microbiologically Induced Corrosion (MIC) is, evident. The cleaning pig ensures fair amount of the pipeline internal cleaning; thus regular pigging is considered as first step towards corrosion mitigation.

1.10.4 INSTRUMENTED PIG SURVEY (IPS) OR IN LINE INSPECTION (ILI)

In addition to monitoring though corrosion coupon and ER probes discussed above, which gives indirect result regarding corrosive environment, for the direct assessment of corrosion both internal and external, periodical inspection through Instrumented PIG is carried out. As per OISD standard, each cross country pipelines is mandated to undertake this survey once in 10 year for pipelines less than 25 years old and 8 years for more than 25 years old pipelines. The off shore pipelines, ILI is mandated for once in 5 years. However, in case of Indian Oil, IPS survey is carried with less than 10 years' period i.e. generally between 7-8 years for cross country pipelines and 5 or less than 5 years for offshore Pipelines. In addition, the after commissioning of the pipeline, the ILI is carried out for base line corrosion data capturing.

Generally following two types of technologies are used in the intelligent pigging:

Magnetic Flux Leakage based Pig (MFL-IPIG)

A series of Hall effect sensors mounted on the tool capture the magnetic flux leakage emanating from regions of change in wall thickness due to internal / external corrosion. These signals are continuously recorded with reference to the pipeline distance. MFL-IPIG is widely used for the detection of localized corrosion and pitting. This facilitates determination of extent, location, depth, and internal / external position of defect. The ultrasonic i.e. US-IPIG besides detecting the internal and external corrosion provides information on the presence of cracks particularly in the welds and the heat affected zone. Magnetic Flux Leakage (MFL) testing is a widely used, Non-Destructive Testing (NDT) method for the detection of corrosion and pitting in steel structures. MFL is often used for integrity assessment of pipeline. The basic principle behind MFL involves magnetizing a ferrous metal object to saturation level with a powerful magnetic field. Where the object has no flaws, the magnetic flux will remain undisturbed. A schematic of the MFL pigs is shown in Fig.1.11.

The tool can detect both internal and external corrosion. The technology is widely used with more than 90% of Probability of Detection (POD). However, this has a limitation as cracks particularly in Heat Affected Zones (HAZ) are often not detected by the MFL technology. In one of the leading oil pipeline in India, the survey was carried out based on MFL technology in 2012, however subsequent to survey the pipeline failure in the form of rupture has taken, resulting into huge release of crude oil and ground contamination etc. The sample test of failed pipe piece in laboratory, indicated, the small weld anomalies in the longitudinal pipe seam HAZ region. This pipe weld anomaly of small nature like micro crack could not be precisely detected by MFL tool being in the HAZ. Accordingly, in that case it was decided subsequently to go for ultrasonic based intelligent pigging.

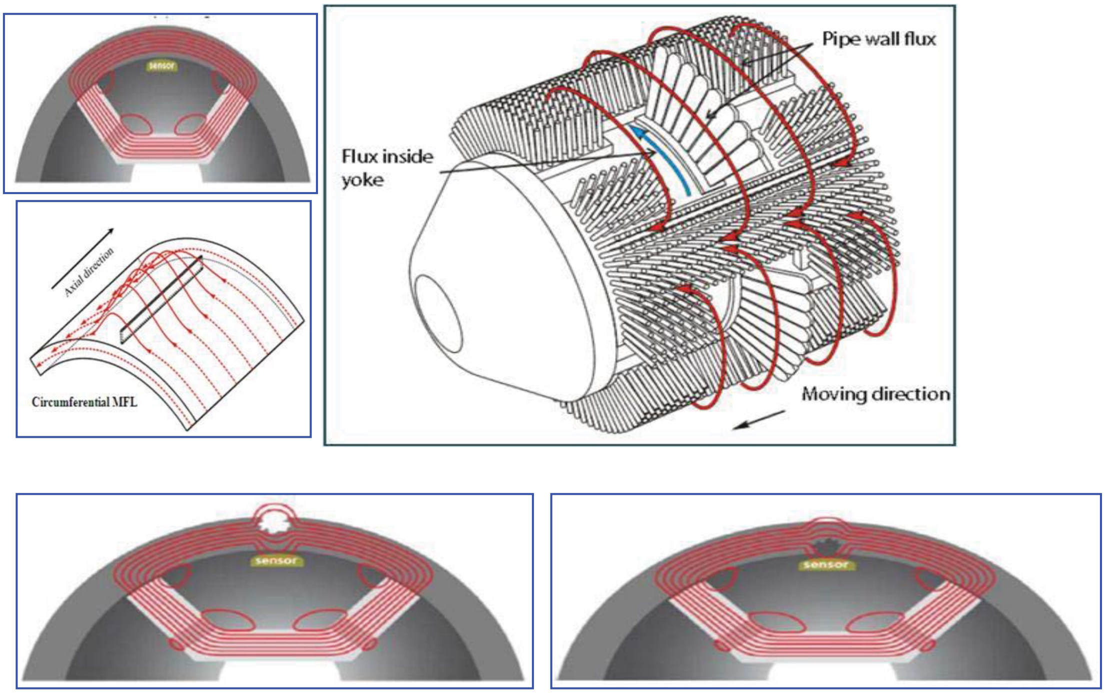


Figure 1.11: Schematic of Axial MFL Based In-line Inspection

Ultrasonic Based Intelligent Pig (US-IPIG)

The technology uses ultrasonic probes to determine the pipe wall thickness. It allows the determination of extent, location, depth, and internal / external position of defect. Ultrasonic based pig requires liquid coupling between transducers and pipeline wall. Its use therefore is restricted for the gas pipeline. It determines the cracks in parent metal and lamination etc. in the precise manner. However, close to girth weld in HAZ, the accuracy of defect detection has still limitations. For the inspection of liquid pipelines ultrasonic tools offer specific advantages with regard to resolution and measurement accuracy. In-line inspection by means of intelligent pigging has become a standard application to ensure safe operation of pipelines worldwide. Ultrasonic inspection tools have proven to be successful for crack inspection as well as for metal loss inspection of liquid pipelines. The above methods indicates the extent of internal corrosion and helps the operators to take a decision based on the severity of corrosion, zone of the pipeline, pressure profile, elevation profile, service condition etc. Often the severely corroded sections of pipeline with higher density of anomalies, is replaced. A schematic of US-IPIG is shown in Fig.1.12

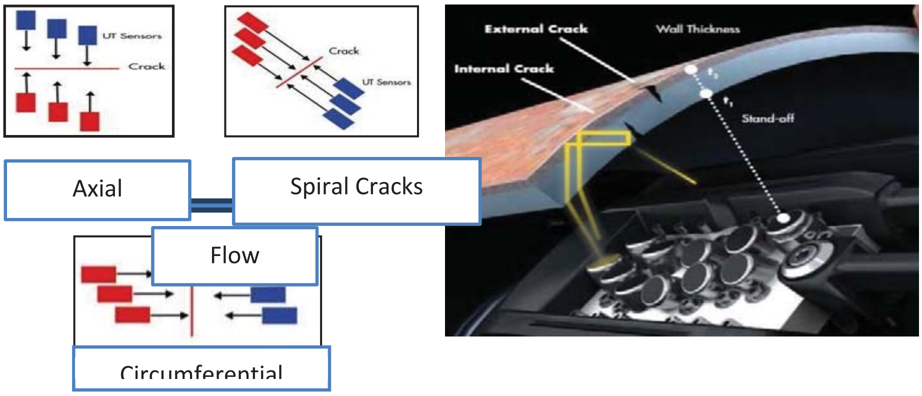


Figure 1.12 Schematic of Axial MFL Based In-line Inspection

1.11 CORROSION INHIBITOR FOR CORROSION CONTROL

As discussed above the Corrosion inhibitor is chemical, it injected in small doses with corrosive fluids flowing through pipeline system. It helps in minimizing the internal corrosion of the pipeline. The corrosion inhibitor tends to form a passive film on the internal surface of the pipeline, thus preventing the corrosive flowing fluid to come in contact with the internal surface, thus the inner wall of the pipeline is protected against the corrosion.

Protection of pipeline from internal corrosion, which mainly occurs, due to corrosive nature of crude oils and petroleum products, flowing through the pipeline, is essential for maintaining the integrity of pipelines. The corrosion inhibitor is normally injected at the originating station for the purpose of mitigation of internal corrosion. The corrosion inhibitor forms a protective layer on inner surface of the pipeline, so as to nullify the effect of corrosive nature of water and other corrosive elements present in the hydrocarbons. The use of corrosion inhibitors constitutes one of the most economical ways to mitigate the internal corrosion, protect metal surfaces against corrosion and preserve industrial facilities.

1.11.1 CLASSIFICATIONS OF CORROSION INHIBITORS

Corrosion inhibitors are chemical additives that modify the pipeline internal surfaces when added to the hydrocarbon medium. There are various classifications of the corrosion inhibitors like inorganic, organic etc. (Fontana, 2005) Further, the inorganic corrosion inhibitors can broadly be divided into two categories:

- Anodic inhibitors
- Cathodic inhibitors

Anodic inhibitors (also called as passivation inhibitors act by a reducing anodic reaction, that it thus blocks the anode reaction and supports the natural reaction of passivating of metal surface. It also forms an adsorbed film on the metal. In general, the inhibitors react with the corrosion product, initially formed, thus results in a formation of cohesive and insoluble film on the metal surface. On the contrary, cathodic inhibitors slow the reaction at the cathode or precipitate cathodic areas in order to increase the impedance on the surface, thus limiting diffusion of reducible species. The nature depends on the material to be protected or agents to be neutralized. The deposited metal promotes the cathodic depolarization by over voltage reduction and formation of an adherent deposit. Among the metals used for this purpose mainly are mercury (Hg), palladium (Pd), iridium (Ir), platinum (Pt), rhodium (Rh) and rhenium (Re).

The effectiveness of corrosion inhibitor depends upon fluid composition, quantity of water and flow regime. A common mechanism of inhibiting corrosion involves formation a coating often a passivating layer, which prevents access of corrosive substance to the metal.

Moreover, there are inorganic anions providing passivation / protection of metal surfaces through their incorporation into the oxide layer. The most widely used of these are:

- Chromate(CrO_4),
- Nitrate (NO_2)
- Molybdate (MoO_3)
- Phosphate (H_2PO_3)
- Silicates

In addition, organic inhibitors have been the most widely used in petroleum refining processes because of their ability to form a protective layer on the metal surface in a media with high hydrocarbons content. At present there are a number of organic inhibitors belonging to different chemical family’s i.e. Fatty amides, Pyridines, Imidazolines and other azoles and polymers which have demonstrated excellent performance as corrosion inhibitors.

1.11.2 MECHANISM FOR CORROSION INHIBITOR

Corrosion inhibitors are used in low concentrations in aggressive environments to prevent, inhibit or minimize corrosion. The inhibition mechanism are generally described as following:

1. CI gets adsorbed on the surface through chemisorption (Chemical adsorption) on the surface of the corroding metal. It forms a protective thin layer. The film act as protective layer or inhibition effect is a combination with metallic surface and inhibitor ions.
2. Inhibitor forms an oxide protection layer to protect the base metal.
3. The corrosive component in the aqueous media was targeted for reaction with the corrosion inhibitor.

Generally, the corrosion inhibitors are divided based on their inhibition mechanisms. The details of inhibitive actions are detailed in this section.

Passivation or anodic inhibitors act by a reducing anodic reaction. These kinds of inhibitors inhibit the anodic reaction and passivate the metal surface by natural reaction. It further forms a films which is adsorbed on the metallic surface. At large, a corrosion product is formed during inhibition process, which results in formation of an insoluble and cohesive film on the metallic surface.

As the name suggests, the cathodic corrosion inhibitors inhibits or prevents the occurrence of the cathodic reaction in corrosion process. Metallic ions in these inhibitors that can cause a cathodic reaction due to alkalinity. This reaction produces insoluble chemical compounds which selectively precipitate on cathodic reactions sites. This deposition over the metal creates an adherent and compact layer restricting the diffusion of species participating in cathodic reactions. It reduces oxygen diffusion and impedance of the surface reducing the corrosion rates.

Some organic compounds also act as corrosion inhibitor. Few of the them are also naturally occurring and their performance can be enhanced by slight modification in the inhibitor or y addition to other compounds. Organic inhibitors are designated as film-forming inhibitors that act by surface adsorption process. These inhibitors may occasionally act as anodic, cathodic or together. These molecules have a strong affinity to metal surface. This property leads to good efficiency for corrosion ignition. Some of them are naturally occurring and hence have relatively lower environmental risk. The film, which forms during adsorption, is hydrophobic in nature and hence acts a barrier for metal dissolution in electrolyte.

1.11.3 CHARACTERIZATION & PERFORMANCE EVALUATION OF CORROSION INHIBITORS

The corrosion inhibitor chemicals are required to be evaluated for a) their compatibility to transportation & refining systems, b) dosage rate optimization and c) performance efficacy. While the inorganic and organic amine derivatives may perform well in protecting pipeline corrosion, some of them can cause fouling in desalter, coking of preheat circuits as well as upset in pH of overhead streams causing ammonia stress corrosion cracking of brass components. Therefore, chemical compatibility to the alloys in refinery system needs to be given the utmost priority while selecting corrosion inhibitors. The compatibility of corrosion inhibitor chemical also needs to be studied with respect to the MIC causing microbes. Often the inhibitor chemicals are seen to act as nutrients to the microbes thereby annulling their effect in corrosion protection. Also, the synergistic or antagonistic effect of the corrosion inhibitor chemicals to other specialty chemicals added to the pipeline such as drag reducer additives, scavenging chemicals etc. needs to be studied prior to their selection for corrosion protection.

Corrosion inhibitors are generally based on an active chemical dispersed in hydrocarbon or water as carrier. The strength of the active constituent determines the effective dosage rate of the inhibitor. A quick evaluation of the film-forming tendency and the film strength of the inhibitor can be evaluated using the Electrochemical Impedance Spectroscopy (EIS) (Matt Lacey, 2018). A Linear Polarization Resistance (LPR) (Natarajan, 2018)measurement can give the adequacy of protection of metals with respect to the dosage rate. The EIS and LPR can be used for quick evaluation of the candidate inhibitor chemical.

For the performance evaluation of the corrosion inhibitor for a given hydrocarbon, a variety of tests can be conducted. The simplest being the ASTM immersion test (ASTM NACE G31, 2012)which is a static test. The weight loss of the immersed coupon determines the effectiveness of the inhibitor film. This test being static doesn't represent the field conditions of the pipeline. The wheel test (NACE 1D182, 2017) is a dynamic test involving the immersion of coupons in the medium treated with inhibitor. This is a gravimetric test providing the percentage inhibition. However, the use of the test as a quantitative comparison is generally discouraged in view of large scatter obtained in the results.

The efficacy of the corrosion inhibitor is assessed as

$$I_{Eff} = (R_0 - R_i/R_0) \times 100 \text{ ------- } (1.7)$$

where 'R_0' is the corrosion rate without inhibitor and 'R_i is the corrosion rate with inhibitor

At present, the ASTM D664 test method modified for this purpose by NACE USA as (NACE TM 0172, 2015) is the most acceptable method for performance evaluation of corrosion inhibitors. In this method, a cylindrical rotating spindle is used as the corrosion coupon. Intentional addition of water to the treated hydrocarbon medium provides the accelerated corrosion medium. A qualitative assessment is made in the form of gradation through visual examination of pitting corrosion on the spindle surface. Quantitative assessment of the spindle has been made possible recently using image analysis.

Recently rotating disc, rotating cylinder and rotating cage electrode tests have come into existence which facilitates for conducting electrochemical measurement of the corrosion occurring with respect to different wall shear stresses signifying the Reynolds number of flow conditions within the pipeline

(Baboian, 2005). These tests are shown to correlate well with the field corrosion data and hence closely simulate the pipeline operating conditions.

An inhibitor may be effective in one set of system, while same not be compatible to another system. Therefore, it is imperative to consider the following critical factors in the selection of inhibitors keeping in view their specificity:

- Chemical structure of the inhibitor component
- Chemical composition of the corrosive medium
- Nature and composition of the metal surface
- Surface roughness of metal and presence of deposits / scales
- Global and local Operating conditions (temperature, pressure, pH, etc.).
- Thermal stability of the inhibitor.
- Solubility and dispersibility and stability of the inhibitor in the carrier medium

1.12 PROBLEM STATEMENT

Currently, India meets nearly 80 % of crude oil requirement through import of various crude oil. The various crude oil includes high sulphur, high TAN (Total Acid Number) and heavy crudes, which are imported at port locations and transported through pipelines to the inland refinery locations. Presently, India imports cheaper, high sulphur, heavy, high TAN crude oils containing sulphur, nitrogen, hydrogen sulphide, water etc. The corrosive nature of the crude oil like sulphur, carbon dioxide, acids, hydrogen sulphide as dissolved in liquid hydrocarbon as well as water / moisture etc., causes internal corrosion in mild steel pipelines. Periodical corrosion monitoring results largely corroborate the phenomenon of internal corrosion in pipelines. In most of the crude oil transportation pipelines in the country, dosing of corrosion inhibitors is not practiced. However, the same is used in petroleum product pipelines and some of the offshore crude oil pipelines. However, considering the incident of internal corrosion in crude oil pipelines, the requirement of injection of corrosion inhibitor for crude oil pipeline is largely felt and accordingly is under active consideration for implementation. The corrosion inhibitors are mostly organic or inorganic chemical compounds. The sourcing of corrosion inhibitor is done as per an industry accepted specification with rigorous laboratory evaluation for their performance (MIL-PRF-25017 Rev H, 2011).

The inhibitor is chemically adsorbed (chemisorption) on the surface of the metal and forms a protective thin film with inhibitor effect or by combination between inhibitor ions and metallic surface or inhibitor leads a formation of a film by oxide protection of the base metal or the inhibitor reacts with a potential corrosive component present in aqueous media and the product is a complex.

The conventional corrosion inhibitors make use of chemical substances consisting of heavy metals and inorganic chemical substances such as chromates and phosphates that are harmful to the human health. Inorganic corrosion inhibitors containing arsenic and lead are carcinogenic in nature and known to induce multiple organ damage at low concentration. High concentrations of chromium can lead to DNA damage. High concentration of phosphates in humans can lead to hypophosphatemia with extensive tissue damage. At present there are a number of organic inhibitors belonging to different chemical families' i.e. Fatty amides, Pyridines, Imidazolines and other azoles and polymers which have demonstrated excellent performance as corrosion inhibitors. While many inorganic, organic and polymeric compounds have showed good performances as corrosion inhibitors for different metals and alloys, many of these compounds are toxic and do not fulfill completely the requirements expected by the environmental standards. Because these are not environment friendly, bio degradable corrosion inhibitors and their sustained exposure is harmful to human being.

1.12.1 GREEN CORROSION INHIBITOR

In view of the above, the extensive use of these corrosion is now being restricted due to the findings about their toxic effects to human and to environment. Natural products are being studied extensively as corrosion inhibitors, both in product mixtures extracted from natural sources such as plants or essentially pure products derived from plants. From the economic and environmental viewpoints, plant extracts are excellent and viable alternative as inhibitors because of their ease of availability and biodegradability. These extracts are obtained in a simple way with minimum purification methods. The extracts are generally obtained from cheap solvents that are widely available, at a low cost and having low toxicity. These extracts contain a variety of natural products such as essential oils, tannins, pigments, steroids, terpenes, flavones and flavonoids, among other well-known active substances that are used as potential corrosion inhibitors. These natural products having corrosion inhibiting properties are generally termed, as **Green Corrosion Inhibitors (GCI)** (Amitha Rani & Basu, 2011). Extension of these to the pipeline internal corrosion problem needs to be studied extensively. The clear white space exists for the proposed research work. Extension of these green corrosion inhibitors for solving petroleum pipeline internal corrosion problem requires to be studied extensively and conclusively.

1.12.2 SCOPE OF THE PRESENT STUDY

Through the process of extensive literature search some of the plant extract are identified which can be used as potential corrosion inhibitors in petroleum product pipelines, based on their solubility, dispersibility and compatibly with the petroleum product. The aim and objective of study is to extraction and characterization of suitable plant produce like Neem, Jatropha, Karenjia, Hibiscus and Eucalyptus for their physical properties like density, viscosity, solubility / dispersibility in hydrocarbon and water etc. Evaluation of their chemical composition and molecular structure of identified green corrosion inhibitors, using IR spectrum, NMR spectrum, Raman Microscopy etc. In addition to above, laboratory scale performance evaluation with the established ASTM codes, standards & practices, at different doses level. The testing protocol includes NACE TM 0172, Rotating spindle test, Static Emersion test, Rotating wheel test etc. Doses optimization studies of natural substances as corrosion inhibitors for hydrocarbon product along with study of synergistic effects with other organic additives, also required to be extensively undertaken.

1.13 ORGANIZATION OF THE THESIS

The Thesis is organized into six chapters. The first chapter provides an **Introduction** to the subject in terms of the Global & Indian Energy scenario, fossil fuels as a predominant component of Indian energy mix, Impetus on growth of oil sector, role of pipeline transportation as an important element of supply chain, challenges in maintenance of pipeline infrastructure against corrosion, cost associated with corrosion monitoring and mitigation, means of corrosion monitoring and mitigation, role of inhibitors in prevention of internal corrosion of pipelines, state of the art of inhibitor chemicals and their effect on sustainability and the defining problem statement for current work.

The second chapter deals with a comprehensive **Literature review** on the various types of corrosion inhibitors, their mechanisms, studies on extraction of plant produce / extracts for application as green corrosion inhibitors in various industrial applications, performance evaluation of green corrosion inhibitors for corrosion prevention in various metallic systems etc. From the literature review, gap areas in availability of suitable and relevant green corrosion inhibitors for internal corrosion protection of petroleum pipelines have been identified. From the identified gap areas, a conceptual frame work for studying potential plant extracts as green corrosion inhibitors for pipeline application have been identified with an outline of the physiochemical performance evaluation methodology.

The third chapter deals with **Research Methodology**. The method adopted for under taking the research has been elaborated, including test medium used, test conducted to collect primary data etc.

The fourth chapter deals with the **Extraction, Physical and Chemical characterization** of extracts of seeds of Jatropha, Neem, Karenjia and the leaves of Hibiscus and Eucalyptus. Physical parameters such as density and viscosity and chemical analysis in terms of molecular structure using IR, NMR and Raman spectroscopy etc. is, undertaken.

The chapter five deals with the **Performance evaluation of Green Corrosion Inhibitors-Part One**. This includes the studies on rotating spindle test of ASTM D669 (NACE TM 0172) for dosage optimization and interactive effects of potential extracts with different concentrations of antioxidants and surfactants on the potential green corrosion inhibitors. Results of the static immersion test as per ASTM G31 are also reported. Further, comparative results of the potential extract for their film persistency, corrosion rate and percentage inhibition are reported through rotating wheel test. Discussion of the results and the inferences are summarized.

The chapter six deals with the "**Performance Evaluation of Green Corrosion Inhibitors-Part Two** deals with electro chemical evaluation of green corrosion inhibitors using the Linear Polarization Resistance (LPR) tests through Tafel extrapolation conducted at room temperature and elevated temperature as per ASTM G 59 and ASTM G 102. The study of electrochemical behavior of the inhibitor doped medium have been studied for them. Qualitative and directional performances of green corrosion inhibitors in terms film persistency and passivation potential have been inferred.

The chapter seven deals with summary of work, Conclusion, recommendations and future research etc.

Chapter 2: LITERATURE SURVEY, GAP AREAS & RESEARCH OBJECTIVE

2.1 INTRODUCTION

The conventional corrosion inhibitors make use of chemical substances consisting of heavy metals and inorganic chemical substances such as chromates and phosphates that are harmful to the human health. Inorganic corrosion inhibitors containing arsenic and lead are carcinogenic and known to induce multiple organ damage at low concentrations. High concentrations of chromium can lead to DNA damage. High concentration of phosphates in humans can lead to hypophosphatemia with extensive tissue damage. At present there are a number of organic inhibitors belonging to different chemical families' i.e. Fatty amides, Pyridines, Imidazolines and other azoles and polymers, which have demonstrated excellent performance as corrosion inhibitors. While many inorganic, organic and polymeric compounds have shown good performances as corrosion inhibitors for different metals and alloys, many of these compounds are toxic and do not fulfill completely the requirements expected by the environmental standards. Because these are not environment friendly, bio degradable and their sustained exposure is harmful may be harmful to operators.

2.2 LITERATURE REVIEW

The author has conducted extensive literature survey on green corrosion inhibitors. The green corrosion inhibitors are mostly found as plant produce. The literature available in the public domain i.e. web sites, publications, books, journals has been examined extensively. The published literature indicates the various studies have been extensively undertaken focusing of use of plant produce as green corrosion inhibitor for prevention of corrosion in metallic surfaces.

Research on green inhibitors has concentrated more on moving from inorganic to organic inhibitors. However, not all organic inhibitors are green. Current trend in research on green organic inhibitors are concentrating on natural product as corrosion inhibitors (Amitha Rani & Basu, 2011)**.** The newer green inhibitors have resulted in the reduction of many of the toxic amine compounds or salts. Increasing use of aliphatic amines in place of aromatic amines is seen. Interestingly, the first patent in corrosion inhibitor by Robinson et al (Musa, 2012)as early as 1900 specified the use of molasses and vegetable oils for pickling of sheet steel in acids. They have used starch a bio degradable material for the same.

Use of natural product as green inhibitor has been growing in popularity. Obeyesekere et al (Obeyesekere, Naraghi, & McMurray, 2001) have synthesized and evaluated biopolymers as corrosion inhibitors. Ficus Religiosa leaves extract have been shown to be effective in preventing aluminum corrosion from phosphoric acid by Rathod et al (Rathod & Vashi, 2016)$^{.}$ The Bacopa Monnieri extract provides a green inhibition of copper metal against HNO_3 solution as reported by (Patel & Vashi, 2016). (Mobin & Rizvi, Polysaccharide from Plantago as a green corrosion inhibitor for carbon steel in 1 M HCl solution, 2017) have reported studies on Plantagopsyllium extract as green corrosion inhibitor for mild steel in 1M HCl solution. Effectiveness of some non-ionic surfactants as bio degradable corrosion inhibitor for low carbon steel in NaCl solution is reported by (Bhattarai, Rana, Bhattarai, & Joshi, 2016; Aslam & Mobin, 2016)$^{.}$ The effect of Callistemon plant extract as green corrosion inhibitor for mild steel in HCl and NaCl solutions has been studied and reported by (Bhattarai, Rana, Bhattarai, & Joshi, 2016)In another study, Aqualeria crassna leave extract is shown to have good inhibition efficiency under 1M HCl solution for mild steel (Helen, Rahim, Saad, Saleh, & Raja, 2014).

Given below is a brief list of literature reviewed and summary of these paper/ articles/publications/ reports etc.

(Abdallah, A. Radwan, Shahera, & Abdelhamed, 2010) mentions that galvanic and potentio dynamic anode polarization models are discussed to study inhibiting effect of parsley, lettuce and reddish oils on corrosion of carbon steel used N 0.5 NaOH solutions for accelerated pitting. Study demonstrates that inhibiting effect increases with the increase in the concentration of the oils which is due to absorption of oil, on the surface of the steel. The inhibiting effect of organic compound is manifested as result of their absorption on metal surface. Paper discusses that the chemical structure of compound, nature and charge of metal surface, charge distribution in molecule of the compound, type of corrosive medium affect the absorption effect of the process. The absorption efficacy is determined by molecular absorption of basic component of oils on the surface of steel. The degree of surface filling as function of concentration of oil used to select the isotherm that best describes the absorption process. The absorption of oil on the surface of metal can be described as process of substitution of water H_2O molecules of oil in the aqueous face on the surface of steel. Paper concludes on the note of comparison of various oils as corrosion inhibitor.

(Sangeetha, Rajendran, Muthumegala, & Krishnaveni, 2011) deals with the replacement of environmentally hazardous chromates, several non-chromates which are presently used, with extracts of plant materials as corrosion inhibitors. The plant extracts are environmentally friendly, nontoxic and easily available. These extracts contain many ingredients including several organic compounds and have polar atom such as O, N, P and S. They are absorbed into metal surface through these polar atoms and a protective film is formed. The paper identifies more than 100 references used in various studies of natural corrosion inhibitors.

(Helen, Rahim, Saad, Saleh, & Raja, 2014) deals with anticorrosive behavior of agarwood leaves extract in 1 M HCl solution on mild steel study using gravimetric methods (weight loss method), electrochemical methods, potentio dynamic polarization and scanning electron microscope (SEM). The extracts have shown good inhibition efficiency in various testing protocols for the gravimetric and electrochemical methods. EIS analysis revealed that increase in concentration increases the charge transfer resistance, thus increased inhibition efficiency. The adsorption mechanisms for both extracts were mainly physiorption. In this study, potentio dynamic polarization measurements showed the extracts acted as mixed type inhibitors with predominantly cathodic effectiveness. SEM techniques supported the success of corrosion inhibition with the presence of inhibitors and the methanol extract best fitted the Temkin adsorption isotherm while the aqueous extract best fitted the Langmuir and Temkin adsorption isotherms.

The studies made by (Suleiman, Abdulwahab, & Awe, 2016) on the effect of plant extracts i.e. Umbrella Thorn (Acacia Tortilis) with mild steel using gravimetric and electrochemical corrosion techniques in 0.5 M H2SO4 . The evaluations using linear regression equation and analysis of variance (ANOVA) were employed to investigate the effect of process parameters on the corrosion rate of samples. The results indicated that temperature, inhibitor concentration and time are statistically significant. The adsorption followed Langmuir adsorption isotherm. The SEM morphology of the adsorbed protective film of mild steel surface confirmed high performance of inhibitive effect. Paper concludes that the inhibitor efficiency increases with increase in concentration & decreases with increase in temperature and halide ions.

(Kesavan, Gopiraman, & Sulochana, 2012) compares the existing corrosion inhibitors, aspect of toxicity of substances like chromate, increasing interest in the green inhibitors. Corrosion is an unavoidable but a controllable process. Due to the issues of toxicity of substances like chromate inhibitors, there is an increasing interest in exploration and utilization of eco-friendly inhibitors, which are also known as green inhibitors. This review briefly discusses some of the interesting features of the green inhibitors reported during the last decade.

(Amitha Rani & Basu, 2011) highlights that the environmental toxicity of organic corrosion inhibitors has prompted the search for green corrosion inhibitors as they are biodegradable, do not contain heavy metals or other toxic compounds. As in addition to being environmentally friendly and ecologically acceptable, plant products are inexpensive, readily available and renewable. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic, amino acids, and organic dyes of plant origin are of interest. In recent years, sol-gel coatings doped with inhibitors show real promise. Although substantial research has been devoted to corrosion inhibition by plant extracts, reports on the detailed mechanisms of the adsorption process and identification of the active ingredient are still scarce. Development of computational modeling backed by wet experimental results would help to fill this void and help understand the mechanism of inhibitor action, their adsorption patterns, the inhibitor metal surface interface and aid the development of designer inhibitors with an understanding of the time required for the release of self-healing inhibitors. The present paper consciously restricts itself mainly to plant materials as green corrosion inhibitors.

In recent years, plant extracts have become the focus of corrosion inhibitor research due to their low toxicity, easy availability and economical preparation. (Mo, Luo, & Li, 2016) presents most of the recent contributions made to the application of plant extracts as corrosion inhibitors for steel in sulphuric acid, as well as in both hydrochloric acid and sulphuric acid. The constituents, properties, adsorption modes and inhibition mechanisms of these natural products are discussed. Evaluation methods and the factors that influence the corrosion inhibition efficiency of plant extracts are also summarized

(Papavinasam, 2000) provides a list of methods for determination of effectiveness of corrosion inhibitor. Study elaborates that in principle, any method to determine the corrosion rate can be used to test a corrosion inhibitor. The primary criterion for evaluation is the inhibitor efficiency. Inhibitors having sufficiently high efficiency are tested for "side effects," which include environmental compatibility, emulsion formation, viscosity and pour point density. Finally, the inhibitor formulation is tested in the field. In general (Papavinasam, 2000) specifies, the process of evaluation and selection of corrosion inhibitors involves three steps: (1) laboratory evaluation, (2) evaluation of compatibility (including cost), and (3) field evaluation

(Acharya, Chouhan, Dixit, & Gupta, 2013) presents a brief research carried out in field of green corrosion inhibitor research. It cites the works carried out on corrosion inhibition ability of several naturally occurring chemical compunds containing tannis, alkaloids, organic amino acids and organic dyes. Corrosion control of metal is of technical, economic, environmental and aesthetical importance. The use of inhibitor is the best way to prevent metal and alloys from corrosion. There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. These efforts are motivated by the desire to replace toxic organic corrosion inhibitors used for mitigation of corrosion of various metals and alloys in solutions. Plants represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. The green corrosion inhibitors are bio degradable, nontoxic, environmentally benign, and low cost, are obtained from renewable resources with minimal health and safety concerns. Investigations of corrosion inhibiting abilities of tannins, alkaloids, organic amino acids and organic dyes of plant origin are of interest. Development of computational modeling backed by wet results would help in understanding the mechanism of inhibition action, their adsorption patterns, inhibitor-metal surface interface and help in the development of designer inhibitor with an understanding of the time required for the release of self-healing inhibitors. The present paper restricts itself mainly to the plant materials as “Green Corrosion Inhibitor”.

(Fouda, Elewady, shalabi, & Habouba, 2014) investigated anise extract as green corrosion inhibitor of carbon steel in 1 M HCl solution using weight loss, potentio dynamic polarization, electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) techniques. Surface morphology was tested using scanning electron microscope (SEM) and energy dispersive X-ray (EDX). The adsorption of the inhibitors on carbon steel surface was found to obey the Langmuir’s adsorption isotherm. The activation and adsorption parameters were calculated and discussed. Study concludes that anise extract show good performance as a corrosion inhibitor in the subject media.

(Olusegun, Adeiza, Ikeke, & Bodunrin, 2013) used Jatropha Curcas leaves extract as green corrosion inhibitor for mild steel in corrosive media of 1M solution using gravimetric analysis. The study was conducted to identify the order of reaction. Effect of temperature on corrosion inhibition properties were studied for this combination. Adsorpotion isotherms were drawn to and it was observed that the adsorption follows Langmuir isotherms. Paper concludes that Jatropha Curcas extract works acts as an effective inhibitor in acidic media.

(Badoni, 2013) The papers deal with fundamental of corrosion, facts and cause of corrosion. Formation of rust, theories of corrosion, three main types of corrosion like oxidation corrosion, wet or electro chemical corrosion and acid theory. Further it deals with economic aspect of corrosion. Types of corrosion like galvanic, erosion corrosion, crevice corrosion, pitting corrosion, differential aeration corrosion, water line corrosion, microbiological corrosion, stress corrosion cracking factors affecting chemical corrosion, protection and corrosion control, risk assessment flow chart etc.

(Patni, Agarwal, & Shah, 2013) Identifies the various types of corrosive media across the processing industry. Paper further find the references of studies where several green corrosion inhibitors have been used for different applications. Paper further reiterates that corrosion inhibitors can be divided into two categories, One, those that enhance the formation of protective oxide film by oxidizing effect and others that inhibit corrosion by selectively adsorbing on the metal surface and creating a barrier that prevents access of corrosive agents to the metal surface. Research comparison shows that almost all organic molecules containing heteroatoms such as nitrogen, sulphur, phosphorous, and oxygen show significant inhibition efficiency. Paper further indicates that despite these promising findings about possible corrosion inhibitors, most of these substances are not only expensive but also toxic non-biodegradable thus causing pollution problems. Hence, these deficiencies have prompted the search for their replacement.

To overcome these issues, several studies mainly plants naturally occurring compounds, some with complex molecular structures and having different chemical, biological, and physical properties are being studied aggressively for corrosion inhibition. The naturally occurring compounds are luctraive as they are environmentally acceptable, cost effective, and have abundant availability. These advantages are the reason for use of extracts of plants and their products as corrosion inhibitors for metals and alloys under different environment. Different plant extracts can be used as corrosion inhibitors commonly known as green corrosion inhibitors.

Paper further identified Tannins and their derivatives which can be used to protect steel, iron, and other tools from corrosion. Based on studies in the field paper concludes that mild steel in 2 M HCl solutions can be protected from corrosion using extracts from leaves can be used. Paper also identified researches where extracts of tobacco from twigs, stems, and leaves can protect steel and aluminium in saline solutions and strong pickling acids. Paper also identifies that Black Pepper, *Acacia* gum, castor seed, and lignin are also good corrosion inhibitors for steel in acidic media. Paper iterates that Mango peel extract is one of the most effective corrosion inhibitor for Al and Zn, and pomegranate fruit shells extract is also suitable for Cu. It was found that all extracts were more efficiently corrosion inhibitors in HCl solution as compared to H_2SO_4 solution .Paper also reinstate that aqueous extracts of *Eucalyptus* leaves protect mild steel and copper in 1 M HCl solution from corrosion. Inhibition efficiency of plant extracts can be tested by various methods such as galvanostatic polarization, mass loss measurements, and surface characterization techniques. SEM studies provide the confirmatory evidence for the protection of mild steel by the inhibitor.

(Chigondo & Chigondo, 2016) starts with the economy of using mild steel, with an associated perennial problem of corrosion associated with the material. However, challenge is using regular mild steel has low corrosion resistance specifically in acidic environments. One of the major nodes for addressing the problem is corrosion inhibition which is most economical & practical technique to control corrosion on metals. In a typically corrosion Inhibition mechanism, inhibitors are adsorbed on the metal surface, forming a protective barrier, and interact with anodic or/and cathodic reaction sites to decrease the oxidation or/and reduction of corrosion reactions. Paper identifies & list several studies where plant extracts have been proposed to replace synthetic organic and inorganic inhibitors given their success story in literature. Paper further deals with the mechanism of action of green inhibitors depending on the structure of the active ingredient. Further to describe the theory for chemical inhibition several theories have been published. One proposition suggests that the active compounds form onium ions (H^+ or R^+) in acidic solutions and are adsorbed on the cathodic sites of the metal and interfere with the cathodic reaction. Paper further discusses active constituents of natural inhibitors which vary from one plant species to another but their structures are closely related to their organic counterparts. (Chigondo & Chigondo, 2016) gives examples such as garlic contains allyl propyl disulphide, mustard seeds contain an alkaloid berberine which has a long chain of aromatic rings and an N atom in the ring, and, at several places, carrot contains pyrrolidine and castor seed contains the alkaloid ricinine. Eucalyptus oil contains monomtrene-1,8-cineole. Lawsonia extract contains 2-hydroxy-1,4-naphthoquinone resin and tannin, coumarin, gallic acid, and sterols. Gum exudate contains hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, and reducing and non-reducing sugars. Garcinia kola seed contains primary and secondary amines, unsaturated fatty acids, and bioflavonoids. Calyx extract contains ascorbic acid, amino acids, flavonoids, pigments, and carotene.

(de Souzaa, Rippera, Perrone, & D’Elia, 2016) studied the behavior of roasted coffee extract and its isolated high molecular weight fraction as carbon steel corrosion inhibitors in HCl solution. Study uses weight loss measurements, potentio dynamic polarization curves, electrochemical impedance and scanning electron microscopy analysis. Results showed that the high molecular weight fraction, rich in melanoidins, present an important role in the inhibitory action of the roasted coffee extract in the acid corrosion of carbon steel. The chemical composition of the roasted coffee (*Coffea canephora*) includes caffeine (2.4%, w/w) and trigonelline (0.7%, w/w), chlorogenic acids (3.8%, w/w), carbohydrates (37.3%, w/w), pectin (2.0%, w/w), protein (7.5%, w/w), lipids (11%, w/w) and Maillard reaction products (melanoidins). Paper identifies that caffeine and chlorogenic acids (especially 5-caffeoylquinic acid) are, together with melanoidins (which represent 25%, w/w), major constituents of roasted coffee and therefore could be possibly responsible for its corrosion inhibitory properties. The objective of this paper is to investigate the inhibitory action of roasted coffee extract as well as its isolated high molecular weight fraction on carbon steel corrosion in acidic medium by weight loss measurements and electrochemical techniques, as well as through surface analyses using Scanning Electron Microscopy (SEM).

The study of corrosion is of paramount importance because of the direct and indirect losses caused by this scourge. At the economic level, more than a quarter of the world's steel production is degraded due to a corrosion problem. (Lgaz, Salghi, & Ali, 2018) discusses, inhibitory effect of 9-Hydroxyrisperidone (HRD) on the mild steel corrosion in hydrochloric acid solution (1M HCl) was studied using chemical, electrochemical (PDP and electrochemical impedance spectroscopy), Density Functional Theory (DFT) and Molecular Dynamic (MD) simulations studies. The mild steel morphologies were evaluated with the aid of SEM.

A green corrosion inhibitor namely, 9-Hydroxyrisperidone (HRD) was investigated for their influence on mild steel corrosion in 1 M HCl using weight loss, Tafel polarization, electrochemical impedance spectroscopy (EIS) and surface morphology techniques. Quantum chemical calculations were also conducted to corroborate experimental findings. The tested compound is mixed type inhibitor following Langmuir adsorption isotherm and involved competitive physiorption and chemisorption mechanisms. The results from electrochemical impedance spectroscopy tests reveal an increase in polarization resistance. Scanning Electron Microscopy (SEM) analyses of steel surfaces in acid-inhibitor solutions showed that tested compound protects mild steel surface effectively.

(Singh, Kumar, Quraishi, Haque, & Singh, 2018) in the study have synthesized two novel corrosion inhibitors Bispyranopyrazoles 1 and 2 and evaluated their corrosion inhibition property on mild steel (MS) in acid solution through weight loss and electrochemical corrosion techniques. The corrosion test results reveal that both compounds inhibit corrosion by an adsorption mechanism and display inhibition efficiency more than 95%. From the surface analysis of the protective film on MS, it was corroborated that adsorption of inhibitor molecules occurred on the MS surface through chemisorption, which further suppresses the corrosion rate. Paper further identifies that the experimental results were in good agreement with the quantum chemical observations.

(Khadom, Abd, & Ahmed, 2017) studies the corrosion inhibition of low carbon steel in 1 M HCl was studied in the absence and presence of Xanthium Strumarium Leaves (XSL) as friendly corrosion inhibitor. The effect of temperature and inhibitor concentration was studied using weight loss method. The results indicated that XSL reduces the corrosion rate. The inhibition efficiency was found increased with the increase in the concentration of inhibitors. The adsorption of XSL was found following the Langmuir adsorption isotherm model

Due to the harmful nature of the traditional inhibitors, in recent years researchers have an interest in using eco-friendly corrosion inhibitors. The plant extracts exhibit efficient corrosion inhibition properties due to the presence of a mixture of organic constituents starting from terpenoids to flavonoids. In the study by (Bhuvaneswari, Vasantha, & Jeyaprabha, 2018) the inhibition of corrosion of mild steel in 1 N H_2SO_4 solution using the leaf extract of Pongamia pinnata (P. pinnata) was investigated by the weight loss method, potentiodynamic polarization method and electrochemical impedance spectroscopy (EIS) technique. Characterization of the leaf extract of P. pinnata was carried out using Fourier transform infrared spectroscopy (FTIR) and gas chromatography mass spectrometry (GCMS) analysis. The effect of temperature and immersion time on the corrosion behavior of mild steel in sulfuric acid with different concentrations of P. pinnata was also studied. From the results it was found that the inhibition is mainly attributed to the adsorption of inhibitor molecules on the mild steel electrode surface. It was found that the adsorption of inhibitor molecules takes place according to the Langmuir, Temkin, and Freundlich adsorption isotherms.

(Ansari & Siddiqui, 2018) throws light on ways to combat corrosion of steel. A variety of inhibitors for steels corrosion in the acidic solutions are dealt here. A great emphasis has been made on HCl solutions in drilling and acidizing operations low grade steels, at high temperatures. A combination of corrosion inhibitors with surfactants, solvents, natural extracts as well as intensifiers in order to improve the strength or we can also say the efficiency of each individual compound at higher temperatures. The aim of this research is to give a pretty good idea about the corrosion problems encountered in drilling and acidizing operations and the inhibition techniques adopted in order to tackle the problem.

(Cookey, Tambari, & Iboroma, 2018) discuss the inhibition effect of green tip forest lily leaves on steel in acid media. paper further identifies the several synthetic corrosion inhibitors such as polyethylene glycol and inorganic related inhibitors, such as those containing phosphate, chromate, and other heavy metals were widely used and comments on their limitations. However, due to the high cost and toxicity of these synthetic inhibitors, the need to find alternatives became obvious. In recent times, corrosion inhibitors of natural origin are now being preferred as they are eco-friendly, biodegradable and possess no threat to the environment. In this study, corrosion tests were performed on mild steel to evaluate the effect of concentration of inhibitor, varying immersion period and temperature on the corrosion inhibition properties of Clivia nobilis leaves extract. This was done in H_2SO_4 and HCl acid solutions using weight loss and gasometric methods. From the weight loss results, corrosion rate and degree of surface coverage were evaluated and plotted as a function of inhibitor concentration at various immersion times. The volume of the cathodic hydrogen gas evolved was also plotted as a function of inhibitor concentration. The efficiency of inhibition in H_2SO_4 and HCl solutions were also compared. It was observed that corrosion inhibition efficiency increased with increasing concentration of Clivia nobilis leaf extract but not with prolonged immersion period

In the paper (Koshel, 2013) deals with effect of corrosion in environment like leakage of natural gas can lead to H_2S environment, effect of H_2S, handling of hazardous materials and precautions. A case study of the BP Pipeline failure was mentioned by author. Author also mentions corrosion related failures in oil fields, causes of corrosion and corrosion monitoring mechanism like visual examination, weight measurement, electrochemical, ultrasonic, iron content, hydrogen probe, down hole inspection and intelligent pigging etc.

The chapter (Palou, Xomelt, & Likhanova, 2014) deals with use of corrosion inhibitor is one of the economic ways to mitigate the corrosion. He mentions about the inorganic and organic type of corrosion inhibitors and their effect on corrosion mitigation. Then author describes the use of environmentally friendly corrosion inhibitors, their advantages and suitability for various industries.

(Ismail, 2016) undertakes study regarding effect of green corrosion inhibitor for mild steel in sea water. He has selected the green corrosion inhibitors mainly on account of their biodegradability, bio accumulation, bio compatibility. He mentions some of the green corrosion inhibitors that are being used for corrosion prevention in carbon steel.

(NACE TM 0172, 2015) deals with testing procedure and protocol of determining corrosive properties of the gasoline and distillate fuels and also included information on test specification preparation.

In this paper, (Miksic & Furman, 2009) evaluated several types of corrosion inhibitors. The active ingredients in those inhibitors included long chain amines, fatty amides, imidazolines, fatty acids and their salts. The inhibitors tested in the concentration range from 50- 200ppm in the electrolyte and electrolyte hydrocarbon mixture in presence of CO2 and H2S in static & dynamic conditions. Several evaluations were performed when corrosion inhibitors were added into electrolyte containing flow modifiers. The results, which include the corrosion inhibitors, are effective in studied range of flow rates and compatible with flow modifiers

(Pokhriyal, 2013) deals with the general description of petroleum pipeline design and operation, Requirement of pipelines as safe, economical, reliable, convenient, energy efficient mode of transportation of petroleum products. The pipelines are inherently prone to corrosion being laid underground. Hence it is required to be well protected against various time dependent and time independent threats. Corrosion threats are generally time dependent threats which have major impact on life and integrity of pipeline. The weakening of the pipeline by corrosion will reduce the resistance to the pipeline against external forces and bring out material and fabrication weakness. The CAPEX for laying pipeline is enormous; therefore it is necessary to protect the pipelines against corrosion. The prevention of corrosion thus required throughout the life cycle of the pipeline. The corrosion management is part of the integrity management of the pipeline. Author deals with the types of corrosion inhibitors used for protection against internal corrosion. This briefly talks about the different types of corrosion in the pipelines, description of available crude oil, Gas and product pipelines in India. Author also mentions that existing practices in the corrosion management including corrosion assessment.

A comparative electrochemical study has been performed by (Wang, 2011) to evaluate corrosion inhibition property of several film-forming corrosion inhibitors provide by Akzo Nobel on carbon steel in a chloride solution. For carbon steel exposed to 1 M NaCl solution with and without added inhibitor, electrochemical measurements including electrochemical impedance spectroscopy (EIS), linear polarization resistance (LPR) at different exposure time intervals, and potentio dynamic polarization at the termination of the exposure, have been performed to investigate the film-forming process and to evaluate corrosion inhibition efficiency of the inhibitors, as well as its evolution with time. (Buchweishaija, 2009)

There is an intensive effort underway to develop new plant origin corrosion inhibitors for metal subjected to various environmental conditions. (Buchweishaija, 2009) summarizes the early efforts which have been motivated by the desire to replace toxic inhibitors used for mitigation of corrosion of various metals and alloys in aqueous solutions. Plants represent a class of interesting source of compounds currently being explored for use in metal corrosion protection in most systems, as possible replacement of toxic synthetic inhibitors. In this review article, research results on the use of eco-friendly phytochemicals as corrosion inhibitors have been summarized. A general introduction to the topic of corrosion mitigation by inhibitors is presented followed by extensive literature survey on the use of natural inhibitors for corrosion control of metals and alloys in different corrosive media.

(Al-Senani, Al-Aaeedi, & Almufarij, 2015) investigated the effect of Green Leafy Vegetables (GLV) extracts namely Lactuca sativa (Lactuca), Eruca Sativa (Arugula), Petroselinum crispum (Parsley), and Anethum Graveolens (Dill) for inhibition of corrosion of carbon steel in 1 M HCl solution using gravimetric (weight loss) method. Paper shows that the inhibition efficiency has increased as concentration of the extract increased. The inhibition efficiency has decreased as the temperature increased. The results obtained showed that GLV extracts inhibited the corrosion process by a physical adsorption mechanism that followed the Langmuir, Freundlich, and Temkin adsorption isotherm models. The adsorption thermodynamic parameters that were calculated include, free energy of adsorption, activation energy, enthalpy of adsorption, and entropy of adsorption are proposed for the corrosion of carbon steel in 1 M HCl in the absence and presence of GLV extract.

(Mahat, Kamarudin, Isa, Bonnia, & Jani, 2012) investigated the effect of extract of Azadirachta excelsa leaves as corrosion inhibitor on mild steel in hydrochloric acid medium using weight loss method. corrosion rate (CR), inhibition efficiency (IE) and surface coverage were calculated using the experimental data. Extracts of Azadirachta excelsa leaves in different concentration were used as natural inhibitor to identify the optimum dosage rate. The inhibition efficiency of mild steel in 1 M hydrochloric acid increased as the increasing of concentration of plant extract. The surface morphological changes were recorded using the FESEM analysis. Study proved that Azadirachta excelsa leaves extract was nontoxic, cost effective corrosion inhibitor for mild steel in acid medium.

(M.M.B.El-Sabbah, H.F.Y.Khalil, M.H.Mahross, B.N.A.Mahran, & Gomaa, 2015) studied the aqueous extract of ginger (AEG) as a possible green inhibitor for corrosion of mild steel in 1 M HCl in a temperature range 25-55°C using the gravimetric method, Open circuit potential (OCP), linear and Tafel polarization techniques. Effect of AEG was also studied in presence of a commercial biocide to reduce the microbial activity at the surface of the extract. The inhibition efficiency was found to increase with increasing concentration of the inhibitor and with decreasing temperature. Study shows that adsorption of aqueous extract of ginger on the mild steel surface obeys the Langmuir adsorption isotherm. Polarization studies indicate that the aqueous extract of ginger is mixed type inhibitor. The thermodynamic functions of adsorption processes were calculated from weight loss at different temperatures data and were used to analyses the inhibitor mechanism. The surface morphology of the mild steel specimens was evaluated using SEM and EDAX analysis.

(Jiang, et al., 2018) isolated & investigated the extract of Raphanus sativus L (Sinapine thiocyanate, Inhi-ST) as green inhibitor by the dried and powdered semen raphanin from Raphanus sativus L. Characterization was done by ESI-MS, 1H and 13C-NMR. The corrosion inhibition of Q235 steel (QS) by Inhi-ST in HCl solution was evaluated using weight loss and potentio dynamic polarization measurement. The study results indicate that Inhi-ST is an effective green corrosion inhibitor for QS corrosion in HCl solution, the green corrosion inhibitor is a mixed type inhibitor, and the inhibition efficiency increase with Inhi-ST concentration increasing, while which decrease with HCl concentration, temperature and storage time increasing. In addition, the adsorption of Inhi-ST on QS follows Langmuir isotherm, which is the mixed adsorption involving both chemisorption and physio sorption.

(Krishnan, et al., 2018) *tested extract of Turbinaria ornata* (TO) as green corrosion inhibitor on mild steel (MS) coupons in conc. HCl medium. Additionally, antibacterial efficacy of the extract of TO was also performed against 16 S rDNA identified marine biofilming bacteria (MBB) and human pathogenic bacteria (HPB). Fifteen colonies of bacteria were identified & isolated from a ship hull to study the anti fouling effect of soxhlet MeOH extract of TO on marine bacteria. Results including weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy, FT-IR and GC-MS shows 10-Octadecaonic acid as a major corrosion inhibitor from *T. ornata* and is discovered as a novel anti foulant.

(Okewale & Olaitan, 2017) has explored the possibility of using plant extract as a corrosion inhibitor other than the use of conventional organic materials as corrosion inhibitor. Rubber leaf extract which contains the carbonyl groups, aromatic rings, and double bonds as indicated by the GCMS, phytochemical, and FTIR analysis is one of the good natural plant extract as corrosion inhibitor. Gravimetric method was used to determine the weight loss on surface of mild steel at various inhibitor concentrations in 0.1M HCl solution. The highest inhibition efficiency of 86% was achieved using the rubber leaf extract as inhibitor. Adsorption mechanism was investigated using Langmuir, Temkin, and Freundlich isotherms.

(Murthy & Vijayaragavan, 2014) synthesized a new corrosion inhibitor, namely acid extract of leaves of *Hibiscus sabdariffa* and studied its inhibiting action on the corrosion of mild steel in acidic bath (1.2 N HCl and 1.2 N H_2SO_4) by corrosion monitoring techniques. The results of the present study show that this compound has decent inhibiting property for mild steel corrosion in 1.2 N H_2SO_4. Paper further studies the effect emersion period, Inhibitor concentration, acid acid concentration on inhibition efficiency of the extract. Paper also concludes that the extract shows better inhibition in sulfuric acid than in hydrochloric acid.

(Echem, Ideriah, Lucky, & Nwala, 2018) studied the inhibition efficiency of the mixtures of rubber leaf and corn cob extracts on the corrosion of mild steel in 1M H2SO4 acid solution at room temperature using weight loss, AAS and FTIR methods. The mixture of extracts demonstrates the corrosion inhibition of mild steel in 1M H2SO4 solution. Inhibition efficiency was found to increase with increasing concentration of the mixture of extract. Paper first discusses the method of extraction followed by the experimental results. It was recommended that the mixed extract should be used to test inhibitory effect on different metals and in higher concentrations of sulphuric acid

(Shah & Agarwal, 2014) studied the effect of aloe vera as green corrosion inhibitor. Paper discusses effect of aloe vera on the galvanized Iron in HCl and H2SO4 solution. Paper indicates aloe vera as potential corrosion inhibitor. The study used gravimetric method for identification of efficiency of corrosion inhibitor. Paper also concludes that the inhibition efficiency was found to be high in sulfuric acid than in hydrochloric acid.

(Fouda, El-Khateeb, & Elbahrawi, 2017) studied the effect of an aqueous extract of Cupressus sempervirens on the corrosion inhibition of carbon steel in 1M hydrochloric acid solution. Study used mass reduction, hydrogen evolution, electrochemical frequency modulation (EFM), potentiodynamic polarization, and electrochemical impedance spectroscopy (EIS) methods for study of corrosion inhibition of Cupressus sempervirens. The efficiency of Cupressus sempervirens extract was examined with increasing dose of the extract and the temperature. The parameters of thermodynamic of corrosion and adsorption processes were measured and discussed. The extract was adsorbed on surface of metal chemically and was obtain obey Temkin isotherm. The potentiodynamic polarization resulted lead to the extract is mixed inhibitor type. The results given from the weight reduction, polarization EIS & EFM were in agreement.

(Santos, et al., 2017) studied inhibition effect of castor bark powder obtained from *Ricinus communis* on AISI 1020 carbon steel in acidic media (HCl 0.5 mol.L^{-1}) by electrochemical impedance spectroscopy (EIS), polarization curves, scanning vibrating electrode technique (SVET) and weight loss measurements. Characterization was done by Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). The EIS and gravimetric results showed that the inhibitory efficiency increases with inhibitor concentration. Polarization curves indicated that the castor bark powder acts as mixed inhibitor. The adsorption of the powder components on the metal surface follows the Langmuir isotherm. The FTIR analyses indicate the presence of C, N and O heteroatoms, incorporated in functional groups mainly related to the presence of carboxylic acids as ricinoleic acid, which could be responsible for the inhibitory properties of the powder. Paper also brings forth the limitation of the castor bark powder indicating that the inhibitor efficiency decreases with the increase in immersion time.

(Mishra, 2014) starts the study with a note on importance of corrosion being a ubiquitous process, causing huge economic loss to industries. Paper further spefies the increased environmental awareness in last few decades to develop green alternatives to widely used synthetic corrosion inhibitors. Paper identifies various plant extracts studied as green corrosion inhibitors. Paper lists Lowsonia Ficus, Eugeno/derivative, Rosemerry oil, Hibisucus sabdariffa, Phyllantus amaratus, Acacia Senegal, Citrus aurantifolia and others studied as green corrosion inhibitors. This paper intends to highlight the research work reported in this field in last decade. This work focusses on advances made in use of plant extracts as green corrosion inhibitors for mild steel in corrosive fluids due to their industrial importance.

(Varvaraa, et al., 2017) studied inhibitive action of natural propolis on bronze corrosion in a weakly acidic solution containing Na2SO4 and NaHCO3. Study deployed multiscale electrochemical techniques, namely potentiodynamic polarization, electrochemical impedance spectroscopy and scanning vibrating electrode technique measurements for assessment of inhibition efficiency. HPLC-DAD analysis was conducted on propolis to identify its constituents. Surface characterization was performed by SEM-EDX and AFM analysis. Experiments were performed as a function of the propolis concentration and immersion time in the corrosive electrolyte. The obtained results showed that propolis presents good anticorrosive properties on bronze, acting as a mixed type inhibitor, but its protective effectiveness is time-dependent. Study indicates that the inhibitive properties of propolis on bronze corrosion are likely due to the adsorption of its main constituents (flavonoids and phenolic compounds), through the oxygen atoms in their functional groups and aromatic rings, which have been evidenced by FT-IR spectra. Paper concludes that the propolis exhibits good corrosion inhibiting properties for bronze on weakly acidic solutions. The adsorption of propolis on bronze was found to follow Langmuir adsorption isotherm.

(Mobin & Basik, Cissus quadrangularis-zirconium acetate complex as a novel green corrosion inhibitor for mild steel, 2018) synthesized a complex based on Cissus quadrangularis (CQ) plant extract and zirconium acetate (CQ-ZrAc) and studied as a novel green inhibitor against mild steel corrosion in 1 M HCl solution using gravimetric analysis, potentio dynamic polarization (PDP) and electrochemical impedance spectroscopy (EIS). GC-MS and FTIR studies were conducted to assess the active organic species and the functional group present in the extract which caused its adsorption on the mild steel surface. The gravimetric parameters revealed that inhibition efficiency depends both on the temperature of corrosive solution and inhibitor concentration. Adsorption of inhibitor followed Langmuir adsorption isotherm. PDP analysis suggests that compound act as a mixed type of inhibitor. EIS data revealed the formation of a protective film by the adsorption of active species present in the extract. SEM images show better morphology in presence of inhibitor. UV-visible and FTIR results also support the inhibition action of the inhibitor.

(G.Subramanian, 2018) emphasized that 1000 million tons per annum of iron & steel products are being produced in India, & out of this a minimum of 400 million tons of steel products may need eco-friendly surface pretreatment. The extensive utilization/application of the derusting processes (acid pickling, wire brushing, grid blasting & sand blasting) for removing corrosion products on steel and iron components in the long run would result in severe environmental degradation in view of the by products produced during those processes

Green corrosion inhibitors are derived from several parts of a plant such as root, seed, leaf and fruit extracts. The extract obtained is concentrated and dissolved in a solvent to obtain the corrosion inhibitor solution. Plant extracts are viewed as rich source of naturally synthesized chemical compounds that can be extracted by simple procedures with low cost. (Sangeetha, Rajendran, Muthumegala, & Krishnaveni, 2011)

The review of the literature clearly and unambiguously indicates that there are various types of green corrosion for different metals and mostly synthesized in acidic medium. The literature also indicates the growing popularity of the green corrosion inhibitors which are preferred choice over inorganic or organic chemicals, because of their environmentally benign and biodegradability. Hence study and development of the green corrosion inhibitor is not only relevant but also clearly manifests as white space for development and application of these corrosion inhibitors in petroleum environment. The brief extraction methodology for few common green corrosion inhibitors is enumerated as gathered from the literature survey.

Rice husk ash acts as a green corrosion inhibitor due to the presence of silicates as reported (Awizar, et al., 2013).The Nano-size silicate particles adsorb strongly to the cathodic region of the metal surface acing as corrosion inhibitor. To extract the silica, rice husk is burnt to white ash. Subsequently silica is extracted from the white ash by 2.5M sodium hydroxide (NaOH) of solution, boiled for 3hours, filtered, washed and dried at room temperature. A solution of 5M sulphuric acid (H_2SO_4) is added to produce silica with higher purity. Then it continued by refluxing process in acid condition (3M HCl) for 6hours to obtain nano-silica powder followed by filtration and repeated washing. Solutions of 2.5M NaOH and 2.5M H_2SO_4 were added until pH neutral. The precipitating of Nano silica is washed and dried at 50 °C for 24hours. The nanosilicate solution inhibitor is prepared by dissolving 1 g of Nano silica powder in 3M NaOH solution.

Mango and orange peels are a rich source of antioxidants, which includes ascorbic acid, carotenoids, and phenolic compounds that act as corrosion inhibitors. The peels of these fruits are air-dried and then crushed. The crushed peels are added to a Soxhlet apparatus and extracted successively with hexane. The extracts are obtained by simple water infusion (Rochaa, Gomes, & D'Elia, 2014)**.**

Aqueous extracts of olive roots, stems, and leaves act as eco-friendly corrosion inhibitor for steel. An olive seed sample is extracted three times with a solvent (methanol/water: 70/30: v/v) for 2 h in a water bath at 60 °C. The refluxed solution of each sample is filtered, and the filter liquor is evaporated to 100ml of dark brown residue, and then degreased with hexane and extracted with separator funnel. The extract is filtered, and the collected liquid is used to prepare the desired concentrations by dilution (Bouknana, et al., 2015)**.** Jatropha which is known for bio diesel production (Olusegun, Adeiza, Ikeke, & Bodunrin, 2013) can also be used for corrosion inhibitors as shown by a few researchers. The solutions of HCl and H_2SO_4 were prepared by using distilled water. The fresh leaf of Jatropha Curcas plant was taken, washed under water, cut into pieces, air dried and then grounded well and sieves into powdery form. Then, 10 g each of the powdery leaf was put into flat bottom flask containing 200 cm^3 of 4 M HCl and H_2SO_4 aqueous solutions. This concentration was used in order to fasten the rate of reaction between the metal surface and the acidic extract of the inhibitor within the experiment period. The resulting solutions were refluxed for 2hours and left overnight before it was carefully filtered. The stock solution was prepared from the filtrate and into the desired concentrations.

2.3 INFERENCES FROM THE ABOVE SURVEY

Based on the various literature surveys, the details of green corrosion inhibitors under various stages of studies for corrosion inhibition of the various metals under various conditions were thoroughly studied. Subsequently the details of the existing corrosion inhibitors used in the various pipelines and their working methodology were studied in details. Since the subject study was related to the use of the corrosion inhibitors for petroleum product and crude oil pipeline, which are highly quality sensitive product, hence extensive study of the existing Organic and inorganic corrosion inhibitors was done.

It is pertinent to mention that in India, Oil companies in line with the auto fuel policy of the Government of India have adopted periodic fuel quality improvement. From BS II (then EURO II), we have is progressively upgraded the fuel specification. Primarily due to environment pollution considerations so that harmful pollutants from exhaust pipe of vehicles could be substantially reduced. At present country has switched over BS IV specification MS (Motor Sprit) commonly known as gasoline or petrol and HSD (High Speed Diesel) commonly known as diesel. Oil companies are geared up to introduce BS VI grade auto fuel w.e.f. 1st April 2020 for entire country. The National Capital Territory of Delhi has already switched over to BS VI from April 2018. Hence, corrosion inhibitor which is being considered for application in pipeline is required to demonstrate compatibility with BS V1 grade product. Additionally, Pipeline are also using the Drag Reducer Additive (DRA) for flow improvement, which are basically long chain polymers with solvent, the corrosion inhibitor should be compatible with DRA also. From crude oil side, the corrosion inhibitor should not be reacting to crude oil characteristics as crude oil is processed through complex refining process having different catalyst, so that it should not affect the refining process, particularly should not produce any trace metals, Ammonia etc. as the same is harmful to the refining process.

This necessitates that though green corrosion inhibitors should be environment friendly, but for application in pipeline for corrosion prevention, the required doses or effective doses of CI should be compatible to petroleum product and no case either affect the product quality or refining process. The CI should be soluble in the petroleum product and dispersible in water as pipelines often contains small amount of water. The water dispersibility is also required for undertaking electro chemical studies for determination of effectiveness of corrosion inhibitors

In order to undertake the development of these green corrosion inhibitors, the further study regarding methods of characterization was done for various types of the green corrosion inhibitors. Understanding physical and chemical characteristics is the first step in the evaluation process. The associated books, journals and various NACE codes were referred for evaluation and testing of corrosion inhibitors.

2.4 GAP AREAS AND RESEARCH OBJECTIVES

The aim of the study is to undertake laboratory scale experiment of plant produce like Neem, Karanjia seed, Hibiscus, Eucalyptus, Jatropha etc. as green corrosion inhibitor for application in petroleum pipeline. The presently used chemical corrosion inhibitors are having high toxicity impact on the environment thus enviro sensitive petroleum industry requires viable alternatives to the traditional corrosion inhibitors. The present study aims to analyze the impact of plant extracts on corrosion mitigation. The characterization of these plant produce undertaken in detail according to industry codes, testing protocol and practices. The present study also aims to address the impact of small doses of the antioxidant along with the plant extract for further enhancing corrosion inhibition properties.

The main objective of the proposed work is to explore the application of green corrosion inhibitors for the protection of cross country pipelines from internal corrosion. The study will essentially address the various corrosive conditions that prevail in pipelines, identification of potential green corrosion inhibitors, analytical characterization of the inhibitors and their electrochemical evaluation, Toxicity studies, Performance evaluation and dosage rate optimization as well as the scalability studies of identified inhibitor for industrial application

Chapter 3: RESEARCH METHODOLOGY

3.1 REASEARCH OBJECTIVE

The literature suggests that the study of green corrosion inhibitor is inundated with development of corrosion inhibitor with acidic media. Hydrocarbon related green corrosion inhibitor studies are still in its primitive stage. Corrosion inhibitors are required at different stages in hydrocarbon industries; however, using a corrosion inhibitor during transportation of a hydrocarbon product is most common.

In view of scare availability of green corrosion inhibitor for hydro carbon pipelines, it was proposed to undertake a study to develop green corrosion inhibitors for hydrocarbon pipeline system. A hydro carbon pipeline usually consists of many fluids such as natural gas, highly volatile liquid (such as propane/butane), refined petroleum with low relatively low volatility & crude oil (which is a mixture of all kind of hydro carbons).

With the abundance of product pipeline across the country, it was proposed to develop a green corrosion inhibitor.

The research objectives of the study can be summarized as follows:

- Literature review on the available green corrosion inhibitors through internet. Data collection from industry regarding different types of corrosion inhibitors used & its impact on environment etc.
- Undertaking detailed study of the characteristics of the green corrosion inhibitors available in the industry.
- Extraction and characterization of potential natural substances like leaves of plant, other plant produce having practically low or No toxic affect.

- Performance studies of the natural extracts in the laboratory scale including electro chemical studies for determination of their effectiveness, inhibition efficiency and suitable for petroleum product pipelines
- Dosage optimization studies of the natural extracts as inhibitors for hydrocarbon products along with study of synergistic effects with other organic additives

3.2 RESEARCH PROCESS

A detailed process maps has been worked out to complete the research as detailed in the figure

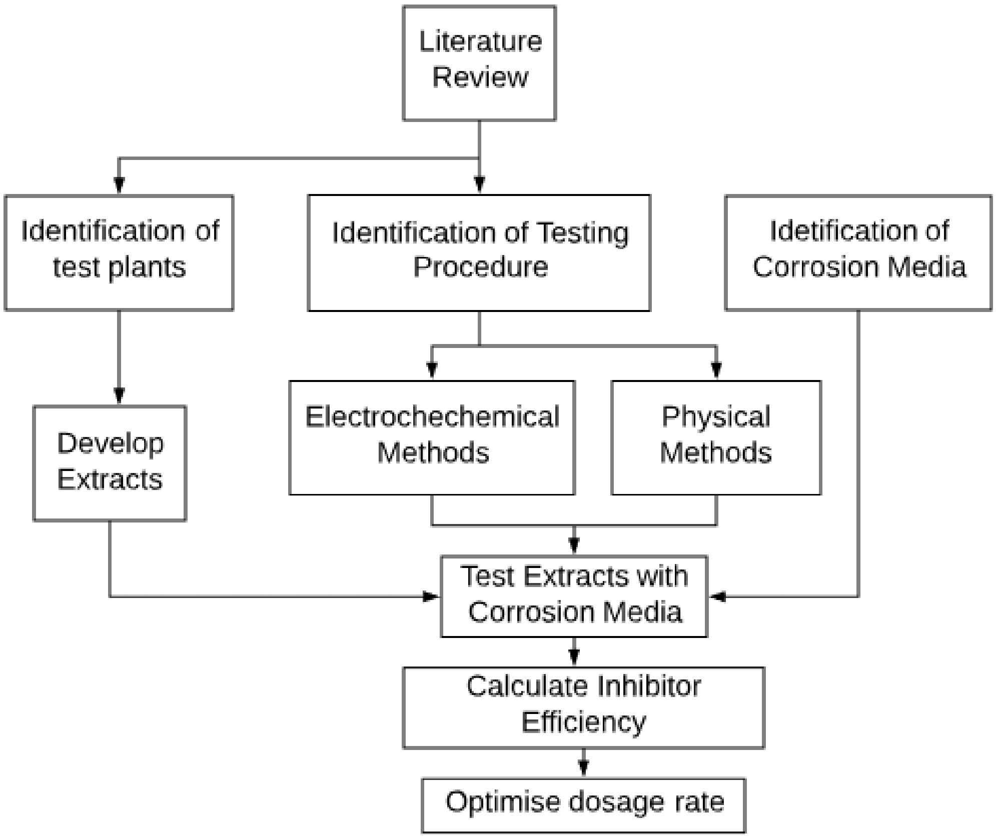


Figure 3.1: Research Process Flow Diagram

3.3 DESCRIPTION OF RESEARCH METHODOLOGY

3.3.1 LITERATURE REVIEW & SURVEY:

However, an extensive literature survey was carried out for green corrosion inhibitor, the research was divided primarily on three points:

1. Plants used in previous studies as green corrosion inhibitors
2. Testing and evaluation of corrosion inhibitor to satiate the study objective
3. Model fitting & optimization of green corrosion inhibitors

Primary purpose of the literature review was to get an idea about the types of plant extracts being used, test methods such as physical as well as electrochemical evaluation, and dosage optimization. Detailed literature review can be found in Chapter 2.

3.4 SELECTION OF TEST MEDIA

Hydrocarbon pipelines pose the high amount of risk to the environment as well as to the encompassing population. Considering the volatility & inflammability of a hydro carbon product a leak or a rupture can pose serious threats to nearby surroundings. Several fatalities / significant damages are recorded in India which has occurred because of pipeline failures (OISD, India, 2019). Moreover, a pipeline failure also poses substantial threat to the business of the operator. However the major vulnerability of a pipeline operation arises as it navigates outside the operators premises.

In the recorded events of pipeline failures, significant has occurred due to corrosion failures (Cunha, 2012). Internal corrosion plays a major role for pipeline failure. Given the industrial significance and associated risk of internal corrosion failure, the study was undertaken for reduction of probability of failure from internal corrosion by introduction of an environment friendly green corrosion inhibitor. Hydro carbon consists of a long range of product, however the present case is limited to jet fuel also termed as Aviation Turbine fuel (ATF)

3.5 SELECTION OF PLANTS GREEN CORROSION INHIBITOR

Several plants have been enlisted in the literature which has been used as green corrosion inhibitors. However, following plants have been considered in the study given their availability and ease of extraction:

1. Neem
2. Jatropha
3. Karenjia
4. Hibiscus
5. Eucalyptus

3.6 EXTRACT PREPARATION & CHARACTERIZATION

Naturally occurring plants are a good source of green inhibitors, as most of their extracts contain elements such as O, C, N, and S, which are active in organic compounds and assist in adsorption of these organic compounds on metals to form a protective film that reduces the corrosion activity. Green corrosion inhibitors are best suited when added in optimum concentrations in ppm level to treat the surface of corroding metals in an aggressive environment. Several plant extracts are rich in naturally occurring chemical compounds that reduces the corrosion rate by adsorption of specific species on metal surfaces through:

1. Changing the rate of anodic or cathodic reactions
2. Effecting the rate of diffusion of corroding ions interacting with corroding surface
3. Forming a non-conducting film which acts as a barrier

For effectively utilizing a plant as corrosion inhibitor, the extracts are prepared which are rick in species which provides protection to the metal. Soxhlet extraction was used for obtaining the chemical inhibitors given its versatility & ease of use for laboratory based extraction. After extraction, the compounds need to be characterized for consistency & verifications of results. Following processes have been used for characterization of these extracted compounds.

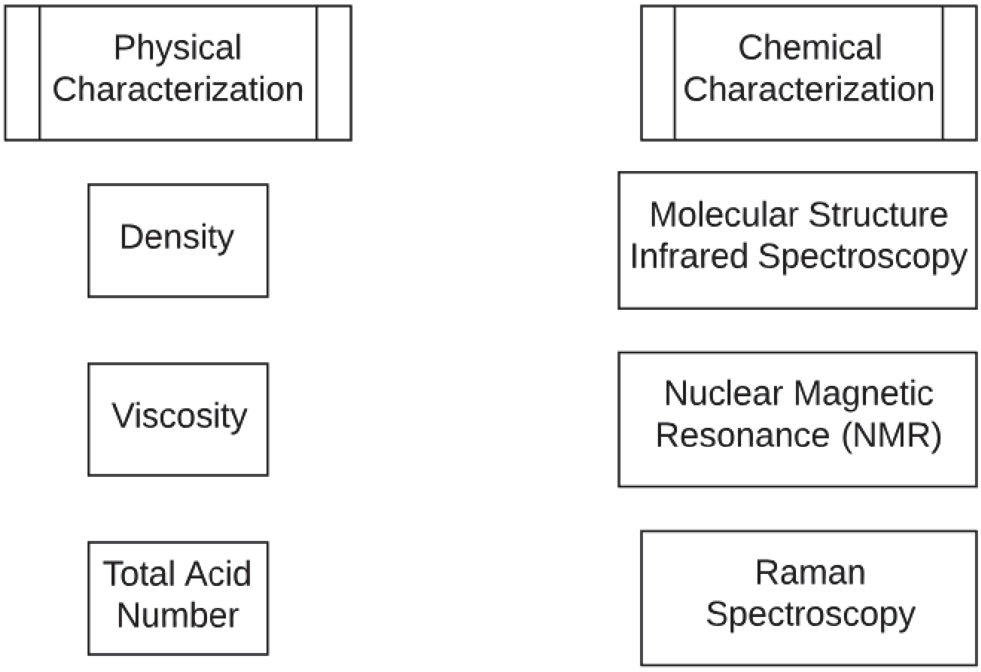


Figure 3.2: Characterization of the Green Corrosion Inhibitor

3.7 SELECTION OF TESTING PROCESS & TEST PROCEDURE

Jet fuel specifications are governed by (IS 1571, 2017) & the corrosion inhibitors for jet fuels are usually tested by (NACE 31215-2015-SG, 2015). The NACE documents specifies both physical as well electrochemical methods for evaluation of corrosion inhibitors by (ASTM NACE G31, 2012) & (ASTM G102-89, 2015) standards respectively.

As part of evaluation of green corrosion inhibitors following methodology were adopted for evaluation by physical methods:

1. Extracts were tested first with rotating spindle test (NACE TM 0172, 2015) & optimization of the dosage rate for comparative inhibition efficiency

2. Extracts were testing subsequently with static immersion test (ASTM NACE G31, 2012)
3. Extracts were tested finally with rotating wheel test for film persistence (NACE 1D182, 2017)
4. Physical characterization of the fuel/media was carried out for further usage in line with reference specifications
    a. Color - Saybolt
    b. Copper strip corrosion, 3h at 50 ºC
    c. Distillation
    d. Percent recovery at 200ºC
    e. Final boiling point, ºC
    f. Flash point (Abel), ºC
    g. Smoke point, mm
    h. Total sulphur, % mass (max.)

Extracts were further evaluated for electrochemical characterization as detailed below:

5. Preparation of micro emulsion with a commercial surfactant (Triton X; a polyethylene glycol based formulation) to facilitate electro chemical evaluation
6. Electrochemical impedance studies were carried out to computed film passivation resistance at optimized dosage
7. Linear polarization resistance (LPR to obtain corrosion rate data & evaluate the corrosion rates through Tafel extrapolation technique.
8. Identification of the mechanism related for inhibitive action of corrosion inhibitor.

3.8 ORGANIZATION OF THE STUDY

The study has been organized in the following chapters:

Chapter 1: Introduction explains the domain of global hydrocarbon transporation industry in general & Indian in particular. The issues related to pipeline related failures have been identified and the importance of corrosion & its mitigation has been explained.

Chapter 2: Literature review explains the various available research being conducted on green corrosion inhibitor. The vast literature suggests the potential scope available in the current research

Chapter 3: Research Methodology covers objective of the study & detailed description of the research methodology

Chapter 4: Extraction & physical characterization describes the processes used for extraction of green corrosion inhibitor from the plants & defines the methodology for its characterization

Chapter 5: Performance evaluation (physical) elaborates several gravimetric & immersion tests conducted on the test media to evaluate the performance of the green corrosion inhibitor. The chapter also explain the details of optimization of the dosage rates of the corrosion inhibitors

Chapter 6: Performance evaluation (electrochemical) describes the test process & results of several electrochemical methods carried on the test media to evaluate the performance of the green corrosion inhibitor.

Chapter 7: Conclusion & Future Research covers the finding of the study & also explains scope of future research areas in the domain of present study

3.9 SIGNIFICANCE OF THE STUDY

The study is done to lay down the basic foundation of usage of green corrosion inhibitors in petroleum study. Presently several synthetic compounds are used as corrosion inhibitors in the hydro carbon industry which are commercially expensive, non-environment friendly & usually toxic in nature. Experimentation & the study identifies the basic process of extraction of green corrosion inhibitors for plant extracts. The study parameters identify the steps for evaluation of corrosion inhibitor and optimization of its dosage. Study further underlines the parameters require comparing two inhibitors.

Chapter 4: EXTRACTION AND PHYISICO- CHEMICAL CHARECTERISATION OF GREEN CORROSION INHIBITOR

4.1 INTRODUCTION

A range of extracts from plant seeds is reported in the literature, for the purpose of application to internal corrosion protection in hydrocarbon pipelines. Seeds of Jatropha and Karenjia offer a commercially viable opportunity not only as bio fuels but also as specialty additives. In this work, extensive studies on extracts from seeds of Neem, Jatropha and Karenjia and limited studies on extracts from Hibiscus flowers and Eucalyptus leaves have been carried out (Fig.4.1)

Figure 4.1 Seeds of Jatropha, Neem and Karenjia, Hibiscus flower and Eucalyptus leaves

4.2 EXTRACTION OF GREEN CORROSION INHIBITOR FROM PLANT PRODUCES

Extraction of oil from Jatropha seeds can be done by either extraction expeller by cold crushing or through a solvent extraction process. Out of these two methods, solvent extraction method has been found to be the only way to improve the oil output. In this study, seeds of Jatropha, Karenjia and Neem were dried and decoated manually. The kernels of the seeds were crushed into small pieces for better extraction of oil and are filled in a Soxhlet apparatus. The Soxhlet apparatus is fitted onto a round bottomed flask containing hexane which is the most favorable commercial medium for oil extraction in industry. The purity of the extract was monitored by testing samples by thin layer chromatography. The solvent hexane containing Jatropha was distilled in a Rota Evaporator to recover hexane from the oil extract. In general, a yield of 30-40% is obtainable by this process. A schematic of the extraction process is shown in Fig.4.2.

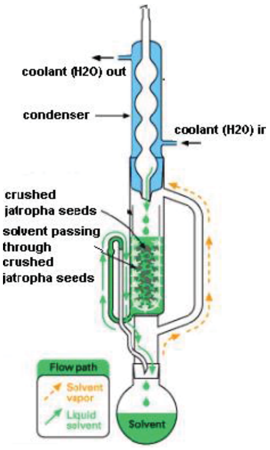


Figure 4.2: Schematic of Extraction of Oil from Jatropha, Karenjia and Neem seeds

In this study, the commercial extracts of Hibiscus and Eucalyptus have been used which are claimed to have been extracted by the cold crushing process. It is obvious from the extraction process described above that green corrosion inhibitors ought to be produced through green route only without producing any harmful effects on the environment. A summary of the plant extracts their extraction process and their dosages for carrying out studies are shown in Table 4-1.

4.3 PHYSICO - CHEMICAL CHARACTERIZATION OF GREEN CORROSION INHIBITORS

The extracts were characterized in the laboratory for their physical properties and chemical composition. The **c**haracterization has been undertaken to understand the chemical and molecular structure of the green corrosion inhibitors and to correlate the same with their performance as corrosion inhibitors. In addition, the study was aimed to understand the antagonistic effects of the green extracts on the industry specification for hydrocarbon products. One of the desirable properties of the green extracts is miscibility with other hydrocarbons. The Green Corrosion Inhibitors (GCI) is miscible in hydrocarbons but immiscible with water. From the density and viscosity values, inference on the flow ability and pumpability of the extract can be drawn.

4.4 PHYSICAL PROPERTIES

The density of the plant extracts at 25ºC was determined on a density meter, Model DMA 4100 M of Anton Paar make (Fig.4.3). The equipment uses Coroilis effect as the measurement principle and is accurate to fourth place of decimal.

The viscosity of the green CI samples was determined on a TA make AR 2000Ex model rheometer (Fig.4.4). Coaxial cylinder geometry was used for measurement of the viscosity. The viscosity was determined in a continuous deformation mode following a viscous model of testing. The sample was charged into the cylindrical sample holder and sheared by a cylindrical rotor at a constant shear rate of 100 Sec^{-1}. The viscosity measurements were made at 25ºC and 40ºC.

The Total Acid Number (TAN) of the green extracts have been evaluated through titrimetric methods. The properties of the extracts of Neem, Karenjia and Jatropha are shown in Table 4-2. The density and viscosity values indicate that these potential green corrosion inhibitors are compatible with hydrocarbons and can be easily injected into a running pipeline using a dosing pump.

Figure 4.3: M/s Anton Paar make DMA 4100 M Density meter

Figure 4.4: M/s TA make AR 2000Ex model Rheometer

4.5 CHEMICAL CHARACTERIZATION

4.5.1 INFRARED SPECTROSCOPY (IR)

IR spectroscopy is a versatile method for analysis at the molecular scale. Molecular species can be identified, and quantified, by specific vibration spectrum with characteristic absorption bands. It is an extremely versatile technology for analysis of organic compounds. It is used by chemists for determination of molecular structure of compounds and their identification. The information content of IR spectra helps in fingerprinting approach especially in organic and biological material identification, as well as in studies of condensed matter.

It is widely used for identification of compounds, especially the functional groups. Functional groups are associated with specific group frequencies and thus used for structural analysis of the molecules. It is possible to identify a functional group in a molecule by comparing its vibration frequency on an IR spectrum to an IR stored data bank.

The molecular structure of the green extracts was studied under Infrared (IR) spectrometer of Shimadzu make (Fig.4.5). The samples have been studied within a range of 4000 to 400cm^{-1} wave length range with a 4cm^{-1} resolution. Approximately 40-100 scans were taken to arrive at the spectrum of each of the extracts. The spectrum output of extracts of Jatropha, Karenjia and Neem are provided in Fig.4.6.

Figure 4.5: M/s Shimadzu make IR spectrometer

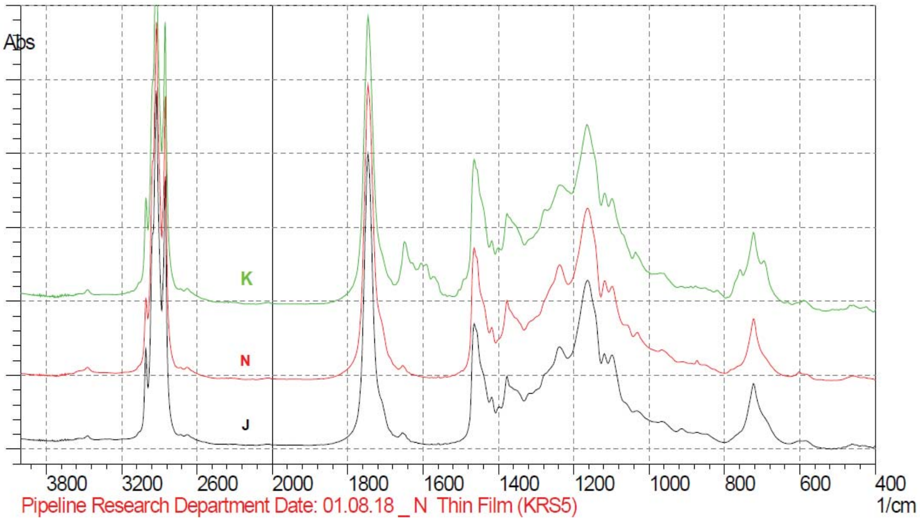


Figure 4.6: IR spectrum of extract from Jatropha(J), Karenjia(K) &Neem (N)

4.5.2 NUCLEAR MAGNETIC RESONANCE (NMR)

Nuclear magnetic resonance (NMR) is a physical phenomenon of resonance transition between magnetic energy levels, happening when atomic nuclei are immersed in an external magnetic field and applied an electromagnetic radiation of a specific frequency. By detecting the absorption signals, one can acquire NMR spectrum. According to the positions, intensities and fine structure of resonance peaks, one can study the structures of molecules. The size of molecules of interest may vary from small organic molecules, to biological molecules of middle size, and even to macromolecules such as nucleic acids and proteins. Apart from these common applications, NMR also plays an important role in analysing inorganic molecules, which makes NMR spectroscopy a powerful technique.

The extracts were also studied on a 500MHz Brucker make ^{1}H proton Nuclear Magnetic Resonance (NMR) spectrometer (Fig.4.7). The combined spectrum outputs of the three extracts are shown in Fig.4.8.

Figure 4.7: M/s Brucker make 1H Proton Nuclear Magnetic Resonance (NMR) Spectrometer

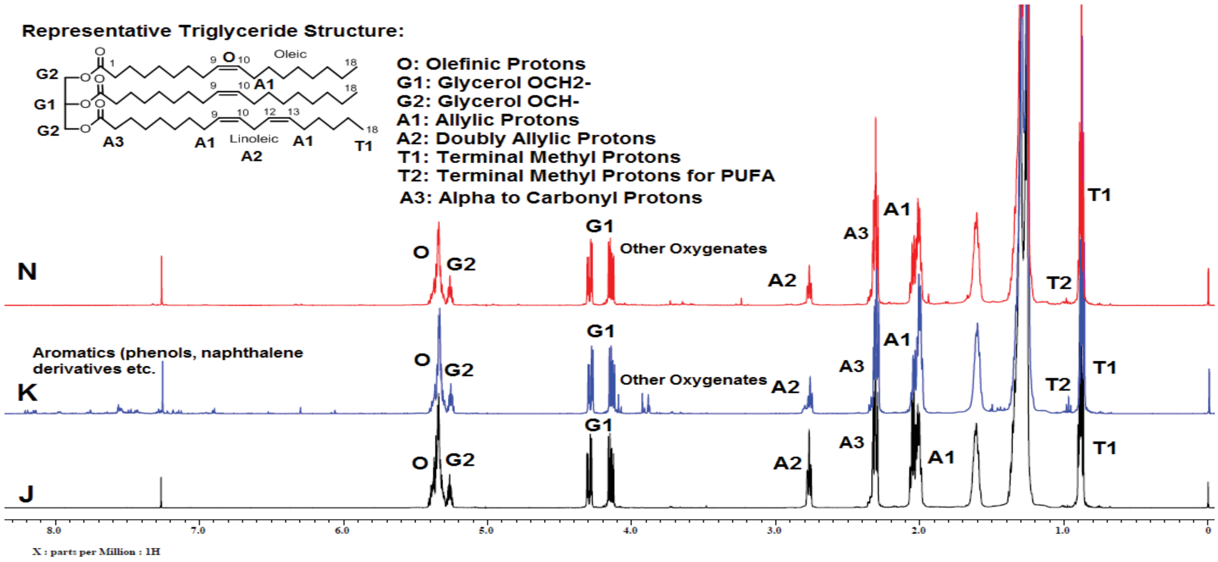


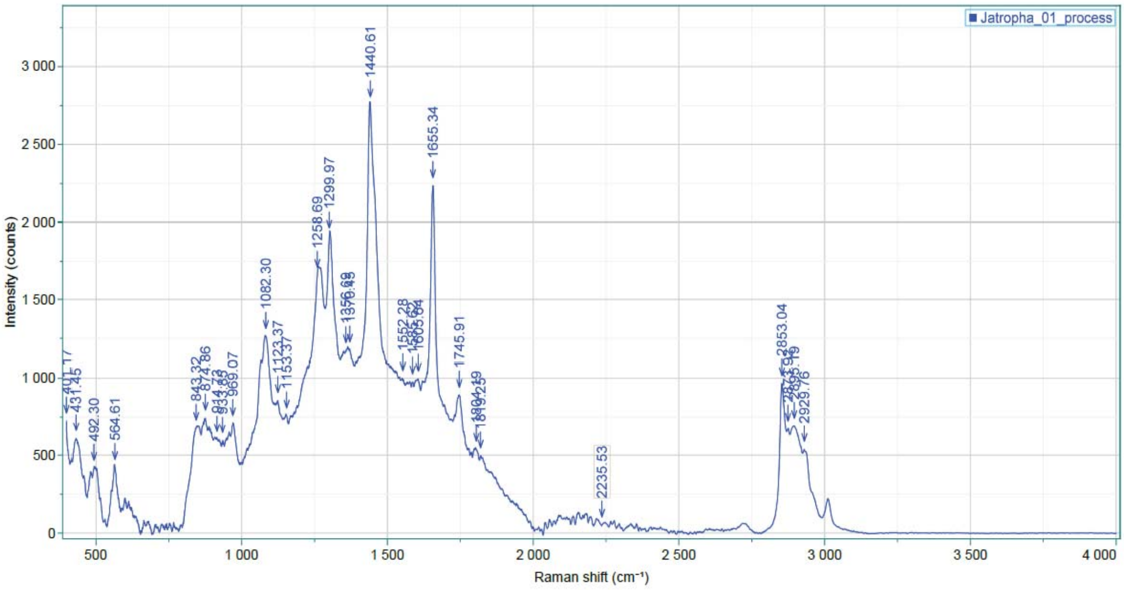
Figure 4.8: ^{1}H Proton NMR spectrum of extract of Jatropha (J), Karenjia (K) and Neem (N)

4.5.3 RAMAN SPECTROSCOPY:

Raman spectroscopy is based on the Raman effect discovered by Sir C. V. Raman in 1928. This method employs scattering of light by a material, where the light is scattered inelastically as opposed to the more prominent elastic Rayleigh scattering. This inelastic scattering causes shifts in wavelength, which can then be used to deduce information about the material. Properties of the material can be determined by analysis of the spectrum, and/or it may be compared with a library of known spectra to identify a substance. The sample is illuminated with a monochromatic laser beam which interacts with the molecules of samples and emits a scattered light. The scattered light having frequency different from that of incident light (inelastic scattering) is used to construct Raman spectrum. Raman spectra arise due to inelastic collision between incident monochromatic radiation and molecules of sample incident radiation.

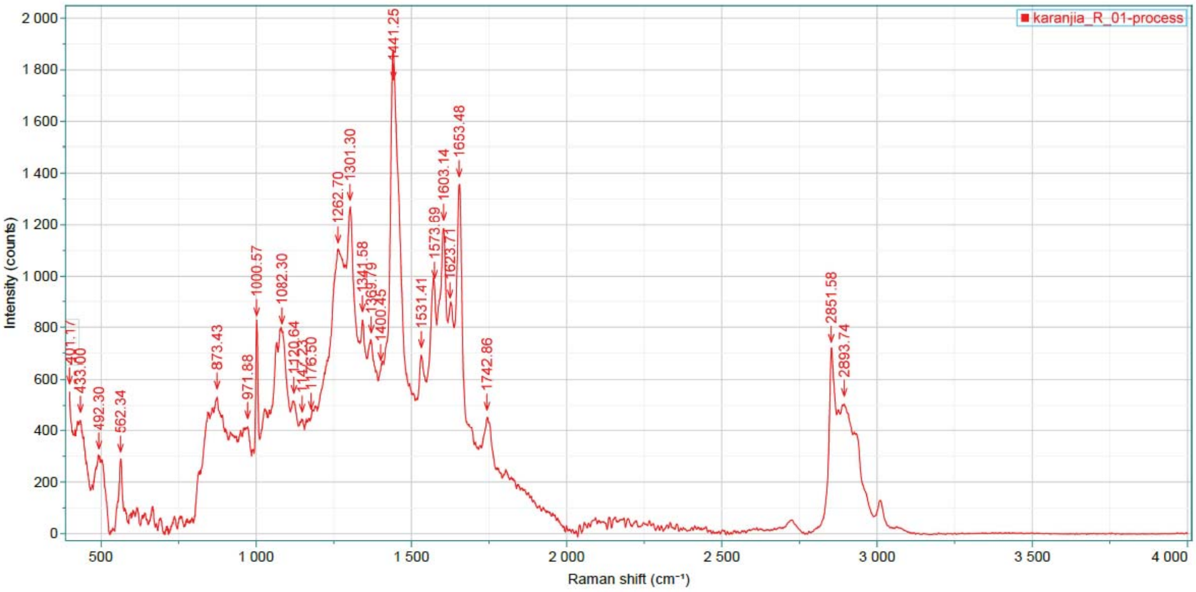
A thin film of the optimum dosage of the green extracts as applied over the metal surface was studied under a Raman Microscope at both low and high laser energies using Raman spectrometer with confocal microscope, on model LabRam HR evaluation model of M/s Horiba, France (Fig.4.9). The acquisition parameters of 785nm laser with 100 % power and a Raman shift range 400 – 4000cm-1 were maintained. Two scans for 20 sec duration each were obtained with 1cm fixed path cell. The spectrum obtained from the extracts of Jatropha, Karenjia and Neem is shown in Fig.4.10 to Fig.4.12 respectively.

Figure 4.9: M/s Horiba make Raman Confocal Microscope



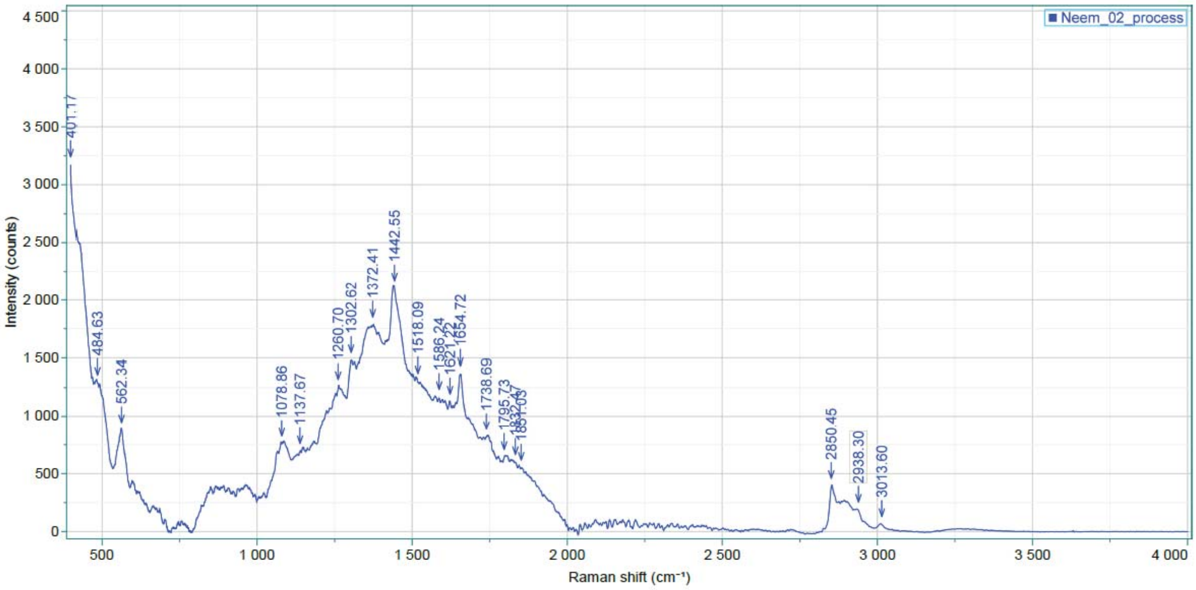
Equipment : Raman Spectrometer / LabRam HR Evaluation / Horiba France
785nm Laser / 100% Power / 10x objective / 1cm Path Cell

Figure 4.10: Raman microscope output of extract of Jatropha



Equipment : Raman Spectrometer / LabRam HR Evaluation / Horiba France
785nm Laser / 100% Power / 10x objective / 1cm Path Cell

Figure 4.11: Raman microscope output of extract of Karenjia



Equipment : Raman Spectrometer / LabRam HR Evaluation / Horiba France
785nm Laser / 100% Power / 10x objective / 1cm Path Cell

Figure 4.12: Raman microscope output of extract of Neem

4.6 RESULTS AND DISCUSSIONS:

From the Physical properties and the chemical analysis of the extracts, the following can be inferred:

1. The extracts are denser than the petroleum products.
2. The viscosities of the samples indicate that the diluted solutions of the extracts are pumpable into pipeline transportation systems.

From the Chemical analysis of the extracts, the following can be inferred:

- The Neem and Karenjia extracts are slightly less acidic than Jatropha extract
- The extracts are deciphered as triglycerides of fatty acids with average acid chain of 17.5 -18. The fatty acids can be saturated, mono-unsaturated, di-unsaturated or poly-unsaturated.
- Jatropha extracts consists majorly of oleic acid (unsaturated) with other saturated acids in small quantizes. Oleic acid is an unsaturated fatty acid that is most widely distributed and abundant fatty acid in nature. It is odorless and colorless oil.
- Karenjia and Neem extracts were seen to have more saturated acids
- Karenjia extract is seen to have significant proportions of poly unsaturated linoleic acids along with phenolic and naphthenic components
- The IR spectra show a sharp band at ~ 3000 cm^{-1} which indicates the presence of olefinic C-H mainly due to presence of Oleate moieties in all the samples.
- From the Raman microscope, presence of unsaturation in long hydrocarbon chain (1655cm-1) and weak signal for ester (1740cm-1) could be inferred in all the samples. The Karanjia extract shows the presence of aromatics which are not seen in Jatropha and Neem extract.
- The Oleate ester moieties can help in the formation of thin films on the metal surface as polar compounds.
- In addition to the carbonyl group C=O, presence of free fatty acids especially the saturated type and the aromatic compounds can enable the film-formation by reacting with metal surfaces.

Table 4-1: Summary of Plant extracts studied

Description of Green CI	**Method of Extraction**	**Dosage range studied (ppm)**	**Biological Name**
Neem Oil	Crushing & Solvent extraction	200 to 2500	Azadirachta Indica
Hibiscus Oil	Cold Pressed	200 to 8000	Hibiscus Rosasinensis
Eucalyptus Oil	Steam Distilled	1500 to 5000	Eucalyptus Globulus
Jatropha Oil	Crushing & Solvent extraction	100 to 8000	Jatropha Curcas
Karanjia Oil	Crushing & Solvent extraction	100 to 8000	Millettia Pinnata

Table 4-2: Physical properties and TAN values of extracts

Green Corrosion Inhibitor	Viscosity		Density @ 20 Deg.C (gm/cm3)	Total Acid Number
	@25 Deg.C (cP)	@40 Deg.C (cP)		
Neem	86.57	47.03	0.9245	6.41
Karenjia	78.45	42.9	0.9306	6.32
Jatropha	57.98	33.2	0.9153	5.96
Fuel Properties				
Aviation Turbine Fuel	1.20	1.00	0.804	0.01

Chapter 5: PERFORMANCE EVALUATION OF GREEN CORROSION INHIBITORS

PART ONE (PHYSICAL)

5.1 INTRODUCTION

The corrosion inhibitor chemicals are required to be evaluated for their performance efficacy and optimized for their dosage rate. While the inorganic and organic amine derivatives may perform well in protecting pipeline corrosion, some of them can cause fouling in desalter unit, coking of preheat circuits as well as upset pH of overhead streams causing ammonia stress corrosion cracking of brass components. Therefore, chemical compatibility to alloys in refinery system needs to be given the utmost priority while selecting corrosion inhibitors. The compatibility of corrosion inhibitor chemical also requires to be studied with respect to the MIC causing microbes. A few conventional synthetic chemical inhibitors are reported to act as nutrients to the microbes, present in pipeline systems that grow under anaerobic conditions at local regions of lower elevations thereby annulling the inhibitor performance. Also, the synergistic or antagonistic effect of the corrosion inhibitor chemicals to other specialty chemicals such as antioxidants and dispersants needs to be studied prior to their selection for corrosion protection.

For the performance evaluation of the corrosion inhibitor for a given hydrocarbon, a variety of tests can be conducted. The simplest being the ASTM immersion tests (ASTM NACE G31, 2012), which is a static test. The weight loss of the immersed coupon determines the effectiveness of the inhibitor film. In addition, using the appropriate medium of petroleum fuel, the corrosion rating as per spindle test of ASTM D665 modified as per (NACE TM 0172, 2015) provides an industry accepted procedure for corrosion mitigation property of the corrosion inhibitor.

This test being static doesn’t represent the field conditions of the pipeline. Further, a wheel test (NACE 1D182, 2017), which simulates the dynamic flow conditions of the transportation pipeline, can be used. This is a gravimetric test which can provide the percentage inhibition efficiency.

The efficacy of the corrosion inhibitor is assessed in terms of percentage inhibition efficiency for a given dosage rate is as follows:

$I_{Eff} = ((R_0 - R_i)/R_0) \times 100$, ----- (5.1)

Where, 'R_0' is the corrosion rate without inhibitor and 'R_i is the corrosion rate with inhibitor

Recently, rotating disc, rotating cylinder, rotating cage type electrode tests have come into vogue which does an electrochemical measurement of the corrosion occurring with respect to different wall shear stresses signifying the dynamics of flow conditions within the pipeline (Bouzidi, et al., 2012). These tests are shown to correlate well with the field corrosion data and hence closely simulate the pipeline operating conditions.

5.2 ROTATING SPINDLE TEST - ASTM D669 (NACE TM 0172)

The ASTM D665 test method modified as NACE standard for "Determining corrosive properties of cargoes in petroleum pipeline" NACE TM 0172 (NACE TM 0172, 2015) is the most acceptable method for performance evaluation of corrosion inhibitors. NACE TM 0172 is a test method meant for assessment of corrosive properties of petroleum products being transported via pipelines. The test method enables concerned users to take the required preventive measures for pipeline protection against internal corrosion caused due to the corrosive nature of the fluid being transported via pipelines. The test does not predict corrosiveness in the standing under aqueous phase nor does it predict Microbial Induced corrosion (MIC).

The equipment used to conduct the tests conforms to ASTM D665 specifications. It can accommodate six sample beakers along with the test specimen conforming to UNS G10150 (Grade 1015) having dimensions within the tolerance limit defined under NACE TM 0172 test protocol. A microprocessor based temperature control with digital display and over temperature protection which automatically interrupts power to the unit when the bath temperature exceeds the programmed cut-off point. Stainless steel stirrer paddles are driven at 1000rpm by drive arrangement fitted with toothed belt drive. Drive train components are protected by a removable fiber glass guard. All exterior surfaces have stainless steel or chemical resistant polyurethane enamel finishes. A typical NACE TM0172 test facility of M/s PETROTEST used in the study is presented in Fig.5.1.

In this method, 300ml of the hydrocarbon medium supposedly containing the corrosion causing constituents such as dissolved H_2S, Chlorides etc. is taken in a specially designed beaker with Poly Methyl Methacrylate (PMMA) cover with provision of insertion of chuck / spindle (Fig.5.2). Carbon steel spindles of dimensions as shown in Fig.5.3 are used.

Initially the surface was prepared by grinding and polishing with emery cloth so as to render the entire surface of the spindle free of rust / corrosion pits till only scratch marks are seen. The test steel specimen is prepared by mounting the steel specimen on a grinding and polishing apparatus. Abrasive cloth of 150, 280, 400 and 1200 grit metal working silicon carbide abrasive cloth were used for test specimen. An electric gear operated grinding and polishing equipment is used which provides adjustable speeds within 1700 and 1800 rpm (Fig.5.4). The steel specimen are prepared initially with 150 grit SiC cloth to remove all surface defects, irregularities, pits and scratches as observed visually. Gradually 240, 400, 1200grit silicon carbide abrasive clothes are used for coupon preparation under application of uniform pressure until the surface appears to be uniformly smooth, free from any circumferential and longitudinal marks. After the specimen preparation, the coupons are rinsed with acetone, dried and preserved in desiccators.

Glass wares are properly cleaned with detergent, dried in an oven at 65ºC. Thereafter the samples are prepared at different dosages (volume by volume) with the help of a micro liter syringe for volume measurement of the corrosion inhibitor. The beaker containing the hydrocarbon sample with or without inhibitor dosage is placed in an oil bath maintained at a constant temperature of 38± 1ºC. So as to suspend the spindle held at the chuck through the PMMA cover. The spindle is thus free to rotate under immersed condition within the hydrocarbon sample contained in the beaker. The oil level in the bath shall not be below the oil level in the test beaker. The spindle is rotated within the solution at 1000 ± 50rpm for 30 min to ensure complete wetting. With the stirrer in motion, 30ml of distilled water is added to the solution through a hole in the PMMA cover, discharging the water on the bottom of the beaker. The stirring at a speed of 1000 rpm is further continued for 3.5hours maintaining the temperature of the bath. At the end of the 4-hour long exposure, the spindles are removed, drained and wiped clean and dipped in a suitable solvent prior to visual inspection. The entire spindle surface is inspected and reported except for the area adjacent to the shoulder.

A qualitative assessment is made in the form of gradation through visual examination of pitting on the spindle surface. Quantitative assessment of the spindle is also possible with a image analysis system. The details of the qualitative performance gradation and the guidelines for their ratings are presented in Table 5-1. In general, Oil industry specification for minimum guaranteed performance of corrosion inhibitors requires B++ or better rating which corresponds to 0.1% of corrosion in the total exposed spindle surface area or 2 to 3 corrosion spots of less than 1mm diameter.

5.2.1 STUDIES ON DOSAGE OPTIMIZATION OF NEAT INHIBITORS UNDER ROTATING SPINDLE TEST

In this work Aviation Turbine Fuel (ATF) has been considered as the hydrocarbon medium for the entire study. The ATF can contain dissolved acid gases and residual chloride content which can cause corrosion of metallic component which are wetted by the fuel. Since the transportation of ATF involves adherence to a very stringent specification and quality norms, the same was chosen for the studies. Initially, all the five potential green corrosion inhibitors, namely, Hibiscus, Eucalyptus, Neem, Karenjia and Jatropha were chosen to check for their corrosion inhibition potential (Olusegun, Adeiza, Ikeke, & Bodunrin, 2013), (Murthy & Vijayaragavan, 2014), (Mishra, 2014) and also assess the orders of concentration of their effectiveness. Spindle test was carried out on ATF doped with various dosages of these GCI and compared with the ratings of undoped ATF. The dosage range in which the GCI were compared is shown in Table 5-2.

5.2.2 STUDIES ON INTERACTIVE EFFECTS OF ANTIOXIDANTS AND SURFACTANTS ON GREEN CORROSION INHIBITORS

Further to the dosage optimization studies of the green corrosion inhibitors, the individual and combined effect of commercial antioxidant additives was studied using the spindle test. The minimum specified requirement of inhibition rating of B^{++} has been kept as the criteria for evaluation. The Neem extracts have been studied under a combination of a range of dosage of inhibitors within 1300 to 2000ppm with both amines based and phenol based commercial antioxidants ranging from a dosage of 1000 to 3000ppm (v/v).

Surfactants are generally added to promote dispersibility of organic compounds in aqueous phase. Pipeline corrosion inhibitors are required to disperse in aqueous phase in order to be more effective at regions of water separation. Keeping this in view, the effect of different dosages of surfactants on the optimum dosages of Neem, Karenjia and Jatropha, were studied. For this purpose, a commercial nonionic surfactant namely TRITON X 100 a Poly Ethylene Glycol formulation within a dosage rate of 50 to 400ppm (v/v) in combination with green corrosion inhibitors has been studied.

5.3 STATIC IMMERSION TEST

Static immersion test is a bottle test carried out as per ASTM standard G31 which involves gravimetric analysis for weight loss in coupons after exposure to hydrocarbon medium. A 30mmx25mmx2.5mm carbon steel coupon has been used for the tests. The metallurgical composition of the coupon is given in Table 5-3. The coupons were seen to have a normal equiaxed Ferrite – Pearlite structure. The microstructure of the coupons as recorded is shown in Fig.5.5.

In the static test, 275ml of ‘E’ rated ATF neat and doped with the optimum dosage rates of green corrosion inhibitors as inferred from the spindle test have been considered. The coupons were hung within the solution fully immersed. The remaining volume of the bottle was purged with CO_2 gas and tightly sealed. The bottles were maintained at a constant temperature of 30 °C within an environmental chamber. Static condition of the solution was maintained with no turbulence. The coupons were removed after 550hours.

The coupons were chemically cleaned with an inhibited acid solution of 1000ml having 1.19 specific gravity HCl with 20gm antimony trioxide and 50gms of stannous chloride. Intermittent mechanical cleaning using a nylon brush was followed by cleaning with acetone and xylene. The cleaned coupons were weighed using a Miller digital balance which has an accuracy of fourth decimal place of a gram. For each coupon, the weight was taken after each cycle of the cleaning procedure, till a constant weight was obtained. The weight loss measurements are presented in Table 5-4.

5.4 ROTATING WHEEL TEST

Rotary wheel test setup is used for evaluation of film persistency of corrosion inhibitors for oil field applications. The wheel test is performed by adding the corrosive fluids and inhibitor to a bottle with a metal coupon suspended in it, purging with a corrosive gas, and capping the bottle. The bottle is then agitated for a period of time by securing to the circumference of a "wheel" and rotating it. The wheel test is best regarded as a screening test for the inhibitor evaluation and can discriminate poor inhibitors from better ones. However, there is no theoretical or hydrodynamic method to determine the flow patterns in a wheel test. Therefore, the rotating wheel test is used for film persisting studies.

A double stainless steel wheel assembly with provision for mounting of 20 bottles with a capability of the rotational speed between 16 to 60RPM and a load bearing capacity up to 12 kg is used. A double walled chamber to enclose the testing wheels with an insulated door is provided. There is a provision of having uniform air circulation throughout the chamber with the help of motorized uniform air circulation facility. Equipment has the provision of setting up of temperature between 50ºC to 150ºC with temperature accuracy of 0.2ºC. The typical rotating wheel test setup used in the study is shown in Fig.5.6.

Generally, the inhibitor to be tested is added to the bottle first. Then the bottle is purged with CO_2 before charging the hydrocarbon and brine mixture. The measured quantities of brine and oil mixture, is charged into the bottle. Then the test specimen is introduced in such a way that the specimen is held at the cap of the bottle using a nonmetallic wire. The bottle is capped and placed on the wheel and rotated at the desired temperature.

At the end of the test, the test specimens are retrieved from the bottles, and prepared for the weight loss measurements as elucidated in earlier. The weight losses are calculated and the results of multiple specimens are averaged out. In the case of a wild result (one that is more than four times the average deviation), are rejected and the results of the remaining specimens are averaged. The percent protection is then calculated as follows:

% (I.E) = Mass loss (Blank–with inhibitor) / Mass loss (Blank) ×100 ---- (5.2)

Many variables, such as the oil / brine ratios, brine concentration, inhibitor dosage rate etc. affect the on corrosion rates and hence the % inhibitor efficiency.

Carbon steel coupons / API 5LX grade B steel coupons are used in the rotary wheel test for evaluation of the green CI with an average dimension of coupon as 30mm x 25mm x2.5mm with an average area of 18.75cm2. The chemical composition of the coupon as analyzed using a spark emission spectrometer is shown in Table 5-3. In the present study, 275ml of total volume of hydrocarbon and brine has been considered with the remaining vapor phase flushed with CO_2 prior to closure. The 3.5 % and 7% brine solutions have been added in different volume proportion to the hydrocarbon to simulate the water retention of transportation pipelines as well as to accelerate the corrosion process within the test duration. The test was run at 30 °C at 10 rpm for a minimum period of 550hours i.e 21 days and more. Extended tests were conducted with periodic removal of coupons for analysis of weight loss and corrosion rate. Experiments with 2 % vol. of aqueous solution of 3.5% NaCl, 10 vol. %. of aqueous solution of 3.5% NaCl and 10 vol. %. of aqueous solution of 7% NaCl have been conducted.

The test duration was 1150hours, 600hours and 430hours respectively. The results in respect of each of these are presented in Table 5-5 to Table 5-7 respectively. Also, the aqueous brine phase separated from the hydrocarbon at the end of the wheel test of inhibitors was analyzed for ‘Fe’ content using inductively coupled plasma spectrometer. The results are presented in Table 5-8.

5.5 COMPATIBILITY OF THE POTENTIAL GREEN CORROSION INHIBITORS WITH TRANSPORTATION FUELS

The compatibility of the Jatropha, Karenjia and Neem extracts at their optimized dosage rates when doped as corrosion inhibitors is required to be studied in terms of composition and physico chemical parameters of the transportation fuel. The samples of motor gasoline, diesel fuel and kerosene oil doped with 1200ppm of Jatropha (J1200), 1400ppm of Karenjia (K1400) and 1600ppm of Neem (N1600), were tested as per relevant IP, ISO and ASTM test specifications. As an industry practice the corrosion inhibitor is not injected in ATF while being transported through pipeline system. The comparative results of the critical physico chemical parameters in respect of the neat kerosene, gasoline & diesel fuels and these fuels doped with optimized dosage of the potential green corrosion inhibitors are presented in Table 5-9 to Table 5-11 respectively.

5.6 RESULTS AND DISCUSSION:

Spindle Tests

a) The undoped ATF was seen to have a worst rating of grade ‘E’ with very extensive corrosion pits on the spindle (Fig.5.7). The Hibiscus and Eucalyptus compositions were seen to possess limited corrosion inhibition potential. However, even at a very high dosage rate of 8000ppm, they were not meeting the minimum specified inhibition rating of B^{++} as required by the oil industry, as shown in Fig.5.8 and Fig.5.9 respectively. Moreover, dosages in the range of 5000ppm to 8000ppm i.e. 0.8 vol. % are practically not desirable or feasible.

b) The Neem, Karenjia and Jatropha compositions were seen to show very good corrosion inhibition potential. The optimum dosages of these three green corrosion inhibitors, was evaluated as 1600ppm, 1400ppm and 1200ppm respectively, which meets the minimum specified inhibition rating of B^{++} as required by the oil industry respectively. Fig.5.10, Fig.5.11 and Fig.5.12 show the photographs of the spindles after the test with varying concentrations of Jatropha, Karenjia and Neem respectively in ATF. The optimized dosage of the inhibitors is inferred and shown as Fig.5.13, Fig.5.14 and Fig.5.15 for 1200ppm of Jatropha, 1400ppm of Karenjia and 1600ppm of Neem respectively. The cumulative performance ratings of the inhibitors at different concentrations are shown in Fig.5.16.

c) Both phenolic and amine based antioxidants are seen to supplement the corrosion inhibition tendency of Neem as green corrosion inhibitor as shown in Fig.5.17 and Fig.5.18 respectively. However, an addition of 3000ppm of phenolic/aminic antioxidant is only effective to the extent of reducing the optimum dosage of Neem for its performance to meet the B^{++} criteria by 100ppm as seen in Fig.5.19 and Fig.5.20 respectively. The performance ratings for different combinations of Neem and both types of antioxidants are shown in Fig.5.21.

d) From the spindle tests, it is seen that the surfactant has a synergistic effect on the performance of all the three potential green corrosion inhibitors. The surfactant is seen to have a pronounced effect on the performance of Neem in comparison to that of Karenjia and Jatropha. A 50ppm addition of surfactant is enough to reduce the optimum dosage level of Neem for its performance by 200ppm whereas for the same reduction of optimum dosage level an addition of 200ppm and 100ppm of surfactant is required in case of Jatropha and Karenjia respectively as shown in Fig.5.22, Fig.5.23 and Fig. 5.24. The performance ratings for different combinations of Neem, Karenjia and Jatropha with the commercial surfactant are shown in Fig.5.25.

Static Test

e) The test bottles containing the exposed coupons at the end of 550hours of static tests for 1200ppm of Jatropha, 1400ppm of Karenjia, 1600ppm of Neem and undoped condition, are shown in Fig.5.26 to Fig.5.29 respectively.

f) The static test results indicate no weight loss whatsoever even after 550 hours of exposure to the 'E' rated ATF sample with and without inhibitors. This implies that corrosion does not occur in neat hydrocarbon solution.

Rotary Wheel Test

g) From the wheel tests, it is seen that in case of ATF with 2% vol. of aq. 3.5% NaCl, in presence of the three inhibitors at their respective optimum dosage rates, the corrosion rates decreased by more than an order of magnitude. Among the three, the Neem and Karenjia provided a lower corrosion rates as compared to the Jatropha extract as shown in Fig.5.30.

h) The percentage inhibition efficiency of all the three potential green corrosion inhibitors showed a value higher than 90% at their optimum dosage rates. However, the Neem and Karenjia extracts clearly show an efficiency of more than 95% as shown in Fig.5.31. The test bottles and the coupons at the end of tests at 1150hours are shown in Fig.5.32 and Fig.5.33 respectively.

i) The corrosion inhibition efficiency of Neem extract is further validated by the very low ‘Fe’ content observed in the separated brine phase at the end of the wheel test as shown in Table 5-8.

j) Similar observations are made in respect of the potential green corrosion inhibitors when tested with 10% volume of 3.5% NaCl. The corrosion rates and the percentage inhibition efficiency are shown in Fig.5.34 and Fig.5.35 respectively. The coupons retrieved after the test duration of 600hours distinctly shows the performance of the potential green corrosion inhibitors (Fig.5.36).

k) In case of tests with 10% volume of 7% brine, the corrosion rates are seen to increase in general. Also, the inhibition efficiencies are seen to decrease marginally. However, the Neem extract still shows a better performance as compared to Karenjia and Jatropha as shown in Fig.5.37 and Fig.5.38. The coupons retrieved after the test duration of 430hours are shown in Fig.5.39.

l) The wheel tests clearly reveal the corrosion inhibition potential of all the three green corrosion inhibitors considered in this study namely Neem, Karenjia and Jatropha extracts under turbulent and dynamic flow conditions.

Compatibility of the potential Green Corrosion Inhibitors with fuels

m) The physico chemical parameters of kerosene, gasoline or diesel fuels commonly transported through pipelines are seen to be well within the specification when dosed with the optimized dosages of 1200ppm of Jatropha, 1400ppm of Karenjia and 1600ppm of Neem. Therefore, it is inferred that the extracts are compatible with the fuels enabling their industrial utilization as green corrosion inhibitors.

Table 5-1: Qualitative Ratings of NACE TM0172 Spindle test

Rating	Percent of spindle surface area corroded
A	0
B^{++}	Less than 0.1 (2 or 3 spots of not more than 1mm)
B^{+}	Less than 5
B	5 to 25
C	25 to 50
D	50 to 75
E	75 to 100

Table 5-2: Dosage rates of Green Corrosion Inhibitors studied

Green Corrosion Inhibitor	Dosage range in ppm (v/v)
Hibiscus	200 to 8000
Eucalyptus	1500 to 8000
Neem	200 to 2500
Jatropha	100 to 8000
Karanjia	100 to 8000

Table 5-3: Composition of coupons

Composition in Wt.%	**C**	**Mn**	**Si**	**S**	**P**	**Fe**
	0.2102	1.1145	0.0421	0.0211	0.0327	Balance

Table 5-4: Static Test results

Inhibitor Dossage	Initial weight of coupons (g)	Weight of coupons after completion of test (g)	Weight loss after 550hrs (g)
Neem 1600ppm	15.0901	15.0900	0.0001
	14.6260	14.6256	0.0004
	14.5102	14.5099	0.0003
	14.7810	14.7809	0.0001
	13.8486	13.8481	0.0005
Jatropha 1200ppm	14.7602	14.7601	0.0001
	14.5980	14.5979	0.0001
	14.3246	14.3239	0.0007
	14.4686	14.4685	0.0001
	14.4999	14.4995	0.0004
Karenjia 1400ppm	14.5544	14.5539	0.0005
	14.4680	14.4678	0.0002
	14.6474	14.6472	0.0002
	14.7012	14.7012	0.0000
	14.6127	14.6125	0.0002
Reference ATF	15.0887	15.0885	0.0002
	14.5957	14.5952	0.0005
	14.4001	14.4001	0.0000
	15.4363	15.4361	0.0002
	14.4887	14.4887	0.0000

Table 5-5: Wheel test results for 2% volume of 3.5%NaCl

Inhibitor Dosage	In. Wt (g)	Fin. Wt (g)	t (hrs)	Wt. loss (g)	Corrosion rate, mmpy	Average corrosion rate, mmpy	% inhibition
Neem 1600ppm	13.7138	13.7106	550	0.0032	0.0037	0.0030	97.65
	14.7098	14.7078	550	0.0020	0.0023		
	14.4973	14.4957	740	0.0016	0.0014	0.0017	98.59
	15.0900	15.0877	740	0.0023	0.0020		
	14.6256	14.6211	900	0.0045	0.0031	0.0031	96.96
	14.8007	14.7898	1150	0.0109	0.0060	0.0032	94.36
	14.5099	14.5089	1150	0.0010	0.0005		
Karenjia 1400ppm	15.5432	15.5384	550	0.0048	0.0055	0.0038	96.98
	14.5713	14.5694	550	0.0019	0.0022		
	14.7465	14.7426	740	0.0039	0.0033	0.0026	97.76
	14.3665	14.3642	740	0.0023	0.0020		
	14.5539	14.5500	900	0.0039	0.0027	0.0027	97.37
	14.4678	14.4632	1150	0.0046	0.0025	0.0035	93.89
	14.6472	14.6389	1150	0.0083	0.0045		
Jatropha 1200ppm	14.6502	14.6442	550	0.0060	0.0068	0.0082	93.50
	14.5510	14.5426	550	0.0084	0.0096		
	14.3438	14.3310	740	0.0128	0.0109	0.0086	92.69
	15.0834	15.0760	740	0.0074	0.0063		
	14.7600	14.7551	900	0.0049	0.0034	0.0034	96.69
	14.5979	14.5927	1150	0.0052	0.0028	0.0041	92.89
	14.3239	14.3141	1150	0.0098	0.0054		
Reference ATF	13.8670	13.7557	550	0.1113	0.1271	0.1264	-
	15.3475	15.2373	550	0.1102	0.1258		
	14.4810	14.3070	740	0.1740	0.1476	0.1173	-
	14.7181	14.6156	740	0.1025	0.0870		

	15.0885	14.9403	900	0.1482	0.1034	0.1034	-
	14.5655	14.4802	1150	0.0853	0.0466	0.0576	-
	14.4001	14.2744	1150	0.1257	0.0686		

Table 5-6: Wheel test results for 10% volume of 3.5 %NaCl

Inhibitor Dosage	In. Wt (g)	Fin. Wt (g)	t (hrs)	Wt. loss (g)	Corrosion rate, mmpy	Average corrosion rate, mmpy	% inhibition
Neem 1600ppm	15.3198	15.3173	250	0.0025	0.0063	0.0063	97.29
	14.7318	14.7266	570	0.0052	0.0057	0.0057	95.42
	14.4421	14.4365	600	0.0056	0.0059	0.0059	95.31
Karenjia 1400ppm	14.5600	14.5533	250	0.0067	0.0168	0.0168	92.73
	14.8152	14.8057	570	0.0095	0.0105	0.0105	91.64
	15.5659	15.5538	600	0.0121	0.0127	0.0127	89.87
Jatropha 1200ppm	14.6680	14.6620	250	0.0060	0.0151	0.0151	93.49
	14.8293	14.8211	570	0.0082	0.0090	0.0090	92.78
	14.5509	14.5423	600	0.0086	0.0090	0.0090	92.80
Reference ATF	14.7553	14.6632	250	0.0921	0.2313	0.2313	-
	14.6453	14.5317	570	0.1136	0.1251	0.1251	-
	14.8378	14.7184	600	0.1194	0.1250	0.1250	-

Table 5-7: Wheel test results for 10% volume of 7.0%NaCl

Inhibitor Dosage	In. Wt (g)	Fin. Wt (g)	t (hrs)	Wt. loss (g)	Corrosion rate, mmpy	Average corrosion rate, mmpy	% inhibition
Neem 1600ppm	14.5705	14.5645	250	0.0060	0.0151	0.0151	94.04
	15.3944	15.3879	400	0.0065	0.0102	0.0102	93.41
	14.5744	14.5677	430	0.0067	0.0098	0.0098	93.69
Karenjia 1400ppm	13.2598	13.2506	250	0.0092	0.0231	0.0231	90.85
	14.7557	14.7462	400	0.0095	0.0149	0.0149	90.37
	14.8410	14.8309	430	0.0101	0.0147	0.0147	90.49
Jatropha 1200ppm	14.3288	14.3201	250	0.0087	0.0219	0.0219	91.35
	14.7822	14.7726	400	0.0096	0.0151	0.0151	90.27
	14.5816	14.5694	430	0.0122	0.0178	0.0178	88.51
Reference ATF	15.7970	15.6964	250	0.1006	0.2527	0.2527	-
	13.4468	13.3481	400	0.0987	0.1549	0.1549	-
	14.6847	14.5785	430	0.1062	0.1551	0.1551	-

Table 5-8: Analysis of separated Brine phase for 'Fe' content

Sample	Fe content in ppm
Neem 1600ppm	< 1
Karenjia 1400ppm	10
Jatropha 1200ppm	32
Neat ATF	3663

Table 5-9: Comparative characteristics of Kerosene fuel doped with optimized dosages of potential Green Corrosion Inhibitors

S. No	Characteristics	Test Method	Base Fuel	Base Fuel + J1200	Base Fuel + K1400	Base Fuel + N1600
1	Color - Saybolt	P:14	+24	+ 24	+22	+ 22
2	Copper strip corrosion, 3h at 50ºC	P:15	No.1	No.1	No.1	No.1
3	Distillation Percent Recovery at 200ºC Final boiling point, ºC	P:18/D:86	61 241	52.5 250.5	60.0 244.5	50.0 251.5
4	Flash Point (Abel), ºC	P:20	39.5	39	38	38
5	Smoke Point, mm	P:31	24	24	23	23
6	Total sulphur, % mass (max.)	P:34/D 4294	0.03	0.03	0.03	0.03

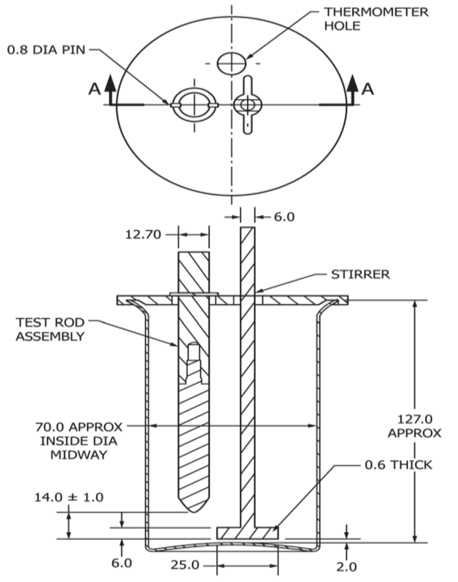
Table 5-10: Comparative characteristics of Motor Gasoline fuel doped with optimized dosages of potential Green Corrosion Inhibitors

S. No	Characteristics	Test Method	Base Fuel	Base Fuel + J1200	Base Fuel + K1400	Base Fuel + N1600
1	Color, visual	-	Orange	Orange	Orange	Orange
2	Density at 15ºC, kg/m^3	ASTM D 4052	737.9	740.2	740.1	739.4
3	Distillation Recovery up to 70ºC, % vol. Recovery up to 100ºC, % vol. Recovery up to 150ºC, % vol. Final boiling point, ºC Residue, % vol	P:18/ISO 3405	30.0 56.0 87.5 192.0 1.0	27.5 55.0 87.5 193.0 1.0	28.0 56.0 87.0 197.0 1.5	27.5 56.0 88.5 193.0 1.0
4	Research Octane No. (RON)	P:27/ASTM D 2699	91.1	91.0	91.0	91.1
5	Gum content (solvent washed), g/m3	P:29/ASTM D 381	12.0	15.0	15.0	12.0
6	Sulphur total, mg/kg	ISO 20847/D 5453	50.0	49.0	49.0	50.0
7	Benzene content, % vol	ASTM D-5580	0.81	0.81	0.82	0.82
8	Olefin content, % by vol, (Max.)	P:23/ASTM D 1319	14.3	14.2	14.0	13.9
9	Aromatic content, % by vol, (Max.)	P:23/ASTM D 1319	28.8	28.8	28.1	28.1

Table 5-11: Comparative characteristics of Diesel fuel doped with optimized dosages of potential Green Corrosion Inhibitors

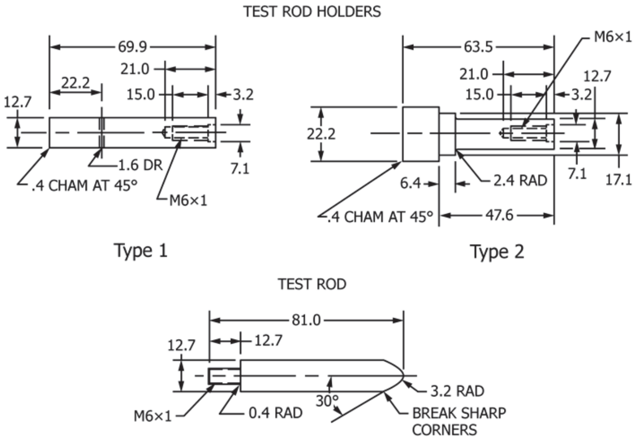
S. No	Characteristics	Test Method	Base Fuel	Base Fuel + J1200	Base Fuel + K1400	Base Fuel + N1600
1.	Cetane Index	ISO 4264	22.5	23.3	22.6	22.7
2.	Distillation, 95 %v/v, recovery, ºC, Max	P:18/ISO 3405	298.0	305.0	304.5	297.5
3.	Flash point, (Abel) ºC	P:20	13.0	14.0	14.0	14.0
4.	Kinematic viscosity, cSt, at 40ºC	P:25	1.24	1.26	1.25	1.26
5.	Density at 15ºC, kg/m3	ASTM D4052	803.7	803.7	803.6	804.0
6.	Total sulphur, mg/kg	ASTM D-4294/D-5453	233	230	231	232

Figure 5.1: NACE TM0172 Spindle test setup



Note - All units are in millimeters, unless otherwise specified.
Tolerances for all dimensions are ± 10% unless otherwise noted.

Figure 5.2: Dimensional details and construction of beakers as per NACE TM0172



Note - All units are in millimeters, unless otherwise specified.
Tolerances for all dimensions are ± 10% unless otherwise noted.

Figure 5.3: Dimensional details of carbon steel spindles as per NACE TM0172

Figure 5.4: Grinding and polishing equipment

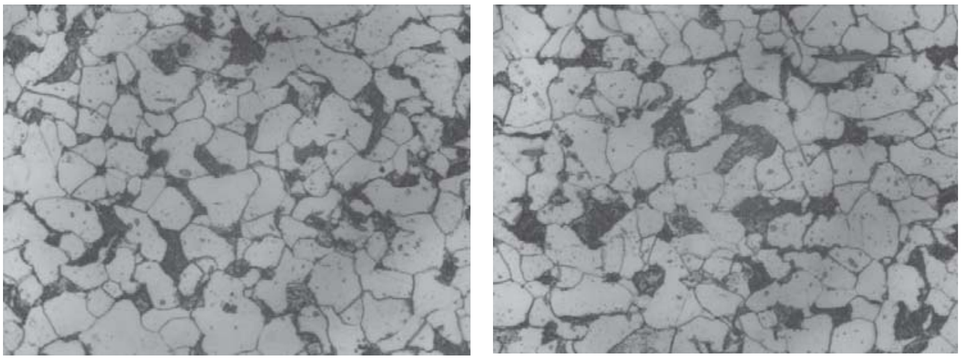


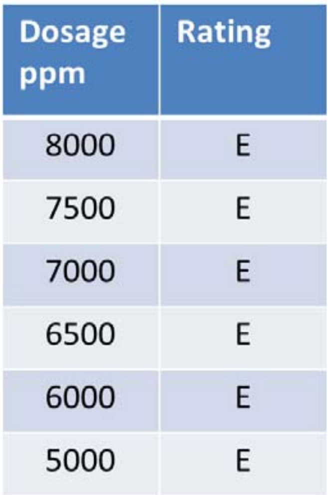
Figure 5.5: Microstructure of Carbon steel coupon showing equiaxed Ferrite and Pearlite (X500)

Figure 5.6: Rotating Wheel Test setup

Figure 5.7: Worst rating of grade ‘E’ with very extensive corrosion pits on the spindle

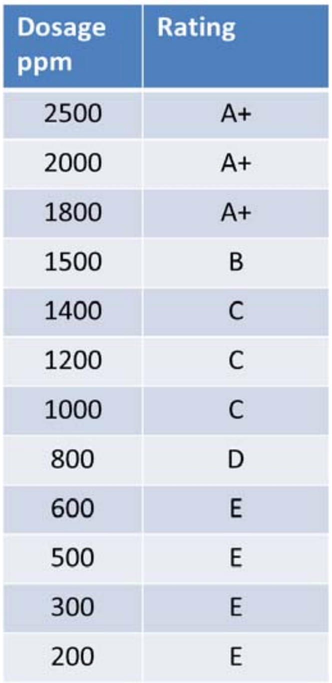
Dosage ppm	Rating
8000	B
7500	B
7000	B
6500	B
6000	B
5000	C
3000	C
2500	D
2000	D
1800	E
1500	E

Figure 5.8: Ratings of spindle with Hibiscus at 8000ppm

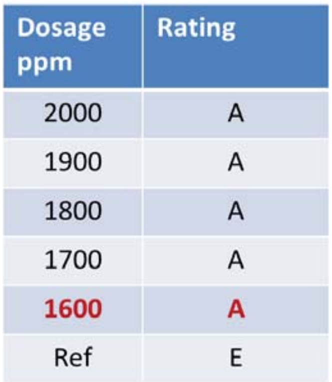


Dosage ppm	Rating
8000	E
7500	E
7000	E
6500	E
6000	E
5000	E

Figure 5.9: Ratings of spindle with Eucalyptus at 5000ppm



Dosage ppm	Rating
2500	A+
2000	A+
1800	A+
1500	B
1400	C
1200	C
1000	C
800	D
600	E
500	E
300	E
200	E



Dosage ppm	Rating
2000	A
1900	A
1800	A
1700	A
1600	A
Ref	E

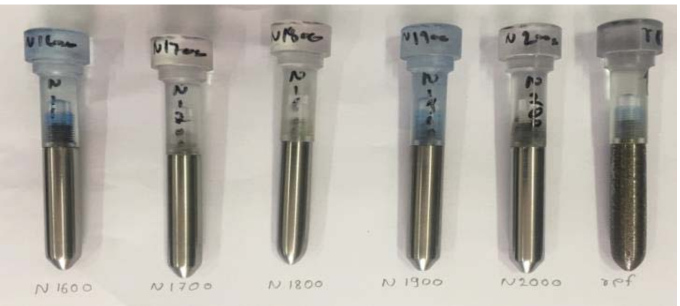
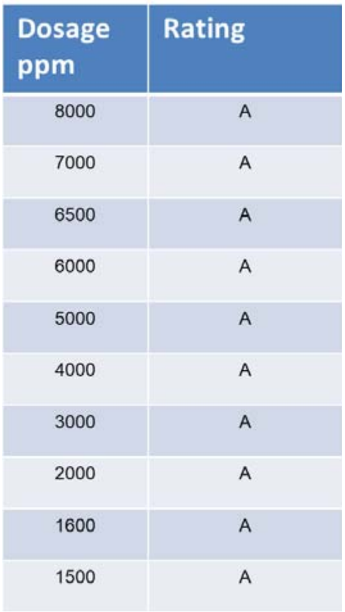
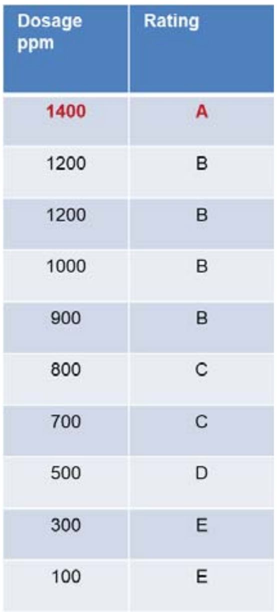


Figure 5.10: Ratings of spindle with Spindles for optimization of dosages for Neem at 1600ppm



Dosage ppm	Rating
8000	A
7000	A
6500	A
6000	A
5000	A
4000	A
3000	A
2000	A
1600	A
1500	A



Dosage ppm	Rating
1400	A
1200	B
1200	B
1000	B
900	B
800	C
700	C
500	D
300	E
100	E

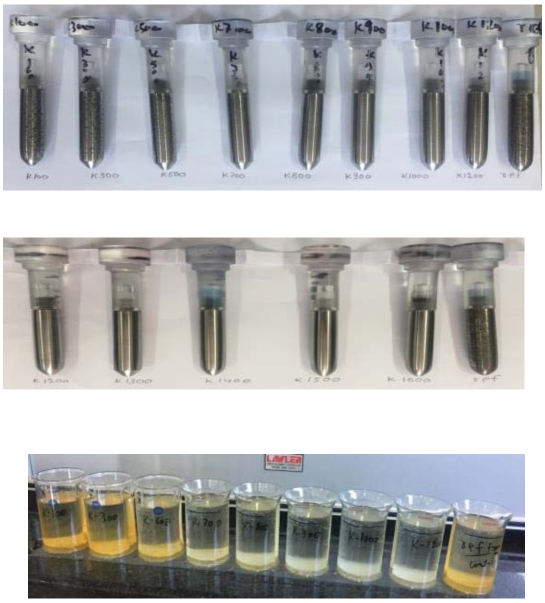
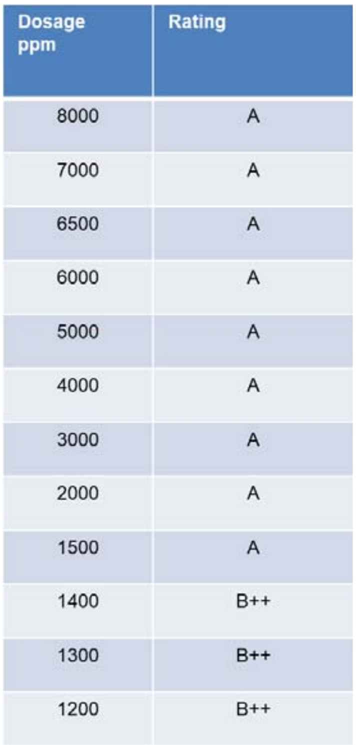
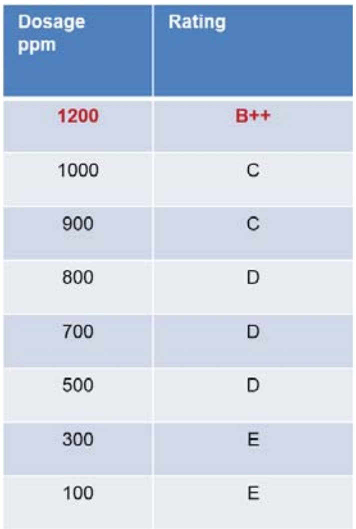


Figure 5.11: Spindles for optimization of dosages for Karenjia at 1400ppm



Dosage ppm	Rating
8000	A
7000	A
6500	A
6000	A
5000	A
4000	A
3000	A
2000	A
1500	A
1400	B++
1300	B++
1200	B++



Dosage ppm	Rating
1200	B++
1000	C
900	C
800	D
700	D
500	D
300	E
100	E

Figure 5.12: Spindles for optimization of dosages for Jatropha at 1200ppm

Figure 5.13: Spindles for optimized dosages for Neem at 1600ppm

Figure 5.14: Spindle for optimized dosages for Karenjia at 1400ppm

Figure 5.15: Spindle for optimized dosages for Jatropha at 1200ppm

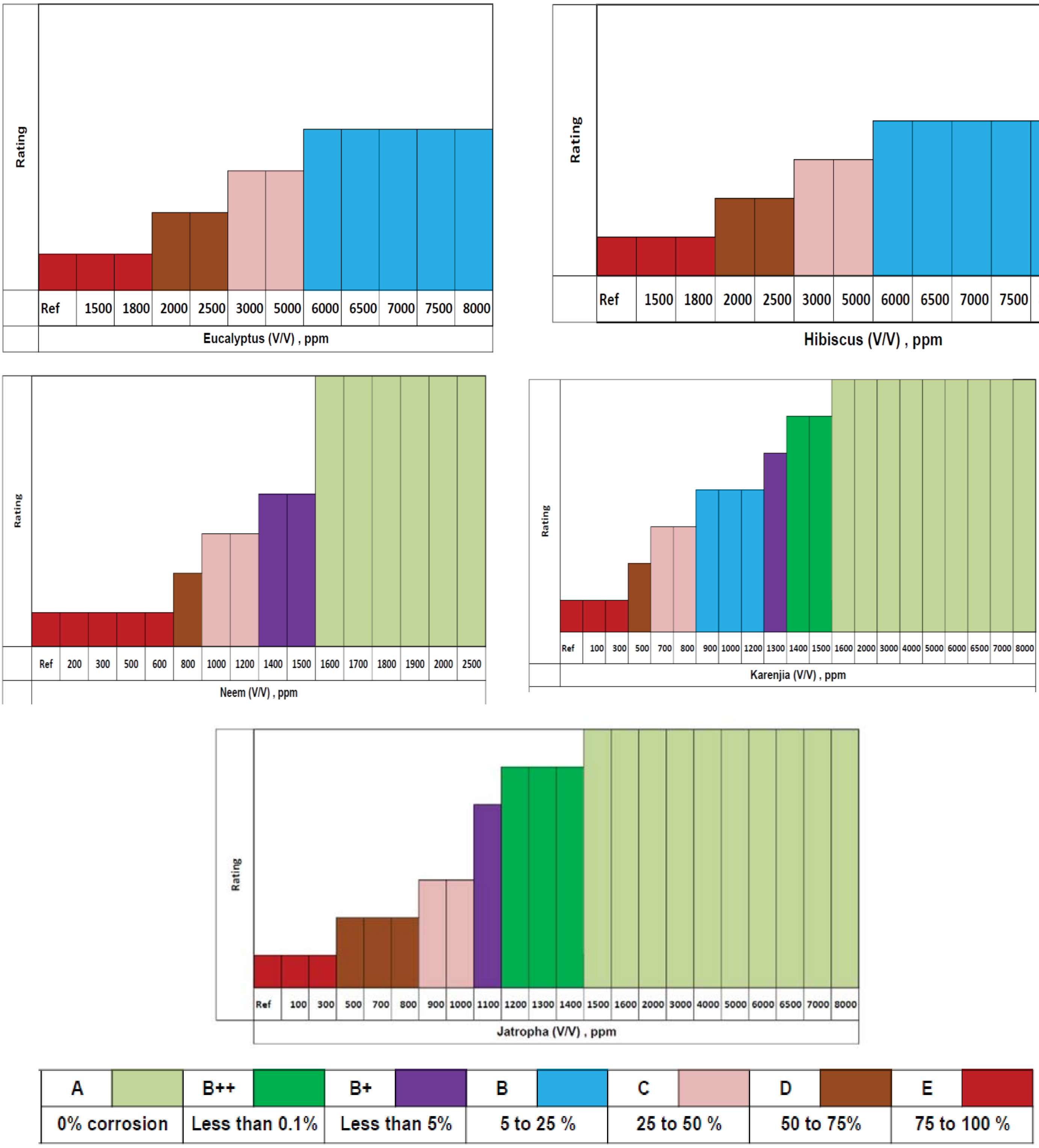


Figure 5.16: Performance ratings of the inhibitors at different concentrations

Figure 5.17: Performance rating of combination of Neem with Aminic antioxidants at different concentrations

Figure 5.18: Spindles showing the effect of Antioxidant on Neem extract

Figure 5.19: Spindles showing the effect of Phenolic antioxidant on Neem extract

Figure 5.20: Spindles showing the effect of Aminic antioxidant on Neem extract

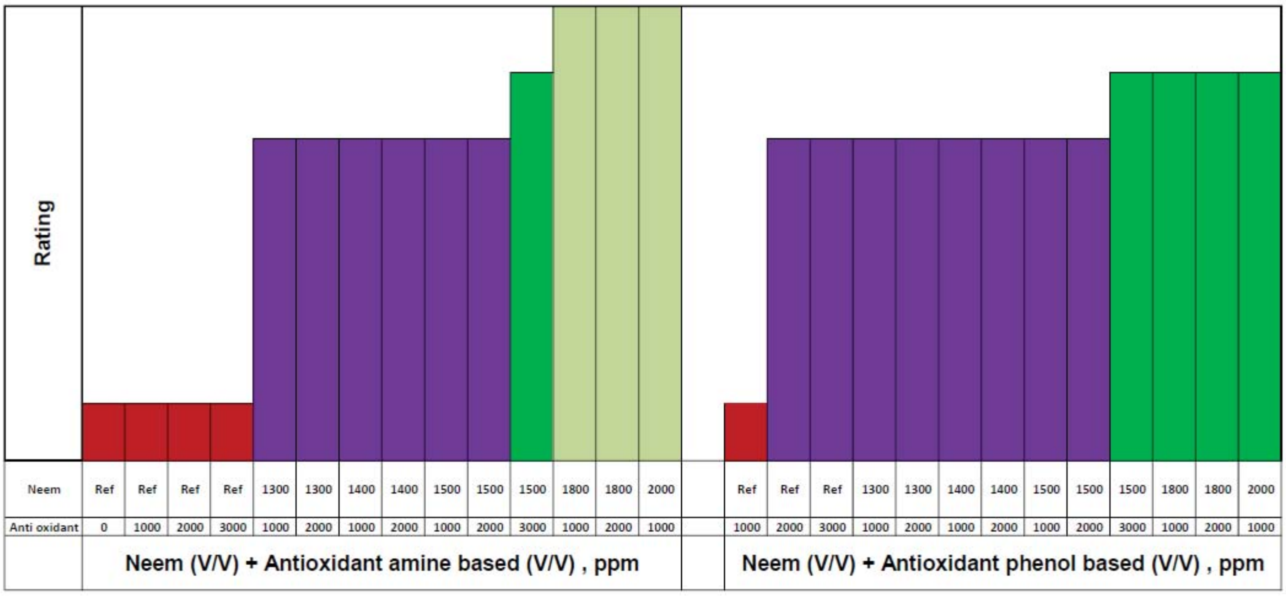
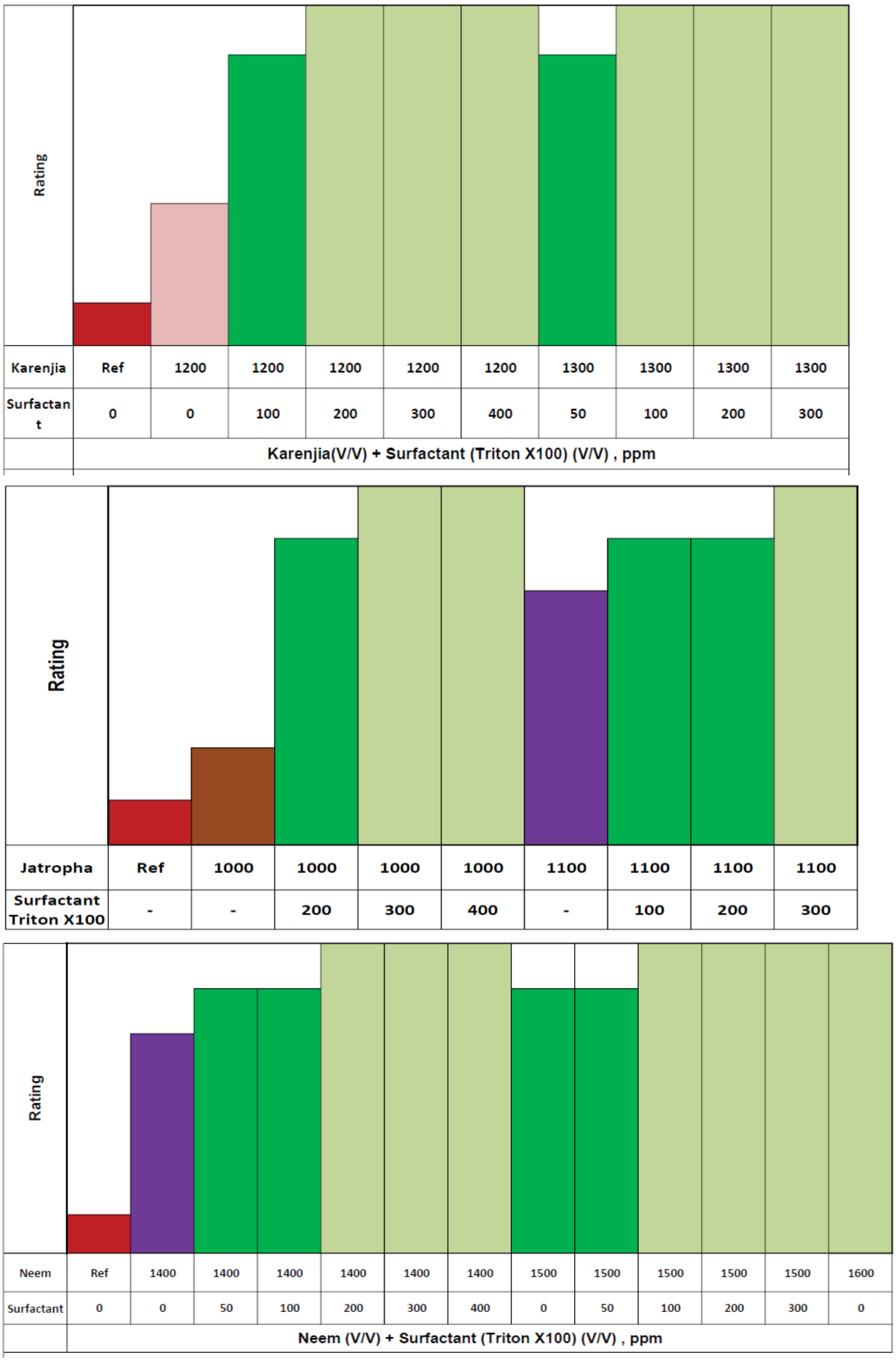


Figure 5.21: Performance rating of combination of Neem with Antioxidants at different concentrations

Figure 5.22: Performance rating of combination of Neem with surfactant at different concentrations

Figure 5.23: Performance rating of combination of Jathopha with surfactant at different concentrations

Figure 5.24: Performance rating of combination of Karenjia with surfactant different concentrations



Karenjia	Ref	1200	1200	1200	1200	1200	1300	1300	1300	1300
Surfactant	0	0	100	200	300	400	50	100	200	300
	Karenjia(V/V) + Surfactant (Triton X100) (V/V) , ppm									

Jatropha	Ref	1000	1000	1000	1000	1100	1100	1100	1100
Surfactant Triton X100	-	-	200	300	400	-	100	200	300

Neem	Ref	1400	1400	1400	1400	1400	1400	1500	1500	1500	1500	1500	1600
Surfactant	0	0	50	100	200	300	400	0	50	100	200	300	0
	Neem (V/V) + Surfactant (Triton X100) (V/V) , ppm												

Figure 5.25: Performance rating of combination of Green Corrosion Inhibitors with Surfactants at different concentrations

Figure 5.26: Test bottles containing coupons at the end of 550hours of static tests for 1200ppm of Jatropha

Figure 5.27: Test bottles containing coupons at the end of 550hours of static tests for 1600ppm of Neem

Figure 5.28: Test bottles containing coupons at the end of 550hours of static tests for 1400ppm of Karenjia

Figure 5.29: Static test bottles of reference ATF with coupons at the end of 550hours of exposure

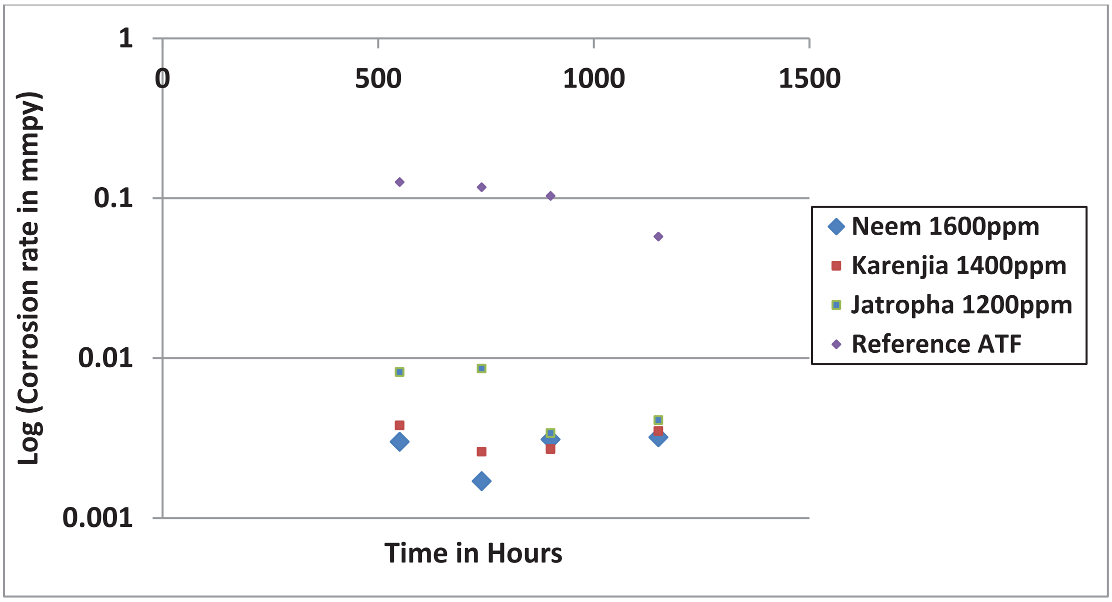


Figure 5.30: Corrosion rates of Green Corrosion Inhibitors with 2% volume of 3.5% NaCl

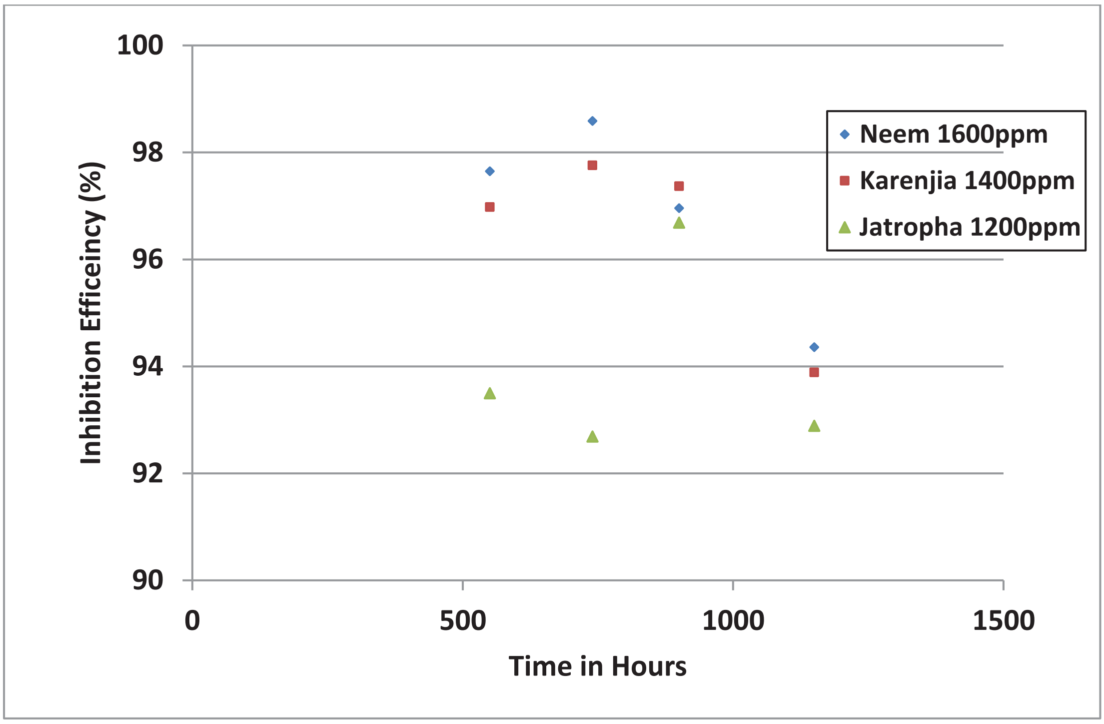


Figure 5.31: Inhibition Efficiency of Green Corrosion Inhibitors with 2% volume of 3.5% NaCl

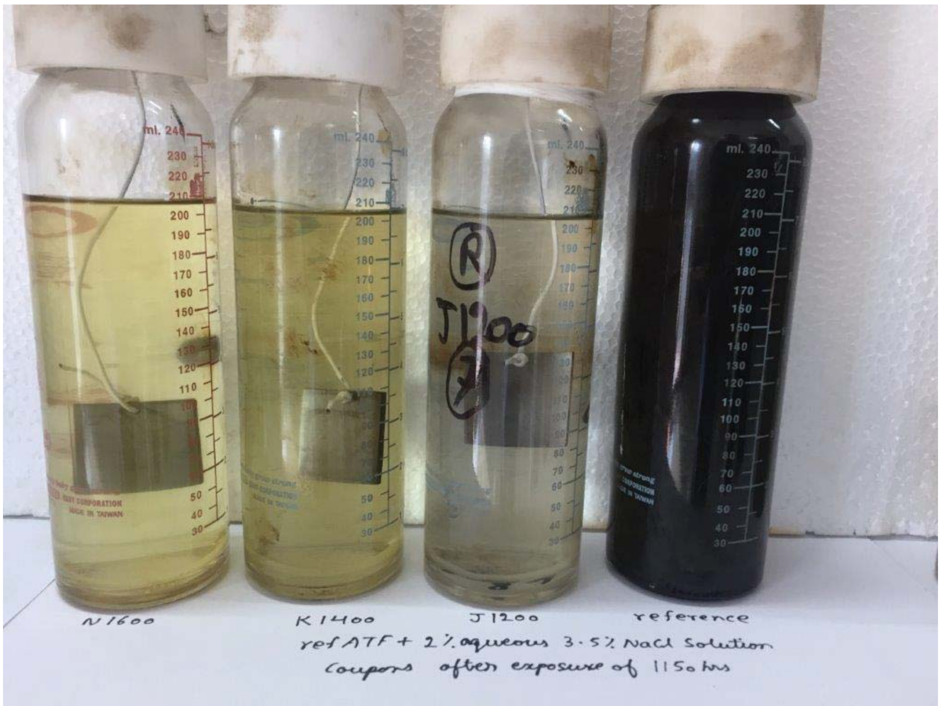


Figure 5.32: Wheel test bottles after 1150hours of test

Figure 5.33: Coupons after testing with 2% volume of 3.5% NaCl after 1150hours

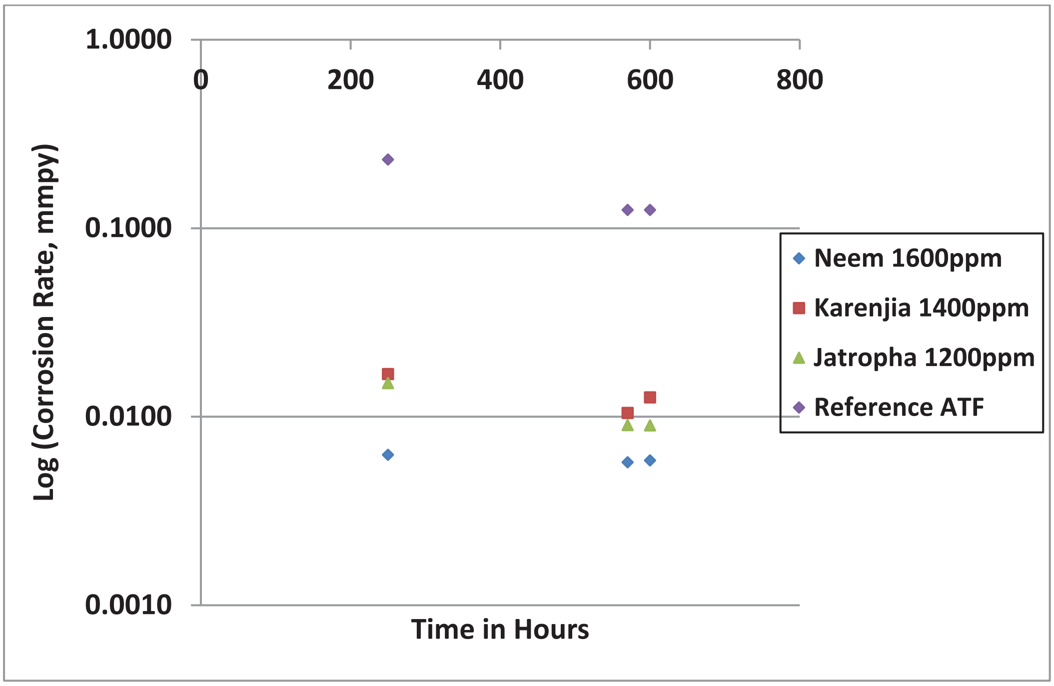


Figure 5.34: Corrosion rates of Green Corrosion Inhibitors with 10% volume of 3.5% NaCl

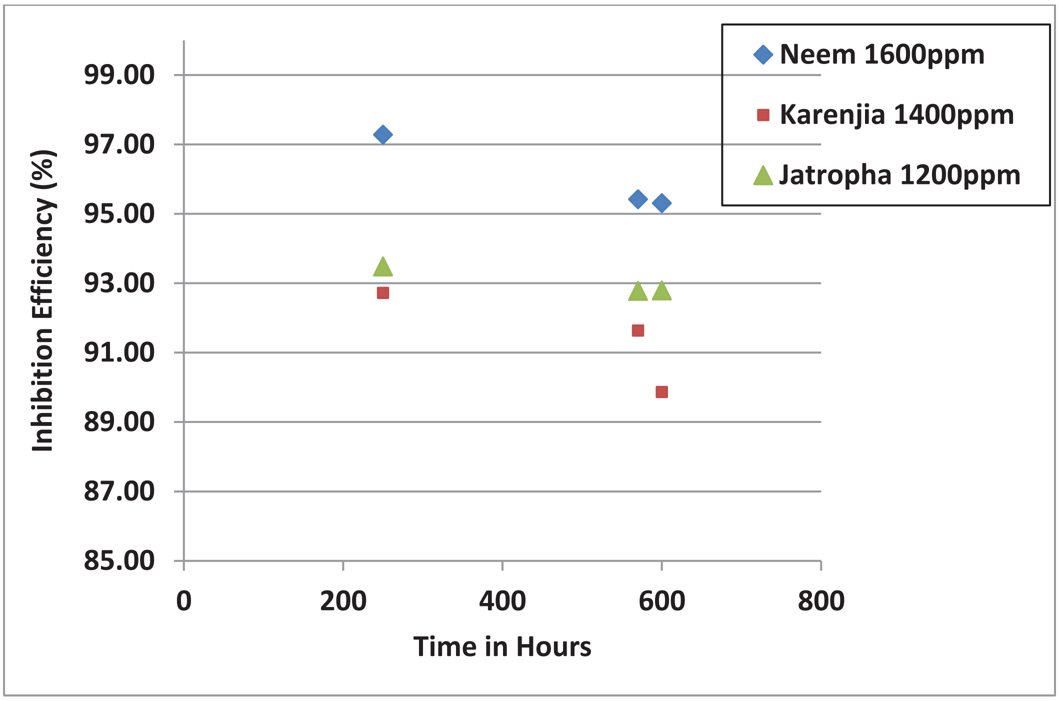


Figure 5.35: Inhibition Efficiency of Green Corrosion Inhibitors with 10% volume of 3.5% NaCl

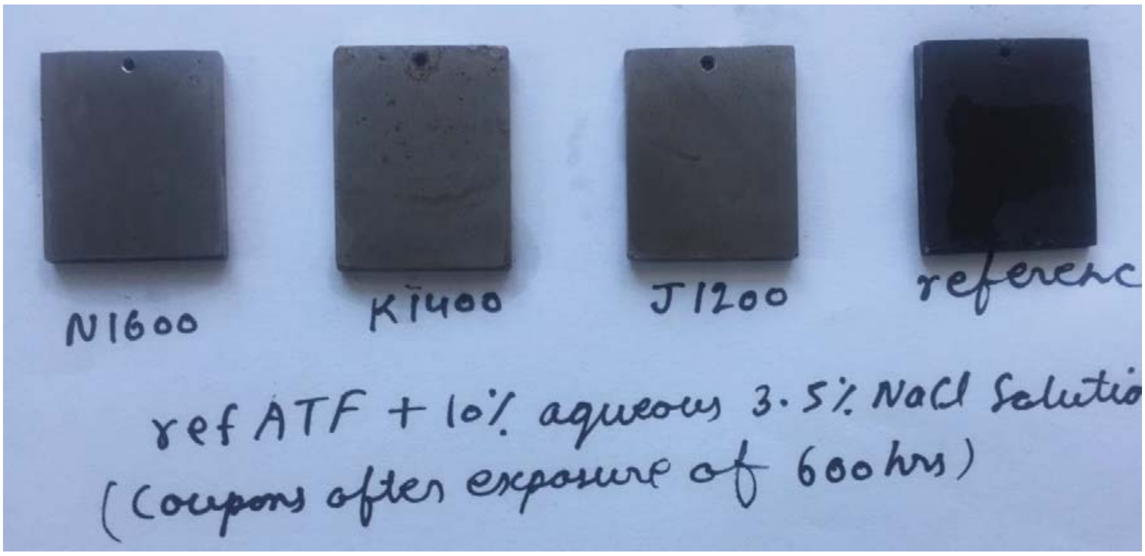


Figure 5.36: Coupons after testing with 10% volume of 3.5% NaCl after 600hours

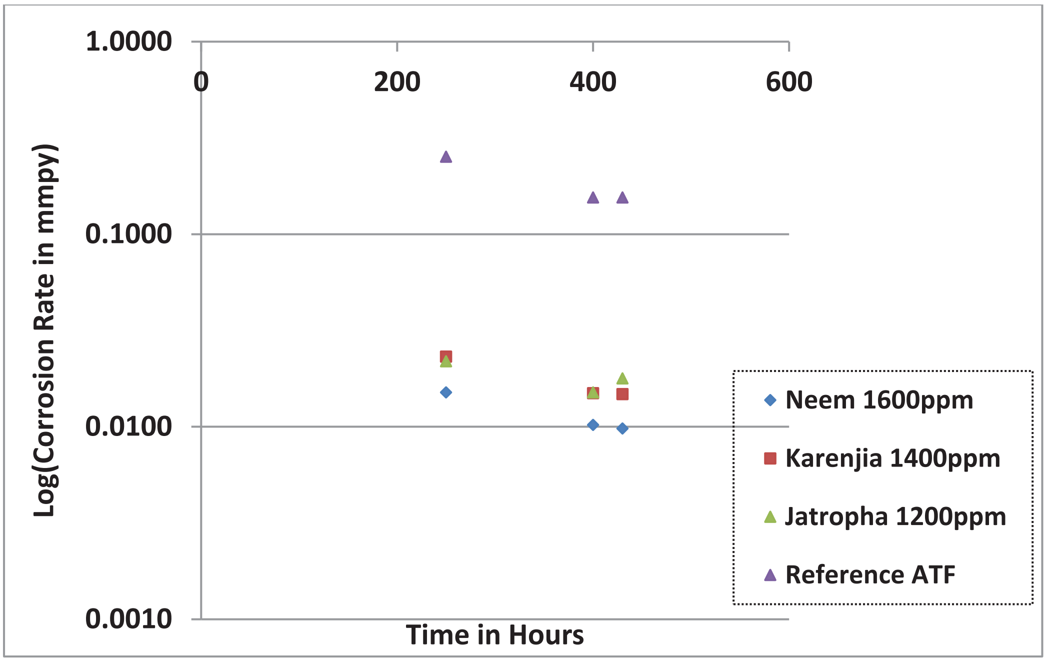


Figure 5.37: Corrosion rates of Green Corrosion Inhibitors with 10% volume of 7.0% NaCl

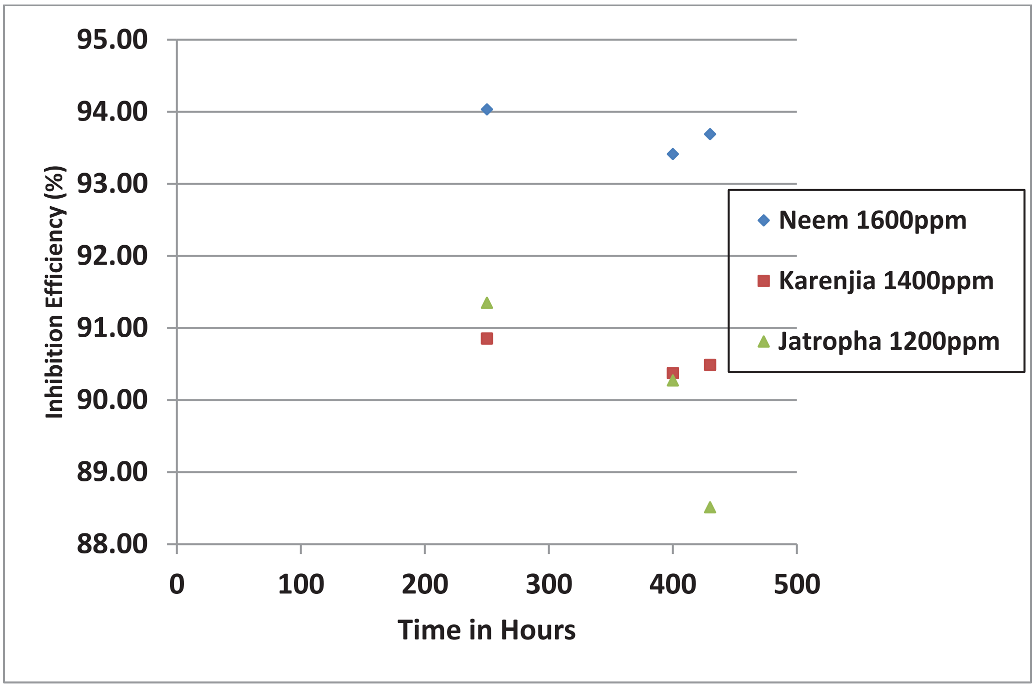


Figure 5.38: Inhibition Efficiency of Green Corrosion Inhibitors with 10% volume of 7.0% NaCl

Figure 5.39: Coupons after testing with 10% volume of 7.0% NaCl after 430hours

Chapter 6: PERFORMANCE EVALUTAION OF GREEN CORROSION INHIBITORS – *PART TWO (ELECTRO CHEMICAL)*

6.1 INTRODUCTION

Electrochemical evaluation of corrosion susceptibility of a given medium can quickly indicate the propensity of the medium to cause corrosion at its natural potential as well as at a range of potentials right from anodic to cathodic levels. In presence of inhibitor films that passivate the metal surface, the electrochemical observation of the solution will have different behavior. Study of the electrochemical behavior of the inhibitor doped medium can thus provide information on the film persistency and passivation potential. The electrochemical tests (Wang, 2011) are nontransient steady state experiments. It may not give a quantitative performance. However, a qualitative and directional performance of the GCIs films can be inferred.

6.2 ELECTROCHEMICAL MEASUREMENT OF CORROSION RATES

The electro chemical corrosion rate measurement often provide results in electrical resistance. The conversion of these values either in mass loss or penetration rates requires additional electro chemical information

Corrosion current values are obtained from galvanic cells and polarization measurements including Tafel extrapolations. The first step involves converting measured current values to current density. This is measured by dividing the total current by geometric area of electrode exposed to the solution. The surface roughness is generally not taken into account while calculating the current density. The assumption is made that the current gets distributed uniformly across the surface area. In case of galvanic couples, the exposed area of anodic specimen may be used. The calculation is expressed as

$$i_{corr} = \frac{Icorr}{A} \text{ ------ } (6.1)$$

Where, i_{corr}= corrosion current density in μA/cm2; I_{corr}=Total anodic current in μA; A= exposed area of specimen in cm2

Electrochemical impedance spectroscopy is a recent and powerful tool in corrosion and solid state laboratories. Electrochemical Impedance Spectroscopy (EIS) also is called AC impedance or just impedance spectroscopy. The usefulness of impedance spectroscopy lies in the ability to distinguish the dielectric and electric properties of individual contributions of components under investigation. Impedance spectroscopy is a non-destructive technique and so can provide time dependent quantitative and time-dependent information about the electrode processes and complex interfaces, extract some characteristics of materials including high resistance materials.

The electrochemical impedance method consists in measuring the response of an electrode to a sinusoidal potential modulation at different frequencies. Often these ac modulations are superimposed either onto applied anodic or cathodic potential, or onto open circuit potential. The mathematical approach of electrochemical impedance data is based on the Ohm's law, i.e. on the linear interdependency between potential perturbation and current response or vice versa. However, the potential-current dependencies of electrochemical systems in general are nonlinear. On the other hand, it is possible to extract a small fraction of this dependence, where the mentioned dependence can be approximated as linear, e.g. in the range of 5–10 mV. Therefore, the measurements of impedance are performed under sinusoidal potential modulation with amplitude 5–10 mV. The sinusoidal perturbations of potential E(t) induces a sinusoidal current I(t) of the same frequency (ω) superimposed onto the steady state current with the phase shift ϕ with the respect to the potential. As for physical electric circuits, the electrochemical impedance of electrode reaction (Z) is defined analogous to Ohm's law as:

$$Z(w) = \frac{E(t)}{I(t)} = (E_0 \, Sin \, wt)/(I_0 Sin \, (wt-\emptyset)) = Z_0 \frac{Sin \, wt}{Sin \, (wt-\emptyset)} \quad \text{---- } (6.2)$$

Where E_0 and I_0 are amplitude of potential and current and 'w=' 2πf is the radial frequency expressed in Hz

Popular format for evaluating the electrochemical impedance data is plotting imaginary impedance data against the real impedance data at each excitation frequency which is termed as Nyquist plot. Nyquist plot has several advantages. Primary one that plot format makes it easy to see the effect of Ohmic (Uncompensated) resistance. If data are taken at sufficiently high frequencies, then it is easy to extrapolate the obtained curve towards the left down to the abscissa to read Ohmic resistance. The semicircle shape of curve often does not change when Ohmic resistance changes.

Another advantage of this plot is that it emphasizes circuit components that are in series. The Nyquist plot format also has some disadvantages such as the frequency does not appear explicitly. Although the ohmic resistance and polarization (charge transfer) resistance can be easily read directly from the Nyquist plot, the electrode capacitance can be calculated only after the frequency information is known

Another format used for evaluating electrochemical impedance data known as Bode plots which consists of the plotting $|Z|$ and ϕ versus log ω. The Bode plot has some distinct advantages over the Nyquist plot. Since frequency appears as one of the axes, it is easy to understand from the plot how the impedance depends on the frequency. The plot uses the logarithm of frequency to allow a very wide frequency range to be plotted on one graph, but with each decade given equal weight. The Bode plot also shows the magnitude ($|Z|$) on a log axis so that you can easily plot wide impedance ranges on the same set of axes. This can be an advantage when the impedance depends strongly on the frequency.

The Bode plot is a useful alternative to the Nyquist plot. It lets you avoid the longer measurement times associated with low frequency determinations of polarization resistance, because the log $|Z|$ versus log ω plot sometimes allows a more effective extrapolation of data from higher frequencies. The Bode plot also has some disadvantages. The greatest one is that the shape of the curves can change if the circuit values change, e.g. uncompensated resistance. Therefore, usually EIS are analyzed both Nyquist and Bode plots. EIS data is commonly analyzed by fitting it to an equivalent electrical circuit model consisting of passive elements that do not generate current or potential such as resistors (R), capacitors (C), and inductors (L).

Typical Nyquist and Bode plots for different electrochemical equivalent circuits are depicted in Fig.6.1. The corrosion rates and related information from the any of the electrochemical measurements are made as per (ASTM G102-89, 2015) and (ASTM G106-89, 2015).

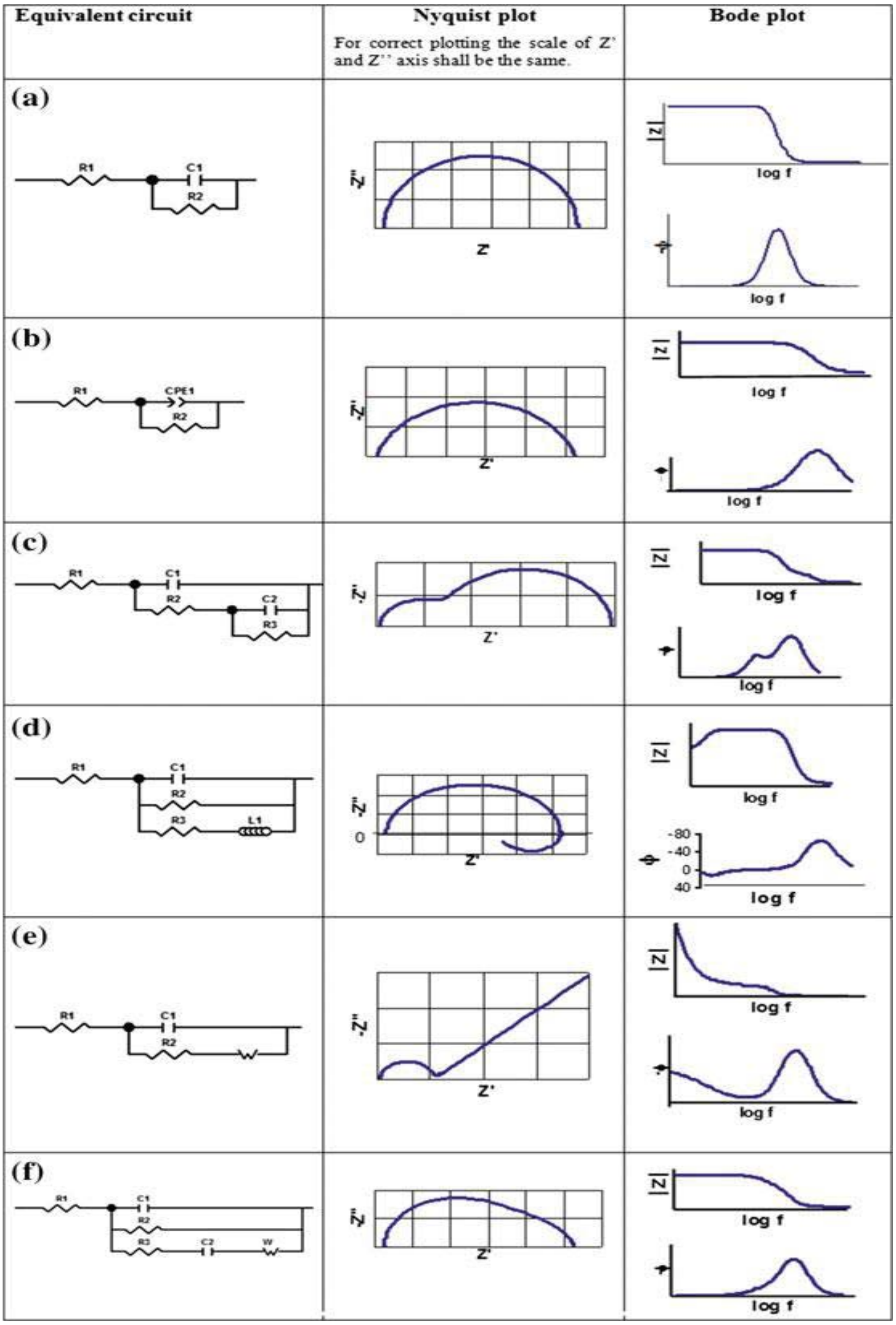


Figure 6.1: Typical Nyquist and Bode plots for different electrochemical equivalent circuits

6.3 MICRO EMULSION OF GCI FOR ELECTROCHEMICAL STUDIES

In order to have a conductive aqueous medium with dispersed inhibitor to facilitate electrochemical evaluation, a micro emulsion with a commercial surfactant (Triton X; a polyethylene glycol based formulation) was made. Initially, 5ml surfactant together with 5ml neat GCI in 50ml demineralized water was used after sonication for 10 minutes. The stable emulsions could be achieved with good dispersion of GCI in water medium. The content of surfactant was further optimized. Stable emulsions were formed at a minimum volume of 0.5ml of surfactant for 5ml inhibitor and 50ml of DM water. For the purpose of electrochemical studies, an aqueous solution 3.5wt.% of NaCl has been used throughout this study.

6.4 ELECTROCHEMICAL TEST SETUP

The Linear Polarization Resistance (LPR) studies were conducted using a multichannel AUTOLAB PGSTAT 204 Potentiostat – Galvanostat. In LPR, a three electrode mode is generally adopted with a working electrode (corrosion coupon), a platinum counter electrode graphite and a saturated calomel electrode as an independent reference electrode. The laboratory setup is shown in Fig.6.2.

A one liter double jacketed electrochemical cell with provision for sample addition / with drawl ports was used in the study. A circular coupon of 15mm diameter and 1.0mm thickness made of 1020 grade carbon steel was used in the study. Prior to the experiments, the steel coupon was metallographically prepared through successive grinding and polishing steps up to 0.5micron alumina to a mirror finish. The general chemical composition of the coupons and its microstructure are shown in Table 6-1 and Fig.6.3 respectively. The high temperature studies were accomplished by circulating heated water through the jackets with a close loop temperature controller sensing the bath temperature.

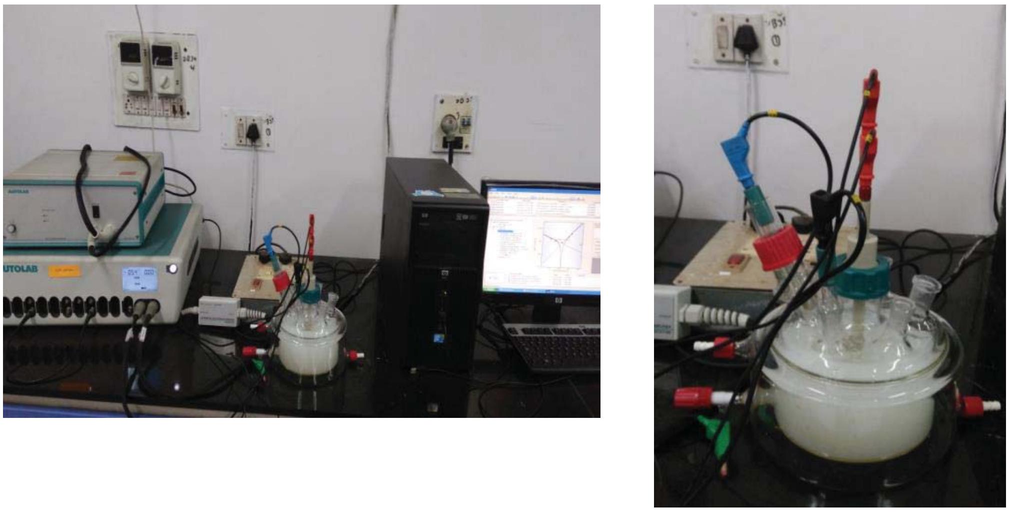


Figure 6.2: M/s AUTOLAB make Electrochemical Test set up

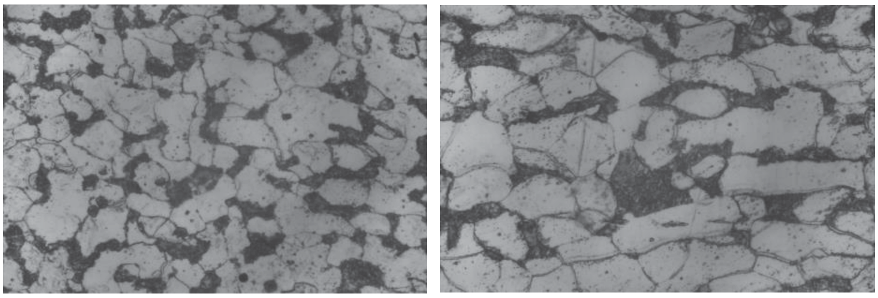


Figure 6.3: Surface and sectional microstructure of Carbon steel coupon showing normal Ferrite and Pearlite (X500)

Table 6-1: Composition of LPR coupons

Composition in Wt.%	C	Mn	S	P	Fe
	0.21	0.45	0.009	0.003	Balance

6.5 ELECTROCHEMICAL IMPEDANCE STUDIES

The electrochemical impedance studies were carried out on the micro emulsified optimized dosage rates of the potential green corrosion inhibitors over carbon steel coupons. The emulsions were prepared as elucidated in section 5.3. The tests were performed at room temperature (27 °C) at the open circuit potential over a frequency range of 1Hz to 100 KHz. The system has provision of computing the impedance values over the set frequencies instantly. The Nyquist plots of reference (No inhibitor), solution with 1200ppm of Jatropha, 1400ppmm of Karenjia and 1600ppm of Neem and the computed resistance of the passivation film / solution (Rp/Rs) are shown in Fig.6.4 to Fig.6.7 and Table 6-2 respectively.

Table 6-2: Computed Resistance of the passivating film from EIS studies

Experimental condition	**R_p in Ohms**	**R_s in Ohms**
Reference without Inhibitor	620.01	13.343
Jatropha 1200ppm	869.76	45.517
Karenjia 1400ppm	987.02	69.3
Neem 1600ppm	1365.2	47.476

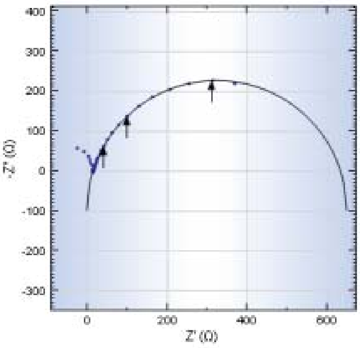


Figure 6.4: Nyquist plot of solution without Inhibitor

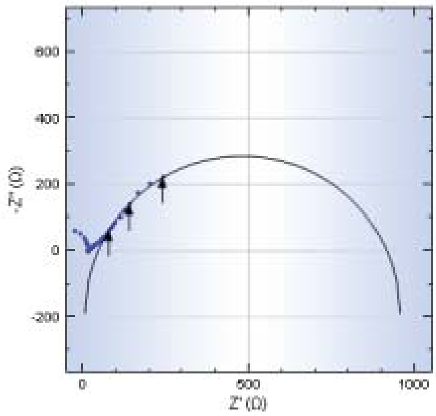


Figure 6.5: Nyquist plot of solution with 1200ppm of Jatropha Extract

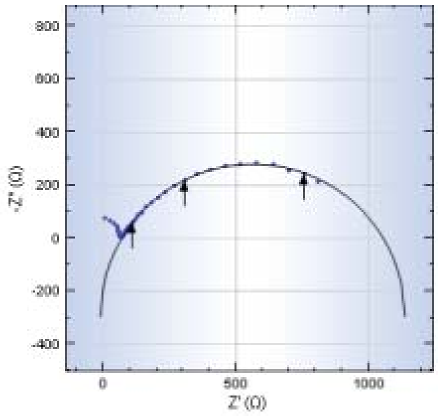


Figure 6.6: Nyquist plot of solution with 1400ppm of Karenjia Extract

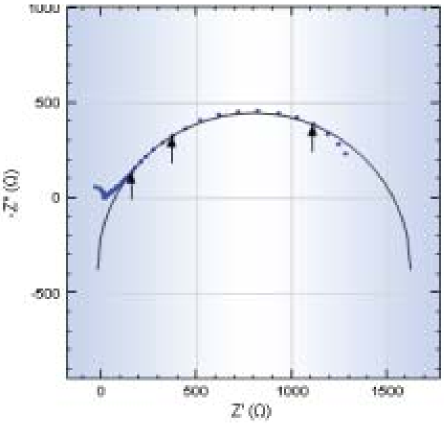


Figure 6.7: Nyquist Plot of solution with 1600ppm of Neem Extract

6.6 LINEAR POLARIZATION RESISTANCE STUDIES

Linear polarization resistance (LPR) is a quick, non-destructive testing technique commonly used in material corrosion studies to gain corrosion rate data. For this method the material is polarized, typically on the order of ±10mV, relative to its open circuit potential (It is potential measured when no net current is flowing). As the potential of the material (working electrode) is changed, a current will be induced to flow between the working and counter electrodes, and the material's resistance to polarization can be found by taking the slope of the potential versus current curve. This resistance can then be used to find the corrosion rate of the material using the Stern-Geary equation.

Linear Polarization Resistance (LPR) is conducted as per as per (ASTM G59-97, 2014) and (ASTM G102-89, 2015). It is adopted to evaluate the corrosion rates through Tafel Extrapolation technique. The electro chemical corrosion rate measurement may provide results in terms of electrical resistance. The polarization resistance can be related to the general corrosion of metal at or near corrosion potential. In this test method, polarization resistance of the corroding metal as a working electrode is measured. The corrosion current values are obtained from galvanic cells with respect to a reference electrode. The measured current value is converted into current density by dividing total current by geometric area of working electrode, in this case the corroding surface of the metal exposed to the solution. The corrosion rate in mm/ year can thus be determined.

The LPR tests require the medium to be conductive. Initially tests under hydrocarbon medium were tried but remained without success. To overcome the challenge of ensuring conductivity for the studies, inhibitor film on coupon was made and retained by dipping in inhibited hydrocarbon samples and drying at 60 °C. Thereafter, the coupons were studied in 3.5% brine solution for their electrochemical response. However, due to the discontinuous inhibitor film on coupons on account of porosity and surface tension effects, the studies were impaired.

6.6.1 LINEAR POLARIZATION STUDIES AT ROOM TEMPERATURE

After setting up the electrochemical cell, the open circuit potential (E_{OC}) of the sample was recorded over the period of time and the transient nature recorded for 10 minutes. The potential – time measurements were made to evaluate the potential at the metal – solution interface as it achieved equilibrium. Fig.6.8 shows the potential – time plot of the potential green corrosion inhibitors in their emulsified form to achieve equilibrium with a 3.5% aqueous solution of NaCl. The open circuit potential is seen to shift toward noble or active direction in presence of the optimum dosages of the extracts.

Thereafter, the system provides a voltage sweep of +or-100mV to the (E_{OC}) (anodic to cathodic range) at a scan rate of 1mV/sec as per ASTM standard, the current values are recorded with respect to the applied potential. The potential vs. current plots are automatically generated with provision to define the anodic and cathodic Tafel slopes (b_c & b_a) by the user by identifying the linear regions. Once identified, the system generates the corrosion potential (E_{corr},), Corrosion current (i_{corr}) and the Tafel slopes (b_c & b_a). The inhibition efficiency is calculated based on the current densities (ratio of i_{corr} to sample exposed area to the solution) with and without the dosage of inhibitors as given below:

$$Inhibition\ efficiency\ (I.E) = \frac{i_a - i_p}{i_a} \text{ -------------- } (6.3)$$

Where, i_a - Current density in the absence of inhibitor and

i_p - Current density in the presence of inhibitor

The LPR studies were carried out at room temperature on the potential green corrosion inhibitors namely Neem, Karenjia and Jatropha at three different concentrations including the optimum concentration established as per performance evaluation in rotating spindle. The typical Tafel curves in respect of these tests carried out with varying concentrations of the Neem, Karenjia and Jatropha in the aqueous micro emulsion along with the reference blank brine solution are shown in Fig.6.9 to Fig.6.11 respectively. The typical output showing the establishment of Tafel slopes in respect of these are also shown in Fig.6.12.The summary of the corrosion potential (E_{corr},), corrosion current (i_{corr}) and the Tafel slopes (b_c & b_a), and current densities (i_a and i_p) and inhibition efficiency (I.E) are compiled and shown in Table 6-3.

Table 6-3: Summary of Room temperature LPR results of the green corrosion inhibitor extracts

Green Inhibitor	Conc. Of extract inppm	Temp (K)	E_{oc} (mV)	E_{corr} (mV)	i_{corr} (µA.cm^{-2})	-b_c (mV.dec^{-1})	+b_a (mV.dec^{-1})	% IE
Reference	0	300	-591	-595.91	31.698	87.436	-592.70	-
Jatropha	600	300	-557	-567.08	25.971	90.986	-701.86	18.1
	1200	300	-598	-594.24	15.913	58.811	981.05	49.8
	1800	300	-606	-614.40	14.005	65.008	1.5824	55.8
Karenjia	600	300	-611	-621.86	22.766	81.175	-568.39	28.18
	1400	300	-539	-543.28	12.383	74.528	241.12	60.93
	1800	300	-530	-530.88	12.266	96.177	478.42	61.30
Neem	600	300	-558	-576.23	23.328	69.088	1838.8	26.40
	1600	300	-535	-534.22	12.77	100.56	235.25	59.70
	1800	300	-517	-521.02	11.38	79.698	279.44	64.08

6.6.2 LINEAR POLARIZATION STUDIES OF JATROPHA AND NEEM EXTRACT AT ELEVATED TEMPERATURE

Similar LPR studies were carried out on aqueous micro emulsion of Jatropha at three different temperatures namely 30ºC, 50ºC and 70ºC. Heated water was circulated within the jacketed electrochemical cell with a submersible pump and closed loop temperature controller. The experiments were performed maintaining the temperature of the electrochemical bath within + or - 1ºC to the set temperature. Experiments on blank brine solution as well as at two different concentrations of aqueous micro emulsion of Jatropha namely 600ppm and 1200ppm were performed. In addition, experiments at RT, 50C and 70C for 600, 1200 and 1600ppm was carried out. The Tafel plots of Jatropha extract studied at different temperature in respect of nil, 600ppm and 1200ppm are shown in Fig.6.13 to Fig.6.15 respectively. Similarly, the Tafel plots of Neem extract studied at different temperature in respect of nil, 600ppm, 1200ppm and 1600ppm are shown in Fig.6.16 to Fig.6.18 respectively. The summary of the corrosion potential (Ecorr,), Corrosion current (icorr) and the Tafel slopes (bc & ba), and current densities (ia and ip) and inhibition efficiency (I.E) for high temperature LPR studies of both Jatropha and Neem are shown in Table 6-4 and Table 6-5 respectively.

Table 6-4: Summary of the high temperature LPR test on Jatropha

Conc. of Jatropha Extract inppm	Temp. ºK	E_{oc} mV	E_{corr} mV	i_{corr} $\mu A.cm^{-2}$	b_c $mV.dec^{-1}$	b_a $mV.dec^{-1}$	% IE
0	300	-591	-595.91	31.6980	87.436	592.700	-
	323	-560	-565.06	45.08	78.61	235.27	-
	343	-621	-623.13	53.48	85.27	2120.8	-
J600	300	-557	-567.08	25.9710	90.9860	-701.86	18.06
	323	-597	-608.11	39.6270	115.430	-314.360	12.11

	343	-553	-550.45	49.436	106.310	-2079.40	7.58
J1200	300	-598	-594.24	15.9130	58.811	981.055	49.8
	323	-566	-566.10	26.539	100.580	298.270	41.12
	343	-609	-595.89	35.321	87.617	-3022.5	33.55

Table 6-5: Summary of the high temperature LPR test on Neem

Conc. Of Extract (ppm)	**Temp. K**	**E_{oc} mV**	**E_{corr} mV**	**i_{corr} $\mu A.cm^{-2}$**	**b_c $mV.dec^{-1}$**	**b_a $mV.dec^{-1}$**	**% IE**
N0	300	-223	-234	12.175	293.940	204.180	-
	323	-305	-321	21.728	416.220	245.990	-
	343	-621	-624	53.480	85.272	2120.80	-
N600	300	-230	-238	9.121	357.900	238.020	25.88
	323	-339	-345	17.788	428.070	306.250	21.13
	343	-630	-599	46.763	100.06	-630.02	16.56
N1200	300	-223	-231	6.964	346.230	234.910	42.02
	323	-325	-332	14.166	938.770	482.460	34.80
	343	-595	-592	40.741	69.0580	510.940	26.04
N1600	300	-240	-252	4.551	416.930	256.860	58.02
	323	-302	-312	10.186	426.290	273.330	46.10
	343	-577	-606	32.863	108.400	92.089	39.85

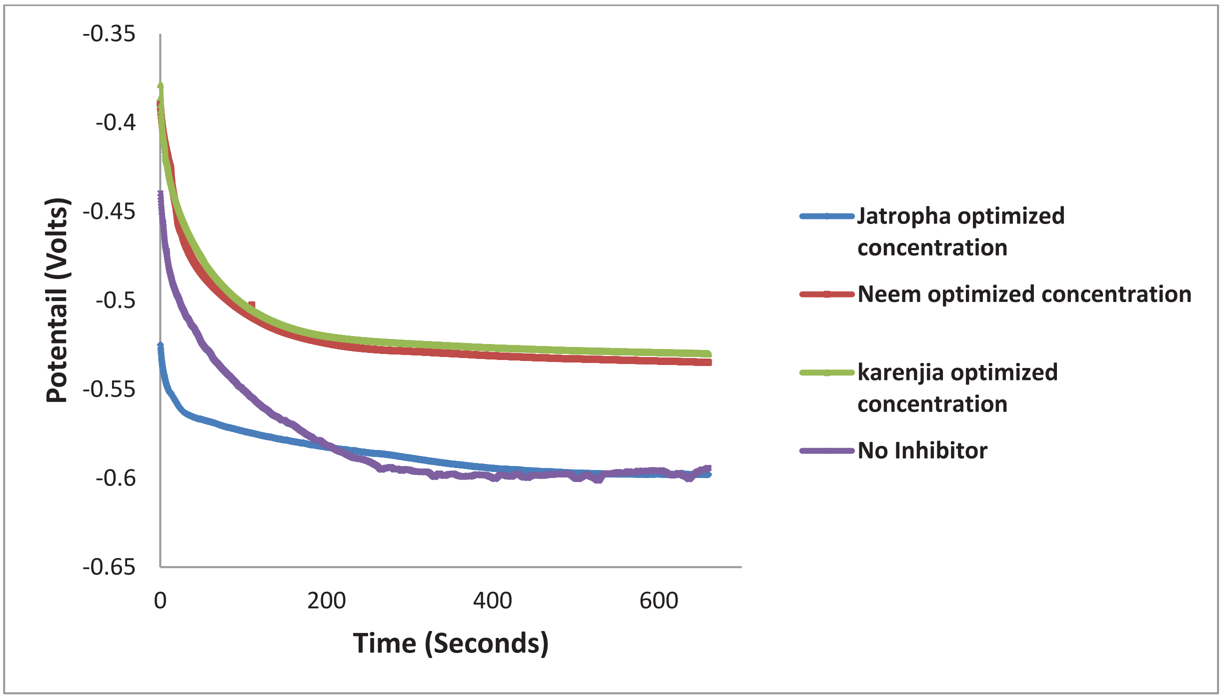
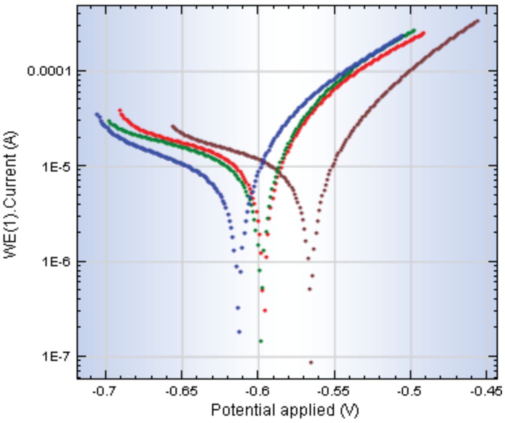
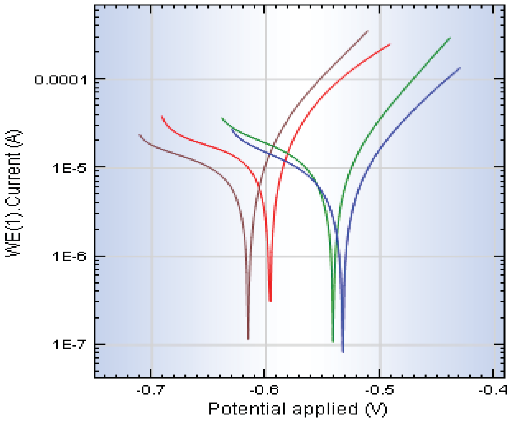


Figure 6.8: Open Circuit Potential vs. Time for the aqueous 3.5% NaCl solutions doped with potential green corrosion inhibitors at their optimized dosage rates



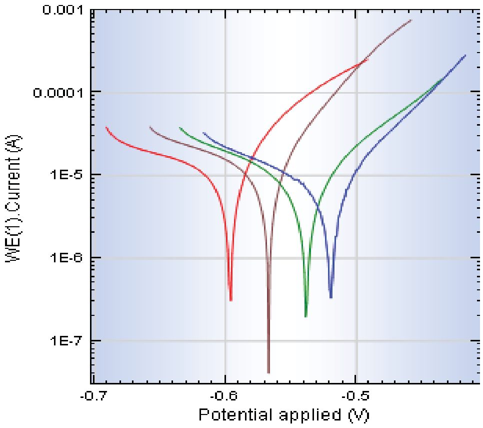
0ppm	600ppm	Optimized concentration	1800ppm
Red	Brown	Green	Blue

Figure 6.9: Tafel plots of solutions with different concentrations of Jatropha extract



0ppm	600ppm	Optimized concentration	1800ppm
Red	Brown	Green	Blue

Figure 6.10: Tafel plots of solutions with different concentrations of Karenjia extract



0ppm	600ppm	Optimized concentration	1800ppm
Red	Brown	Green	Blue

Figure 6.11: Tafel plots of solutions with different concentrations of Neem extract

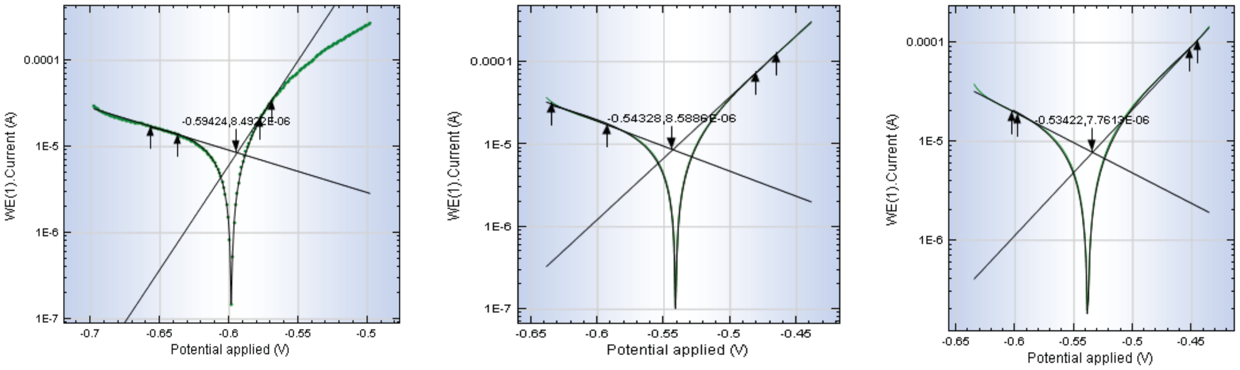
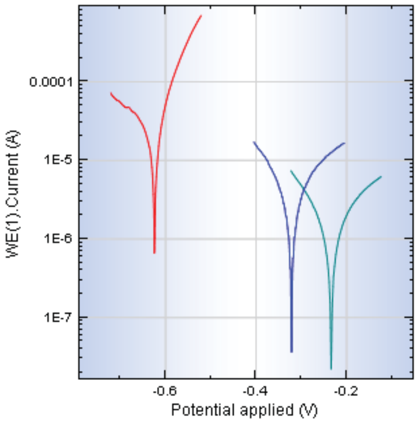
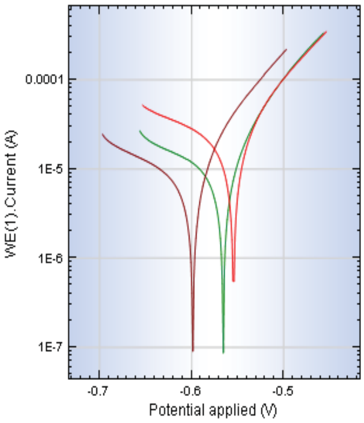


Figure 6.12 Typical Tafel slopes for optimized concentration of (a) Neem, (b) Karenjia and (c) Jatropha extracts



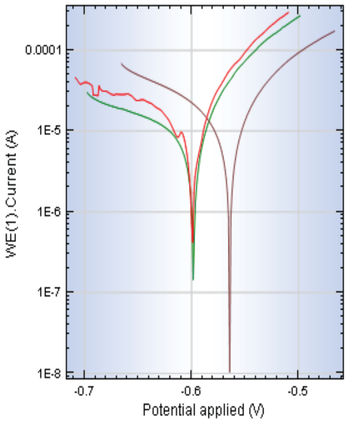
RT	50 deg C	70 deg C
Green	Brown	Red

Figure 6.13: Typical Tafel curves without inhibitor studied at different temperatures



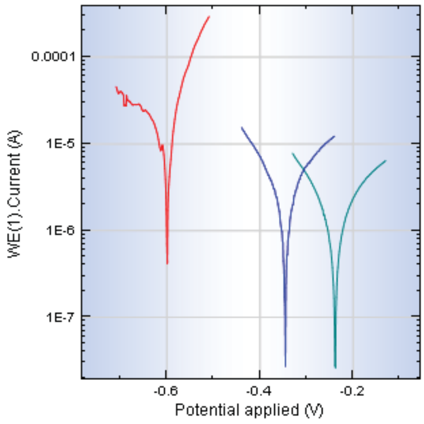
RT	50 deg C	70 deg C
Green	Brown	Red

Figure 6.14: Typical Tafel curves of 600ppm Jatropha extract as studied at different temperatures



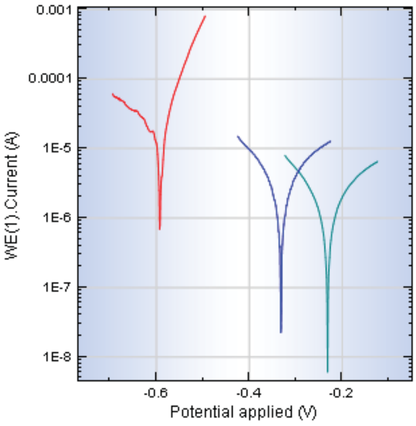
RT	50 deg C	70 deg C
Green	Brown	Red

Figure 6.15: Typical Tafel curves of 1200ppm Jatropha extract as studied at different temperatures



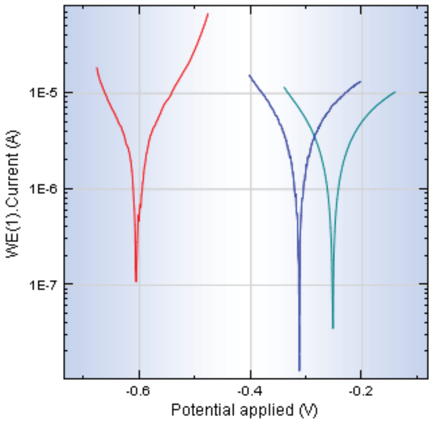
RT	50 deg C	70 deg C
Green	Blue	Red

Figure 6.16: Tafel plots of solutions with Neem 600ppm inhibitor at different temperatures



RT	50 deg C	70 deg C
Green	Blue	Red

Figure 6.17: Tafel plots of solutions with Neem 1200ppm inhibitor at different temperatures



RT	50 deg C	70 deg C
Green	Blue	Red

Figure 6.18: Tafel plots of solutions with Neem 1600ppm inhibitor at different temperatures

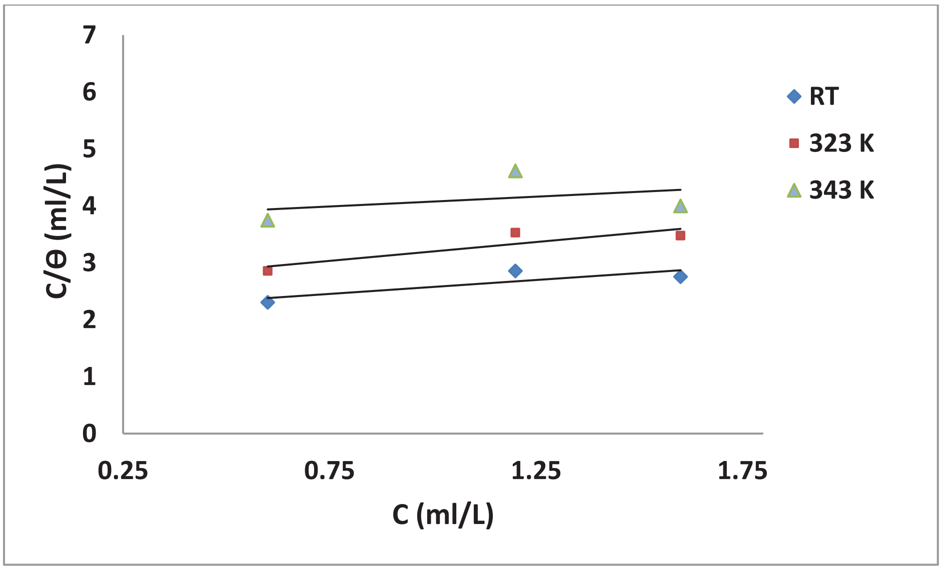


Figure 6.19: Langmuir Adsorption plots for steel in aqueous NaCl medium with different concentrations of emulsified Neem oil extract at three different temperatures

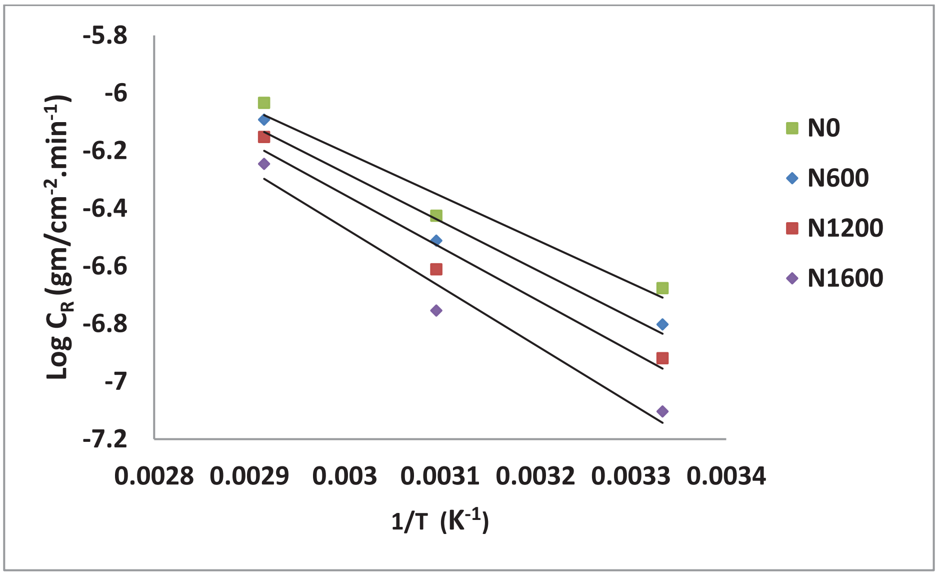


Figure 6.20: Arrhenius plots of the corrosion rate for steel in aqueous medium in absence and presence of Neem oil extract

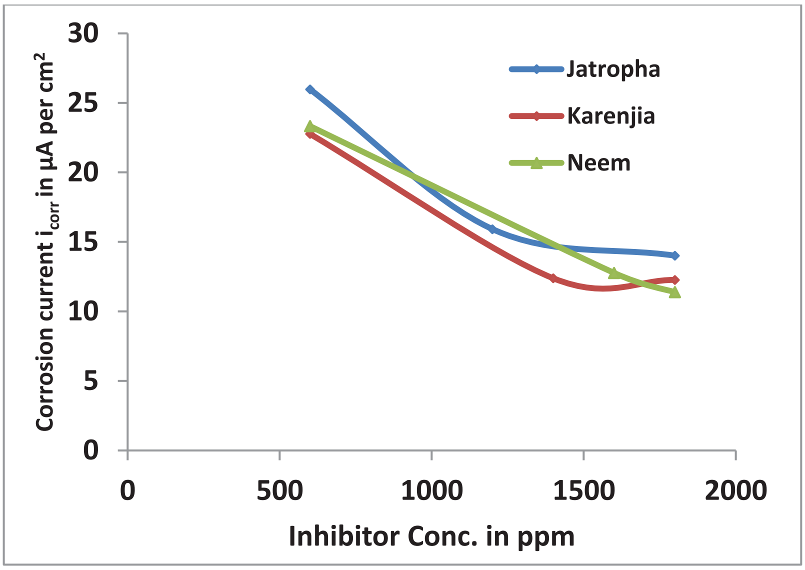


Figure 6.21: Plot of corrosion current with concentration of the potential green corrosion inhibitors

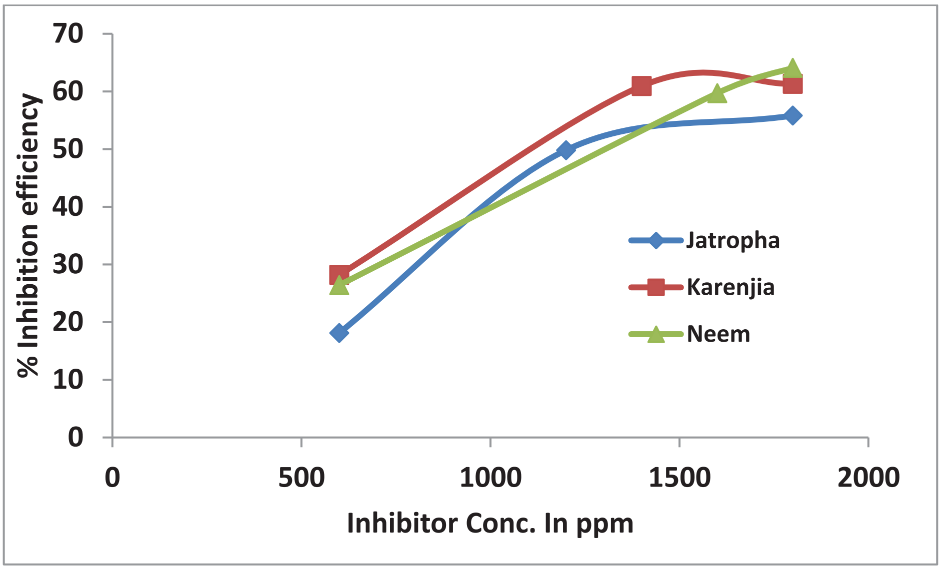


Figure 6.22: Plot of Percentage Inhibition efficiency with concentration

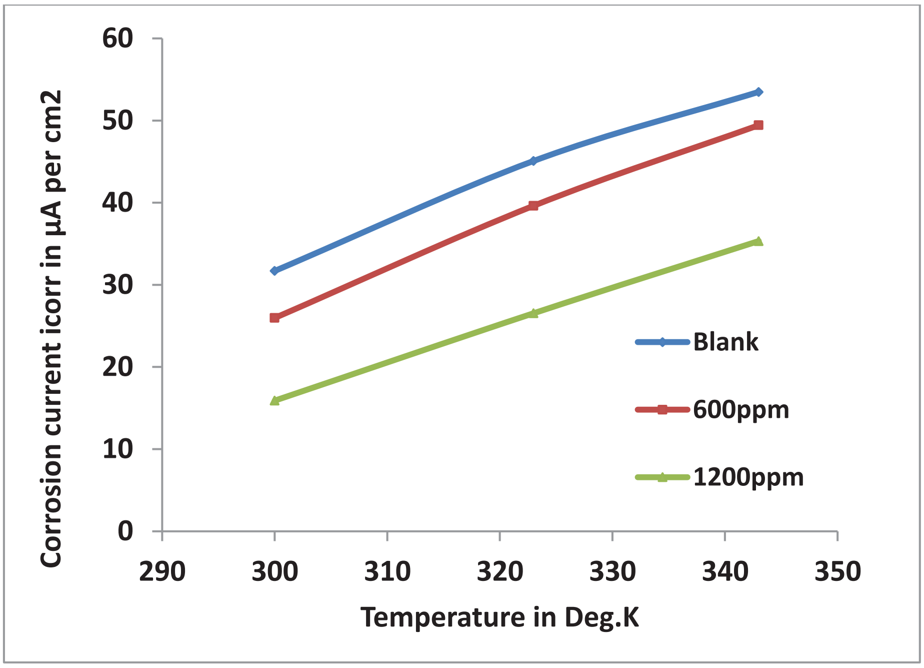


Figure 6.23: Plot of corrosion current with temperature for various concentrations of Jatropha Inhibitor

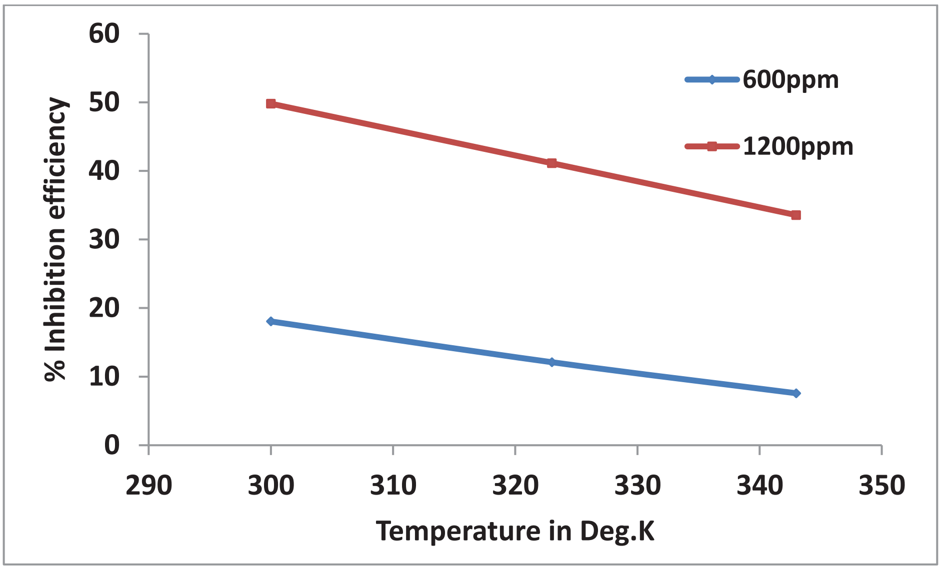


Figure 6.24: Plot of Percentage Inhibition efficiency with temperature for various concentrations of Jatropha Inhibitor

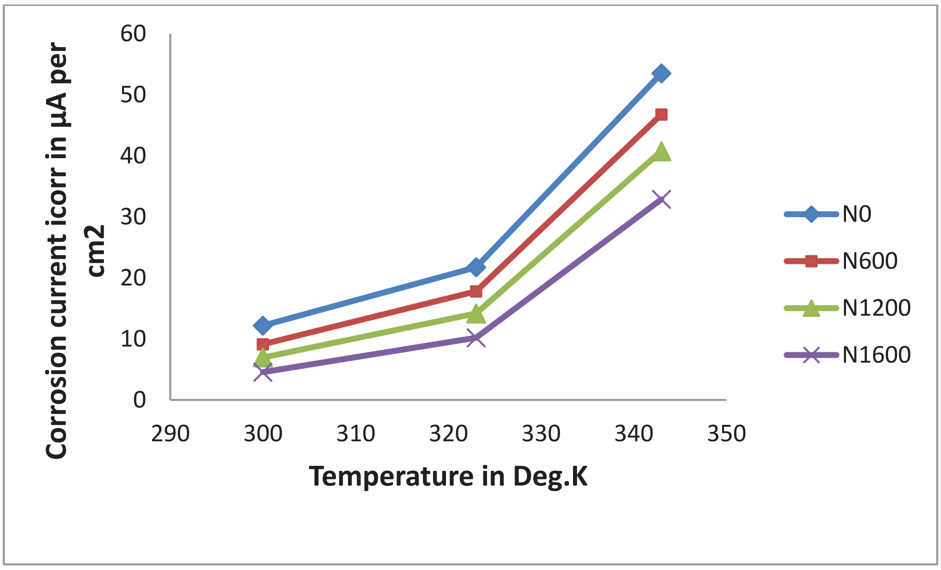


Figure 6.25: Plot of corrosion current with temperature for various concentrations of Neem Inhibitor

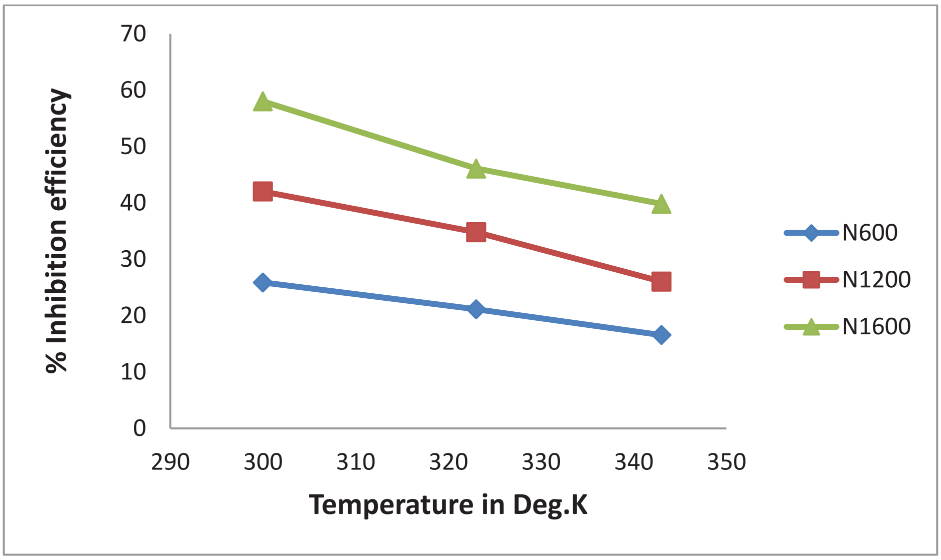


Figure 6.26: Plot of Percentage Inhibition efficiency with temperature for various concentrations of Neem Inhibitor

6.7 CORROSION INHIBITION MECHANISM OF NEEM EXTRACT

The potential Neem extract studied in this work as a green corrosion inhibitor is expected to provide the inhibition of metal surfaces that are covered by the adsorbed water molecules. Researchers elsewhere have reported that the inhibitors react by replacing water molecules with organic molecules (El–Maksoud, 2008) which can be represented as

$$Org.\ molecule\ (aq) + nH_2O \longrightarrow Org.Molecule(ads) + nH_2O\ (soln) \text{-----}\ (6.4)$$

Establishment of the adsorption isotherm can describe the adsorption mechanism of the corrosion inhibitor and also information on the nature of metal inhibitor interaction. Adsorption depends on the charge and nature of the metal surface, adsorption of solvent and other ionic species, electrochemical potential at solution interface and the temperature of the corrosion reaction. The adsorption isotherms can be Langmuir, Frendluich, Temkin, Flory-Huggins, Dhar–Flory-Huggins, Bockris-Swinkles and thermodynamic model of El- Awady et al.

(Ayawei, Ebelegi, & Wankasi, 2017), (Nethaji, Sivasamy, & Mandal, 2013) & (El-Rehim, Ibrahim, & Khaled, 1999).

Towards establishment of the adsorption isotherm prevalent in case of Neem extract as the green corrosion inhibitor, the results of linear polarization resistance studies under taken at 0 to 1600ppm [0-1.6ml/L] aqueous solution of the inhibitor in 3.5% NaCl carried out at 27ºC [300 K], 50 ºC[323 K], 70 ºC[343 K] have been interpreted as follows.

In obtaining the adsorption isotherm, degree of surface coverage[ϴ] for various concentration of inhibitor have been calculated for a given concentration (C) using

$$\Theta = [1- i_p/i_a] \text{ ------------- } (6.5)$$

Where, i_a - Current density in the absence of inhibitor and

i_p - Current density in the presence of inhibitor

The trends of C/ϴ values when plotted against C for each of the test temperature can indicate the adsorption isotherm followed in the corrosion inhibition of a given green corrosion inhibitor. The values and the plot in respect of the Neem extract are shown in Table 6-6 and Fig. 6.19 respectively. From the figure showing a linear relationship between C/ϴ & C, it can be inferred that Neem extract obeys Langmuir adsorption isotherm at all the temperatures at which tests have been carried out.

The response can be represented as

$$C/\Theta = 1/K_{ads} + C \text{ ……… } (6.6)$$

Where, K_{ads} is the equilibrium constant of the adsorption-desorption process

The values of the K_{ads} for the Neem extract are indicated in Table 6-6.

As per the Langmuir's adsorption isotherm assumption that each site of the metal surface holds one adsorbed species the apparent free energy of adsorption for replacement of 1 H_2O molecule with that of the organic inhibitor molecule is calculated as follows (El–Maksoud, 2008)

$$\Delta G^o_{ads} = -2.303RTLog\ 55.K_{ads} \text{-----} \ (6.7)$$

Where, T is temperature in Kelvin

The enthalpy of adsorption i.e ΔH^o_{ads} is further computed using the rearranged Gibbs Helmholtz equation,

$$\Delta G^o_{ads}/T = \Delta H^o_{ads}/T + K_{ads} \text{-------} \ (6.8)$$

The entropy of adsorption (ΔS^o_{ads}) can then be calculated using,

$$\Delta S^o_{ads} = (\Delta H^o_{ads} - \Delta G^o_{ads})/T \text{-------} \ (6.9)$$

The computed values of ΔG^o_{ads}, ΔH^o_{ads}, ΔS^o_{ads} for the Neem extract are shown in Table 6-6

6.7.1 MECHANISM OF INHIBITOR ADSORPTION

The inhibitor mechanism can be well understood only if the mode of adsorption of inhibitor molecule namely molecular or ionic is established. The predominant adsorption mode depends on the composition of the extract, type of the anion and the chemical changes to the extract. The negative surface energy favors the adsorption of cations where as positive surface energy promotes the adsorption of anions. The apparent activation energies (E^*_a) for the corrosion process involving the carbon steel coupon in aqueous 3.5 % NaCl solution with and without the presence of 1600ppm as corrosion inhibitor has been evaluated using the Arrhenius equation as follows.

$$Log\ C_R = log\ A – [E^*_a/2.303RT] \text{----} \ (6.10)$$

Where C_R is corrosion rate in $g.cm^{-2}.min^{-1}$, R is the universal gas constant and T is temperature in Kelvin.

The calculated E^*_a values from the high temperature linear polarization tests for the Neem extract are shown in Table 6-7. A plot of Log C_R with respect to 1/T is shown in Fig. 6.20.

Table 6-6: Thermodynamic functions for adsorption of emulsified Neem oil Extract in 3.5 % NaCl aqueous medium at different temperatures

Concentration (ml/L)	Temperature K	K_{ads}	ΔG_{ads} kJ.mol^{-1}	ΔH_{ads} kJ.mol^{-1}	ΔS_{ads} kJ.mol^{-1}K^{-1}
0.6	300	0.585586	-8.68447	-8.86015	-0.58559
	323	0.443038	-8.60103	-8.74413	-0.44304
	343	0.31746	-8.18295	-8.29184	-0.31746
1.2	300	0.603448	-8.75943	-8.94047	-0.60345
	323	0.429293	-8.51638	-8.65504	-0.42929
	343	0.292793	-7.95224	-8.05267	-0.29279
1.6	300	0.863095	-9.65218	-9.91111	-0.8631
	323	0.532407	-9.09458	-9.26654	-0.53241
	343	0.416667	-8.95857	-9.10148	-0.41667

Table 6-7: Activation energies for adsorption of Neem extract on steel in emulsified aqueous 3.5 % NaCl solutions

Extract	**Conc./ml/L**	**E_a (kJ. mol^{-1})**
Aqueous 3.5 % NaCl medium	-	28.98
Neem Oil Extract	0.6	32.06
	1.2	34.63
	1.6	38.77

6.7.2 RESULTS & DISCUSSIONS

From the electrochemical studies conducted on various concentrations of the potential green corrosion inhibitors both at room temperature and at varying temperatures the following are inferred:

1. The potential–time response of the green corrosion inhibitors in their emulsified form are seen to exhibit a shift towards noble or active direction at their optimized dosage rates.
2. From the Electrochemical Impedance Studies carried out on all the three extracts at their optimized dosage rates, it is seen that the computed film passivation resistance in general increases with the addition of inhibitor. Also, the Neem extract is seen to provide the highest passivation film resistance among the potential green corrosion inhibitors studied.

The Tafel response of all the inhibitors indicate that the E_{corr} values representing the equilibrium corrosion potential of the steel coupon in the aqueous micro emulsion of the inhibitor shifts more anodic values with the increase in concentration. This aspect signifies the potential for all the inhibitors to form more stable films with the increase in concentration.

The corrosion current (I_{corr}) values for all the potential green corrosion inhibitors have been plotted against the inhibitor concentration and the trends are shown in Fig.6.21. The trend clearly indicates that the corrosion current decreases in general with the increase in concentration. However, the rate of decrease in corrosion current falls sharply at concentrations above the optimum concentration as established by the spindle test reported in Chapter 4.

3. Equivalent concentration of Neem and Karenjia oil as inhibitors exhibit corrosion current much less than that of Jatropha.
4. The corrosion inhibition efficiency for all the inhibitors has been plotted against the inhibitor concentration and the trends are shown in Fig.6.22. The trend clearly indicates that the inhibition efficiency increases in general with the increase in concentration. However, Inhibitor efficiency saturates at

concentrations above the optimum concentration as established through spindle test reported in Chapter 4.

5. The Neem and Karenjia oil as inhibitors exhibit higher inhibitor efficiency of around 60% as compared to around 50% of that of Jatropha oil using electrochemical method of evaluation of green corrosion inhibitors.
6. The effect of temperature on the performance of Jatropha oil has been studied. The corrosion current is seen to increase with the increase in temperature as shown in Fig.6.23. This is attributable to the thermal activation of the electrochemical process in which the mobility of the ions in general increases causing the instability of the inhibitor film and its passivation. In line with this, the inhibition efficiency is also seen to decrease with the increase in temperature as shown in Fig.6.24. Similar trend in corrosion current and the inhibitor efficiency is observed in case of Neem extract for varying temperature and dosage rates as shown in Fig. 6.25 and Fig. 6.26 respectively.
7. The studies on adsorption isotherm for Neem extract as a corrosion inhibitor indicate a linear relationship of C/Θ values with C values for each of the test temperatures. It is therefore, inferred that Neem extract obeys Langmuir adsorption isotherm at all the temperatures at which tests have been carried out.

   The thermodynamic properties of the adsorption process of Neem extract as corrosion inhibitor have been calculated for the various temperatures at which tests have been conducted. A negative value of ΔG^{o}_{ads} indicates a spontaneous adsorption, strong interaction between the inhibitor molecules and the metal surface. Generally, values of ΔG^{o}_{ads} upto -20kJ/mol are consistent with electrostatic interactions between charged molecules and charged metal surface indicating physical adsorption. A very small value of K_{ads} further confirms that the inhibitor molecules are physically adsorbed on the steel surface.

An exothermic process (negative ΔH^{o}_{ads}) indicates adsorption to be physisorption or chemisorption while in an endothermic process (positive ΔH^{o}_{ads})

the adsorption is necessarily chemisorption. In case of Neem extract, the negative values of ΔH^o_{ads} clearly supports the physical adsorption phenomenon and further supports the observations made from ΔG^o_{ads} and K_{ads}. Negative values of ΔS^o_{ads} further implies that the rate determining step in the corrosion inhibition step involves association rather than dissociation step reducing the disorder in the system as the metal tends to corrode to form activated complex.

8. To further elucidate the mechanism of physical adsorption of Neem extract on steel coupon and its ionic or molecular mode, apparent activation energies (E^*_a) for the corrosion process have been estimated and studied with respect to temperature. The values are indicated in Table 6-7. The increased apparent activation energy values (E^*_a) of the inhibited solution (1600ppm of Neem extract) with respect to the uninhibited solution at a given concentration indicates the stability of the physically adsorbed inhibitor film on the metal surface.

The potential green corrosion inhibitors derive their inhibitive characteristics from the ability of their molecules to adsorb with a polar group acting as the nodal centre for adsorption process. The adsorbed film provides a barrier between the metal and the corrodent. The efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers. The resultant inhibitive properties are a reflection of their performance under static and dynamic flow conditions encountered in pipeline applications.

Chapter 7: CONCLUSIONS AND FUTURE RESEARCH

7.1 CONCLUSION & SUMMARY OF WORK

In the present work for internal corrosion protection in hydrocarbon pipelines, various plant extracts like seeds of Neem, Jatropha, Karanjia were made available using extraction process and evaluated as green corrosion inhibitors. The extracts from seeds of Jatropha and, Karanjia and Neem were obtained through green route by cold crushing and hexane refluxing at 65-70ºC with periodic monitoring by Thin Layer Chromatography for their purity, followed by distillation of hexane using Rota evaporator. Commercial extracts of Hibiscus and Eucalyptus have been considered which are claimed to have been extracted by the cold crushing process. The limited studies on extracts of Hibiscus flowers and Eucalyptus leaves were also undertaken. However, extensive performance evaluation of extract of seeds of Neem, Jatropha and Karanjia has been carried out.

The Characterization for understanding their molecular structure the Infrared spectroscopy, Nuclear Magnetic Resonance Spectroscopy and Raman spectroscopy was used. Evaluation of performance characterization studies through steady state electrochemical techniques and detailed performance evaluation studies in rotating spindle test, static immersion test and rotating wheel tests have been carried out. This work culminated not only in bringing out the performance potential of the chosen green corrosion inhibitors but also in optimizing their dosage rates. The following enumerates the overall findings of the study:

The extracts were characterized in the laboratory for their physical properties and chemical composition using IR, NMR and Raman microscope. The extracts are denser than the hydrocarbon products. The viscosity indicates that the diluted solutions of the extracts are pumpable into pipeline transportation systems. The Neem and Karenjia extracts are slightly less acidic than the Jatropha extract. The extracts are deciphered as triglycerides of fatty acids with average acid chain of 17.5-18. Jatropha extracts consists of majorly oleic acid (unsaturated) with other saturated acids in small quantities. Karenjia and Neem extracts were seen to have more saturated acids. Karenjia extract is seen to have significant poly unsaturated linoleic acids along with phenolic and naphthenic components

The IR spectra showed a sharp band at ~ 3000 cm^{-1} indicating the presence of olefinic C-H mainly due to the presence of oleate moieties in all the samples. From the Raman microscope, presence of unsaturation in long hydrocarbon chain (1655cm-1) and weak signal for ester (1740cm-1) could be inferred in all the samples. The Karenjia extract shows the presence of aromatics which are not seen in Jatropha and Neem extract. The oleate ester moieties can help in the formation of thin films on the metal surface as polar compounds. In addition to the carbonyl group C=O, presence of free fatty acids especially the saturated type and the aromatic compounds can enable the film-formation by reacting with metal surfaces.

The potential green corrosion inhibitors derive their inhibitive characteristics from the ability of their molecules to adsorb with a polar group acting as the nodal center for adsorption process. The adsorbed film provides a barrier between the metal and the corrodents. The efficiency of inhibition depends on the mechanical, structural and chemical characteristics of the adsorption layers. The resultant inhibitive properties are a reflection of their performance under static and dynamic flow conditions encountered in pipeline applications.

Rotating spindle tests, static test and rotary wheel test have been conducted on various dosages of the candidate GCI extracts in a highly corrosive ATF medium. Through these studies not only the optimum dosage rates but also the effect of synergistic / antagonistic effects of antioxidants and surfactants as well as the effect of dosage rates on corrosion rates and inhibition efficiency have been established. Through the spindle tests on a ‘E’ rated ATF, it is inferred that the Hibiscus and Eucalyptus compositions are seen to possess limited corrosion inhibition potential and they don’t meet the minimum specified inhibition rating of B^{++} as required by the oil industry even at a very high dosage rate of 8000ppm which is also impractical. The Neem, Karenjia and Jatropha compositions are seen to possess excellent corrosion inhibition potential with optimum dosages of 1600ppm, 1400ppm and 1200ppm respectively to meet the minimum specified inhibition rating of B^{++}.

In addition, the phenolic and amine based antioxidants are seen to supplement the corrosion inhibition tendency of Neem as green corrosion inhibitor to a limited extent while a commercial poly ethylene glycol based surfactant has a synergistic effect on the performance of all the three green corrosion inhibitors. The surfactant is seen to have a pronounced effect on the performance of Neem, in comparison to that of Karenjia and Jatropha. A 50ppm addition of surfactant is required to reduce the optimum dosage level of Neem for its performance by 200ppm whereas for the same reduction of optimum dosage level, an addition of 200ppm and 100ppm of surfactant is required for Jatropha and Karenjia respectively.

From the static test, it is clearly inferred that the corrosion does not occur in neat hydrocarbon solutions and presence of aqueous phase or moisture is mandatory. The long term rotating wheel test simulating the pipeline’s turbulent and dynamic flow conditions conducted with various volumes and concentration of brine solution. This indicates a reduction in corrosion rate of carbon steel by more than one order of magnitude through the usage of optimum dosages of all the three green corrosion inhibitors. All the three green corrosion inhibitors demonstrated a percentage inhibition efficiency of more than 90% at their optimum dosage rates. However, the Neem and Karenjia extracts clearly show an efficiency of more than 95% as compared to that of Jatropha. With the increase in concentration of the brine solution, in general the corrosion rates are seen to increase with a decrease in inhibition efficiency. However, the Neem extract still shows a better performance as compared to Karenjia and Jatropha even at increased concentration of brine solution.

The physiochemical parameters of kerosene, gasoline or diesel fuels commonly transported through pipelines are seen to be identical with that of the undoped base fuels when doped with the optimized dosages of 1200ppm of Jatropha, 1400ppm of Karenjia and 1600ppm of Neem. It is inferred that the extracts are compatible with the fuels enabling their industrial utilization as green corrosion inhibitors

In order to have a conductive aqueous medium with dispersed organic inhibitor to facilitate electrochemical evaluation, micro emulsions with a commercial polyethylene glycol based surfactant were made. The content of surfactant has been optimized to achieve stable emulsions. For the purpose of electrochemical studies, an aqueous solution 3.5wt.% of NaCl has been used throughout this study. The potential–time, response of green corrosion, in their emulsified form demonstrated a shift towards noble or active direction at their optimized dosage rates, thus indicating a passivation tendency. From the electrochemical impedance studies carried out on all the three extracts at their optimized dosage rates, it is seen that the computed film passivation resistance in general increases with the addition of inhibitor. Also, the Neem extract is seen to provide the highest passivation film resistance among the three potential green corrosion inhibitors considered in this study.

At the room temperature linear polarization resistance studies, Tafel responses have been evaluated in respect of the three potential green corrosion inhibitors. The Tafel response of all corrosion inhibitors, indicate that E_{corr} values representing the equilibrium corrosion potential of steel coupon in the aqueous micro emulsion of the inhibitor, shifts towards more anodic values with the increase in concentration. This aspect signifies the potential of all the inhibitors to form more stable films with the increase in concentration. The corrosion current (I_{corr}) trend, for all the potential green corrosion inhibitors have been studied with respect to their concentration. The corrosion current is seen to decreases in general with the increase in concentration. However, the rate of decrease in corrosion current decreases drastically at concentrations above the optimum concentration as established by the spindle tests. The equivalent concentration of Neem and Karenjia oil as inhibitors exhibits corrosion current much lesser compared to Jatropha.

The corrosion inhibition efficiency for all the inhibitors has been studied with respect to the inhibitor concentration. The inhibition efficiency increases in general with the increase in concentration. However, inhibitor efficiency saturates at concentrations above the optimum concentration as established through spindle tests. The Neem and Karenjia oil as inhibitors exhibit higher inhibitor efficiency of around 60% as compared to around 50% of that of Jatropha oil using electrochemical method. The electrochemical method is more of qualitative type than quantitative type. Hence absolute value of efficiency doesn’t matter. However, electrochemical studies indicate substantial potential of these GCIs.

The effect of temperature on the performance of extracts of Jatropha and Neem, has been studied. The corrosion current is seen to increase with the increase in temperature which can be attributed to the thermal activation of the electrochemical process, where mobility of ions in general increases, causing the instability of the inhibitor film and its passivation. In line with the same, the inhibition efficiency is also decreases for both Jatropha and Neem extracts with the increase in temperature. From the performance evaluation and electrochemical studies, it is inferred that among the three candidate green corrosion inhibitors studied, Neem extract offers better corrosion inhibition potential as compared to that of Karenjia and Jatropha.

Further, the Neem extract at 1600ppm of dosage rate has been studied for its adsorption characteristics as well as the thermodynamic properties of adsorption to understand the mechanism of corrosion inhibition. The Neem extract is seen to obey Langmuir adsorption isotherm at all the temperatures at which tests have been carried out. The thermodynamic properties of the adsorption process of Neem extract as corrosion inhibitor have been calculated for the various temperatures at which tests have been conducted. A negative value of ΔG^{o}_{ads} indicates a spontaneous adsorption, strong interaction between the inhibitor molecules and the metal surface. Generally, values of ΔG^{o}_{ads} upto -20kJ/mol are consistent with electrostatic interactions between charged molecules and charged metal surface indicating physical adsorption. A very small value of K_{ads} obtained in case of the Neem extract further confirms that the inhibitor molecules are physically adsorbed on the steel surface. In addition, negative values of ΔH^{o}_{ads} clearly support the physical adsorption phenomenon confirming the observations made from ΔG^{o}_{ads} and K_{ads}. Negative values of ΔS^{o}_{ads} further implies that the rate of determining step in the corrosion inhibition involves association rather than dissociation step reducing the disorder in the system as the metal tends to corrode to form activated complex.

In order to further elucidate the mechanism of physical adsorption of Neem extract on steel coupon and its ionic or molecular mode, apparent activation energies (E^{*}_{a}) for the corrosion process have been estimated and studied with respect to temperature. The increased apparent activation energy values (E^{*}_{a}) of the inhibited solution (1600ppm of Neem extract) with respect to the uninhibited solution at a given concentration indicates the stability of the physically adsorbed inhibitor film on the metal surface. The cost of the chemical based corrosion inhibitors presently used in the industry is the range of Rs 175-200 per kg. Extract produced for laboratory scale testing of green corrosion inhibitors has been assessed for cost impact. The cost of Neem seeds obtained various between Rs. 30- 40 per kg. Drying and crushing per kg costed around Rs. 3-4 per kg. Extract of Neem was prepared from the dried sample and with a yield of around 70-80%. Almost similar rates for Karenjia and Jatropha seeds. Hence, the lab scale cost worked out roughly to be Rs 60 per kg. This production cost can be substantially optimized with larger volumes produced with an industrial scale set up. Further reduction of costs can be done by optimizing the dosages of surfactants to increase the performance of the corrosion inhibitor, at lower dosage rate to the feed. Furthermore, the consequential costs on account of their effect in downstream processing units in terms of equipment fouling, corrosion failures and imminent shutdown & environmental benefits of a green corrosion inhibitor makes it more lucrative option than commercially available corrosion inhibitors.

Corrosion Inhibition efficiency and film persistence and stability without hindering the intended physical and chemical properties of the hydrocarbon fuel.

7.2 FUTURE RESEARCH

1. There is great potential of further research in this field. The future research can be under taken by synthesis of other easily available natural plant produce for development as corrosion inhibitors for LPG Pipelines, Gas pipelines and crude oil pipelines etc.

2. Further the identified green corrosion inhibitors namely Neem, Jatropha and Karenjia has potential for commercial scale development, which would be cost effective and environment friendly. The bulk preparation of these materials for large scale testing and exploitation would be a key challenging area for further research. Therefore, large scale commercial exploitation of these identified corrosion inhibitor can be undertaken for economy of scale.

3. The phenolic based and amine based antioxidant as additives to enhance the efficacies of the base green corrosion inhibitors may be an active area of research. Further research work can be undertaken for optimization of the doses of identified corrosion inhibitors as well as other naturally occurring substances.

7.3 BRIEF BIO DATA OF AUTHOR

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Working as Executive Director (Operations) Indian Oil Corporation Limited Pipelines head Office, NOIDA

A Mechanical Engineer joined Indian Oil Corporation in December 1981 as Graduate Engineer Trainee (GET). Handled various assignment in O&M of cross country crude oil, Petroleum Product and Gas Pipeline, project design, Technical services, Project Execution, Contracting Budgeting and Monitoring in different locations, regions etc. Over 37 years of experience in the field of Oil & Gas Pipelines.

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Publications

(1) Paper presented in Pipeline Technology Conference in Berlin in 2015 on Transportation of Crude oil through Heated Pipelines.

(2) Published paper in World Pipelines published from UK December 2016 issue on the development of Stress Corrosion Cracks in Crude Oil Pipeline.

(3) Published paper in NACE Conference CORCON 2018 on 3rd Oct 2018 on Integrity validation revealed Severe Internal Corrosion on a crude oil Jetty –Non piggable Pipeline.

(4) Published Paper case study: Failure analysis of crude oil pipeline rupture, International Research Journal of Engineering and Technology (IRJET) e-ISSN: 2395-0056

(5) Article on Risk Management model of Pipelines published in in-house M&I journal June 2016.

(6) Published: Development of an internal corrosion management plan for a gas pipeline containing black powder in International Journal Of Research And Analytical Reviews, E-ISSN 2348-1269, P- ISSN 2349-5138

(7) Under Publication: Development of an internal corrosion & erosion risk model for an onshore-offshore crude oil pipeline in Development of An Internal Corrosion & Erosion Risk Model For An Onshore-Offshore Crude Oil Pipeline

Technical Report reviewed and edited

1. Study of Pipeline Structural Integrity and Effect of Pressure Cycling. A Case study of various failures in cross country crude oil Pipeline. The draft report was prepared by "Quest Integrity" USA
2. Technical review and editing the Report on in-service failure of cross country Crude Oil Pipeline in Eastern India, due to stress corrosion cracking
3. Technical review of report on Crude Oil in service Pipeline failure due to AC induced Corrosion through HT power Lines crossings of Pipelines
4. Technical review of the report of Direct Assessment of cross country R-LNG Pipeline
5. Providing assistance for comprehensive Centralized Pipeline Integrity Management System of Pipelines. The first Phase implemented

As a Chairman 19th National Corrosion Conference on Corrosion Control organized by National Corrosion Council of India {A body of Central Electro Chemical Research Institute (CECRI), Karaikudi} with asso**ciation of Indian Oil Corporation Limited and Organized "19th National Conference on Corrosion control" at Bhubneshwar, India from** 5-7th December 2018, on the subject of Corrosion in various Industry like Oil & Gas, Building, Automobiles, Shipping, Construction, Aerospace , Concrete , railways etc. Around 40 Technical papers were presented. Nearly 450 delegates attended 3 days conference. The Conference was Inaugurated by Hon Minster for Petroleum and Natural Gas. (www.nccikkdi.in)

I have attended conferences as Session Chairman and speakers in NACE Conference and other conferences including ENVIRO 2017(Organized by Federation of Indian Petroleum Industries). I have attended World Petroleum Congress 2017 at Istanbul Turkey (WPC 2017) in July 2017 as Session Chairman/ Vice Chairman in F09 Track: Oil & Gas Storage and Transportation. I have attended CERA Week Houston as speaker on Renewable Energy in Indian Scenario, during panel discussion.

0n 19th Feb 2019, participated expert Panel Discussion on the occasion of Release of India Specific Corrosion Impact Study report prepared and released by NACE in presence of Industry Experts and Government Officials.

Member

Technical Committee in Pipeline Technology Conference Berlin

- Technical committee Bahrain Pipeline technology Conference
- Member NACE
- Member Pipeline Operators Forum (POF) (Europe). Attended Pipeline Operators Forum meeting at France during October 2018 for review of latest In-line Inspection specifications. Presentation made on the ILI observations, limitations and recent failures of the pipelines.
- Paper selection committee member cum Vice chair for World Petroleum Congress 2017
- Technical advisory Committee Pipeline Technology Conference, Berlin 2016 onwards
- Member selection committee and Session Chair for Quality Governance Track for ASME Conference being held at New Delhi in April 2019
- Member Innovation Council of Indian Oil, R&D Centre

Experience:

(1) Mechanical Design of Pipeline project and station facilities
(2) Execution of cross country Pipeline project
(3) Operation and Maintenance of cross country Pipelines
(4) Corrosion Monitoring and Integrity Management of Pipelines
(5) Maintenance and Inspection of station rotary equipment's like Heavy duty engines, pumps, compressors , DG sets , tank farms and Offshore terminals etc
(6) Maintenance and Inspection of Offshore Terminal (SPM Systems) and shore Crude Oil Tank farms.
(7) upply Chain Management of petroleum
(8) Energy Optimization in the Pipeline transportation and bench marking

Presently working as **Executive Director (Operations), Indian Oil Corporation, Pipelines Head Office NOIDA**, Managing the Operation & maintenance of more than 14000 Kms of the pipelines consisting of 29 number of cross country Pipelines of Crude oil, Petroleum product including LPG, ATF and Gas Pipeline. The area of interest includes corrosion, monitoring of On-shore and Offshore pipeline. Study of predictive techniques for tank bottom condition of crude oil tanks

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Response to Evaluator's Comment

Response of the evaluators has been incorporated in the thesis. However, response of few questions are detailed in this section

Question No.9:

Criteria for choosing the dosage rates for the Inhibitors and Why do they vary?

The dosage rates for the various GCI studied have been chosen based on extensive Spindle tests carried out over a range of a few ppm upto 2000ppm (in some cases upto 5000ppm). Based on the spindle test results the optimum range of inhibitor dosage for detailed investigation through other performance evaluation tests as well as Electrochemical tests were designed. A few photographs of spindle test results for the Neem, Jatropha & Karenjia are presented below:

Neem

Karenjia

Jatropha

Question No.10

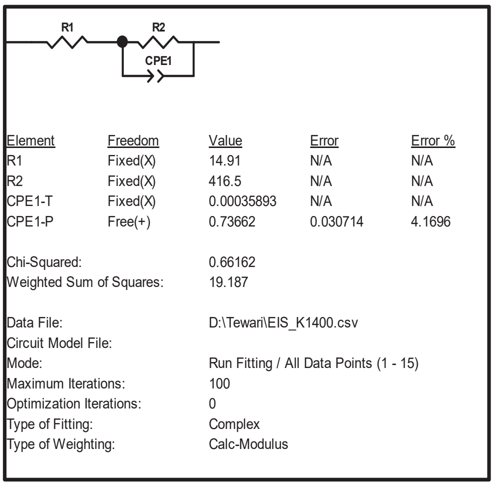
Can the surfactant only act as Inhibitor

The surfactant used in the study (Triton X- a polyethylene glycol based formulation) has a Hydroxyl group as a polar end with Glucose moieties. Being polar, it may act as a film against corrosion. However, its ability to act as inhibitor will depend on its ability to form a strength and stable film on the anodic metal surfaces.

Question No.11

- ✓ **How were the resistances in the Table 6.1 computed?**

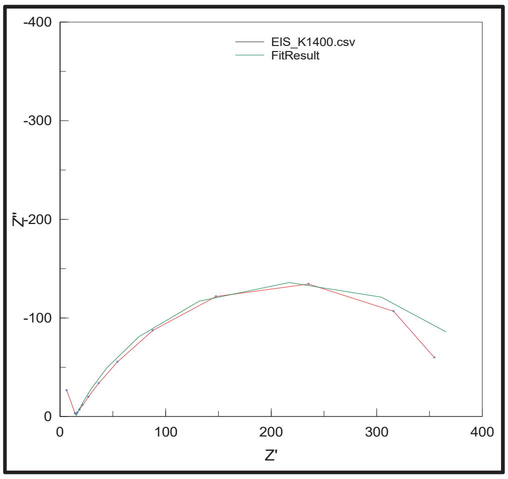
  The resistances were determined from the EIS plots. **R$_s$** and **R$_p$** were determined directly from the Potentiostat-Galvanostat for chosen equivalent circuits and by curve fitting method of the EIS plots. The software of the facility optimizes the resistance values through best fit.



```
Element        Freedom      Value          Error       Error %
R1             Fixed(X)     14.91          N/A         N/A
R2             Fixed(X)     416.5          N/A         N/A
CPE1-T         Fixed(X)     0.00035893     N/A         N/A
CPE1-P         Free(+)      0.73662        0.030714    4.1696

Chi-Squared:                0.66162
Weighted Sum of Squares:    19.187

Data File:                  D:\Tewari\EIS_K1400.csv
Circuit Model File:
Mode:                       Run Fitting / All Data Points (1 - 15)
Maximum Iterations:         100
Optimization Iterations:    0
Type of Fitting:            Complex
Type of Weighting:          Calc-Modulus
```



A typical screen output of the facility is shown wherein R1 represents **R$_s$** and R2 represents **R$_p$**.

✓ **What is the explanation for rapid changes in solution resistance?**

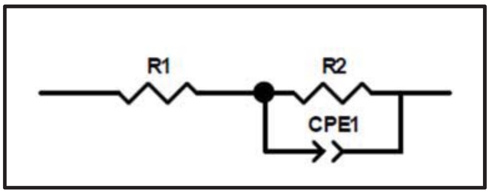
The solution resistance **R_s** depends upon the diffusion coefficient of the solute molecules in presence of surfactants within the aqueous solution. This is directly dependant on the viscosity of GCI. From **Table 4.2**, the Neem is seen to have the highest viscosity among other chosen GCIs for the study. These can be confirmed from the Stokes-Einstein Equation:

$$\boldsymbol{D = \frac{kT}{Br\eta}}$$

D = Diffusion Coefficient
η = Coefficient of viscosity

✓ **What model of the equivalent circuits does the impedance plots of your system fit?**

The equivalent circuit that best fits the system wherein the polar ends of the organic inhibitor molecules diffuse to reach the anodic surface with electron charge transfer has been considered and depicted as follows:



Where R1 is **R_s** (Solution resistance) and R2 is **R_p** (Polarization resistance). Here a Constant Phase Element **(CPE1)** has been considered as against pure capacitance in view of the electrical double layer formation as well as the non impervious nature of the inhibitor film. CPE here represents the double layer capacitance at the interface.

✓ **The Impedance loops of the Nyquist plots are marked with arrows but no explanation was given.**

The plots **shown have been directly obtained from the Potentiostat-Galvanostat.** The arrows are automatically depicted by the system in indicate the data points selected for fitting the curves..

✓ **In Fig.6.9 (Jatropha Extract) and Fig.6.10 (Karenjia Extract) the curves in both cases shifted towards negative and positive potentials with increase in concentration, so what type of inhibitor type can they be classified as?**

The shift in potential with the inhibitor concentrations indicate the film forming ability as well as the stability of the film formed on the anode surface. In case of Jatropha, it can be inferred that the stability of the film is lost with the increase in concentration. Whereas in case of Karenjia, a stable film forms only on addition of a threshold level of inhibitor concentration. From this, it is inferred that the GCI in general behave as mixed type of inhibitors.

- ✓ **Fig. 6.11 (Neem Extract) there was a consistent shift of the curves to the more positive potential and steady decrease in anodic current density with an increase in the concentrations up to the highest tested concentration (1800 ppm), so why is the green curve chosen as the optimized concentration?**

  The electrochemical tests are conducted under static conditions only. Whereas, the optimized concentrations indicated in this work are only based on the Spindle test (NACE TM0172) which closely simulates the dynamic flow conditions that exist in field pipelines.

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PLAGIARISM CERTIFICATE

1. We **Dr R. P. Badoni** (Internal Guide), **Dr Kanan Chandrasekaran** (Co-Guide / External Guide) certify that the Thesis titled "**Development of Green Corrosion inhibitors for protection from internal corrosion of buried cross country pipeline**" submitted by Scholar **Mr Anand Kumar Tewari** having SAP ID **500019845** has been run through a Plagiarism Check Software and the Plagiarism Percentage is reported to be 22 %.

2. Plagiarism Report generated by the Plagiarism Software is attached.

R.P. Badoni

(Dr R. P. Badoni)
Signature of the Internal Guide

(Dr C. Kannan)
signature of External Guide / Co Guide

ATewari

(Anand Kumar Tewari)
Signature of Scholar

15.05.2019

Thesis_Green_Corrosion_Inhibitor

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Reference Identified	Justification
Chapter 1: Introduction	The context uses common terms used across industry/research and in the published papers.
Chapter 2: Literature Review	Some similar context have occurred due to common terms used by the referred literature such as author name, title journal name, year of publication etc.
Chapter-3 Research Methodology	No similar text found
Chapter-4 Extraction and physio-chemical characterization of green corrosion inhibitor	No similar text found
Chapter-5 Performance evaluation of green corrosion inhibitors part one (physical)	No similar text found
Chapter-6 Performance evaluation of green corrosion inhibitors part one (electro-chemical)	No similar text found except for some common terms used across published research and industry
Chapter-7 Conclusion and future research	No similar text found except for some common terms used across published research and industry

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