High Performance Anti-Corrosion Nitrile Butadiene Rubber Lining on Mild Steel Mixed Acid Storage Tanks

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Certificate

This is to certify that work in this thesis has been carried out by **Mr. Asad Mehmood** and completed under my supervision in School of Chemical and Materials Engineering, National University of Sciences and Technology, H-12, Islamabad, Pakistan.

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Submitted through

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National University of Sciences and Technology

Islamabad

Dedication

I would like to dedicate this dissertation to my family for their support to my higher education.

ACKNOWLEDGEMENT

'Behold! In the creation of the skies and the earth and the alternation of night and day there are indeed signs for men of understanding.' [Quran, 2:164]

All the praise for Allah Almighty without whom I couldn't able to achieve my goal. Thank you to the honorable, Dr. Nasir M.Ahamd, as my supervisor, for his trust, encouragement, and valuable instructions throughout the research work. Thanks to Dr. Ahmed Nawaz and Dr Zakir Hussain for helping me in research work. Moreover, thanks to my seniors Mr Abdul Qudeer and Mr Amir Khalid for sharing such valuable knowledge of your research which has guided me in one of the most important phase of my research. My class mate Mr Bashir Ahmad who was a real support during my research at last but most importantly, the position where I am standing wouldn't have been possible without the highest level of care, support, prayers and love of my parents, wife and my siblings. Their prayers have been the ultimate source of encouragement for me.

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Abstract

Corrosion protection has become a multidisciplinary subject, development of new protective techniques and materials with their anticorrosive properties simulating service condition in industries is important to study for their application. In this work effort, has been made to the corrosion protection work by enhancing acid storage tanks service life by making it more corrosion resistance. It is demonstrated that corrosion of mild steel acid storage tank samples was suppressed when we applied lining on them with Nitrile butadiene rubber lining reinforced with carbon black and applied on sampled in hydraulic press machine by compression curing method, while putting them in corrosive environment of dilute and concentrated mixed acid solution and using Electrochemical Impedance Spectroscopy (EIS) for testing of lining stability. EIS shows that these lining were showing good capacitance and high impedance values compare to bare metal sample by proving to be an excellent barrier for charge transport, while Tafel scan results further confirmed that corrosion rate was significantly decreased on rubber lining sample. SEM investigation reveals that lining surface was gradually degraded due to corrosion reaction while corrosion product was developed. These results can prove to be very vital for acid industries facing corrosion issues and in future work different set of composition of lining can be tested in various environments for better comparative study.

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List of Abbreviations:

SBR	Styrene Butadiene
NBR	Acrylonitrile Butadiene Rubber
PBN	N-Phenyl-2-naphtylamine
DOP	Dioctyl Phthalates
MEK	Methyl Ethyl Ketone
E_{oc}	Open Circuit Voltage
EIS	Electrochemical Impedance Spectroscopy
E_{corr}	Corrosion Potential
I_{corr}	Corrosion Current
R_u	Uncompensated Solution Resistance
R_{coat}	Coating Resistance
R_{pore}	Pore Resistance
C_c	Coating Capacitance
R_p	Polarization Resistance
CR	Corrosion Rate
Mpy	Mils per year
R_{sol}	Solution Resistance
Cdl	Double Layer Capacitance
SEM	Scanning Electron Microscope
FTIR	Fourier Transforms Infrared Spectroscopy

Chapter 1

Introduction

1.1 Motivation:

Corrosion is electrochemical destruction of metal because it contact with different vigorous environment. In Acid storage industry and other industries (oil & gas) corrosion can cause huge damage of materials. A must efforts and resources have constantly been made to improve the service life of material. The economic aspect of corrosion are far greater than most people realized that the Industrial nation is spending 5% of its annual income on corrosion damages which can be pay directly in the form of corrosion, production loss, maintenance cost, contaminant of corrosion in the product, extra material design, time wastage resulted because of corrosion.

The idea of corrosion protection is not new because concerned authorities are constantly putting effort to overcome this issue. Many corrosion protection techniques are used such as, anodic or cathodic protection, inhibitors, modification of design, coating (organic or inorganic) and rubber lining.

Rubber lining and coating are basically act as barrier between the metal surface and electrolyte (environment), to prevent redox reaction and charge transfer. With the advancement of material field new research and techniques are being tested and new innovative ideas are being used to protect against corrosion.

In this work, industrial mixed acid storage tanks sampled was protected against corrosion by development of anticorrosion Nitrile butadiene rubber lining reinforced with carbon black. These rubber lining were applied on acid storage tanks (mild steel) sample and tested in corrosive environment of mixed acid solution (H_2SO_4, HNO_3 and H_2O) to check how much electrochemical stability of these rubber lining are provided in this environment.

1.2 Corrosion:

In worldwide, mild steel is most commonly used material for structure application. But its vulnerability to increase corrosion to increase its maintenance cost. In corrosive environment such as sulfuric acid and nitric acid the surface of mild steel formed a passive layer but it not

strong enough as in case of stainless steel, Such interactions harm the materials effectiveness because deterioration of its structural properties such as physical, mechanical, thermal and Appearance etc. [1]

Figure 1: Mild steel tanks corrode in acid storage industries

These specific properties of material as mentioned above play a vital role in understanding material usefulness when material interaction take place with its environment. Every class of material deterioration takes with different mechanism is followed by its appearance, this deterioration phenomena of metal is known as corrosion.

1.2.1 Electrochemical Aspect of corrosion [2]

The corrosion of materials in an electrochemical process, the metal surface which is exposed in environment and is covered with an oxide film, when they contact with its environment this oxide film tends to dissolved. In case of aggressive solutions such as organic and inorganic acids this oxide film tends to be dissolve very rapidly resulting a bare metal surface which is the active state of metal to react with its environment. In case of neutral solution this oxide film dissolved much lower rate as compare to acidic solution. The metal surfaces which is underlying in acidic solutions initially exposed at localized points in the metal where some discontinuity is present. The presence of grain boundary or inclusion on the metal surface the oxide film may be more prone or thinner to dissolution than elsewhere. In case of neutral solution contains anions of inhibiting this dissolution of oxide film may be stabilized or suppressed to form a passivation oxide film which can be prevented effectively for the corrosion of metal because it is in passive state. When the oxide free surface of a metal which is exposed to the solution, The metal ions which are positively charged tend to pass form the metal into the solution, electrons are leaving behind on the metal. The accumulation of negative charge on the metal surface is due to the

residual electrons which can lead to an increase in the potential difference between the solution and metal surface. This difference of potential is called as the electrode potential or simply to say potential of metal which is more negative.

$$M \rightarrow M^{+} + e^{-}$$

The surface of metal involved reaction which is loss of electron and get corroded by the oxidation reaction on the anode while the cathodic side which gain the electron and formed byproduct such as hydrogen gas, water etc. are depended upon the electrolyte.

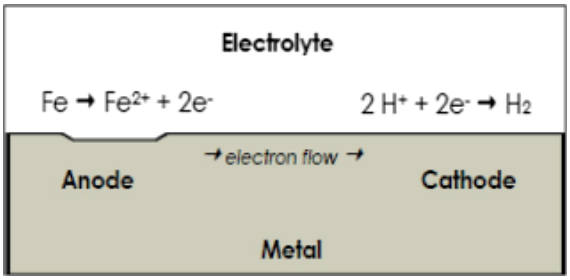


Figure 2: Corrosion phenomena [3]

The diagram shows an electrochemical reaction occurring at the surface of metal which is covered by electrolyte. Two types of reaction are involved in the corrosion, first is metal atoms dissociate into metal ions or free electrons on the anode by the oxidation reaction. These free electrons (metal ions) migrate in the metal and initiate the reduction reaction at the cathode.
Reactions are shown in equation: [4]

Anodic reaction:

$$Fe \rightarrow Fe^{+} + 2e^{-}$$

Cathodic reaction:

$$2H^{+} + 2e^{-} \rightarrow H_2$$

Overall reaction:

$$Fe + 2H^{+} \rightarrow Fe^{2+} + H_2$$

The electrochemical nature of corrosion can be understood by considering a case of zinc (Zn) piece is immersed in dilute hydrochloric acid solution, the reaction that occurs on the surface of metal can be divided into two or more partial reaction of reduction and oxidation is termed electrochemical.

When piece of zinc is immersed in dilute hydrochloric acid a vigorous reaction occurs in zinc dissolves forming a solution of zinc chloride and evolved hydrogen gas.

$$Zn + 2HCl \rightarrow Zncl_2 + H_2$$

Chloride ion is not involved in this reaction. Reaction of zinc with hydrogen can be writen as

$$Zn + 2H^+ \rightarrow Zn^{2+} + H_2$$

So, zinc reacts with H^+ ions in the acid solution and formed zinc ions and hydrogen gas.

For the above reaction equation, it can be observed that during reaction zinc is oxidized to zinc ions and hydrogen is reduced to hydrogen. So we can divide the above corrosion reaction of zinc into two half-cell reactions are shown below.

Oxidation (anodic reaction) $Zn \rightarrow Zn^{2+} + 2e^-$

Reduction (cathodic reaction) $2H^+ + 2e^- \rightarrow H_2$

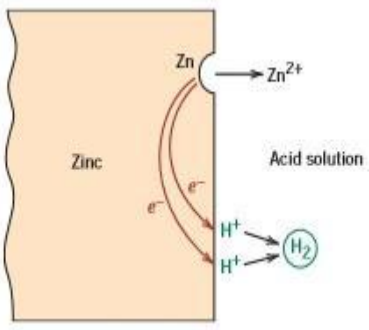


Figure 3: Electrochemical reactions occurring during corrosion [5]

The fundamental principle of corrosion can be explained for the metal is as "**rate of oxidation and reduction reaction are always equal".**

1.3 Polymer rubber lining:

1.3.1Brief introduction of rubber: [6]

In modern society to an indispensable product as steel, wood and mortar is rubber. Two types of rubber is

a. Natural Rubber
b. Synthetics Rubber

All of us use products made of rubber at work, at home, at play, automobile, aircraft industries rely on it for variety of purpose that's why it is truly said that in modern world rubber is omnipotent.

Rubber is an elastic, yellowish, amorphous material obtained from the latex or milky sap like the rubber plants and trees. This latex is pigmented, vulcanized, finished and modified into Varity of products like elastic bonds, tires, electric insulation, gaskets and containers rubber lining.

Today there is not just one product or substance is called rubber, rubber belongs to a class which is made up of a number of different materials that have unique property of their uses.

1.3.2 Type of rubber:

There are different type of rubber in their properties and used.

1.3.3 Natural rubber:

The raw material of natural rubber which actually comes forms trees. Natural rubber can produce compound with high tear strength, tensile strength and abrasion resistance.

Figure 4: Grade of rubber (air dried sheet) [7]

Uses:

Natural rubber can be used at lower compression set, low temperature and high resilience. Not used in concentrated acid and alkalis.

1.3.4 Synthetic rubber:

Synthetic rubber is formed through the polymerization of monomers. Production of synthetic rubber starts with the refining process of oil, hydrocarbons with naphtha is one of desired products. The natural gas combined with naphtha to produce monomers. These monomers are

used for the production of butadiene, isoprene, acrylonitrile and propylene [7] .These monomers are polymerized through the process of steam and catalyst to form rubber intermediaries.

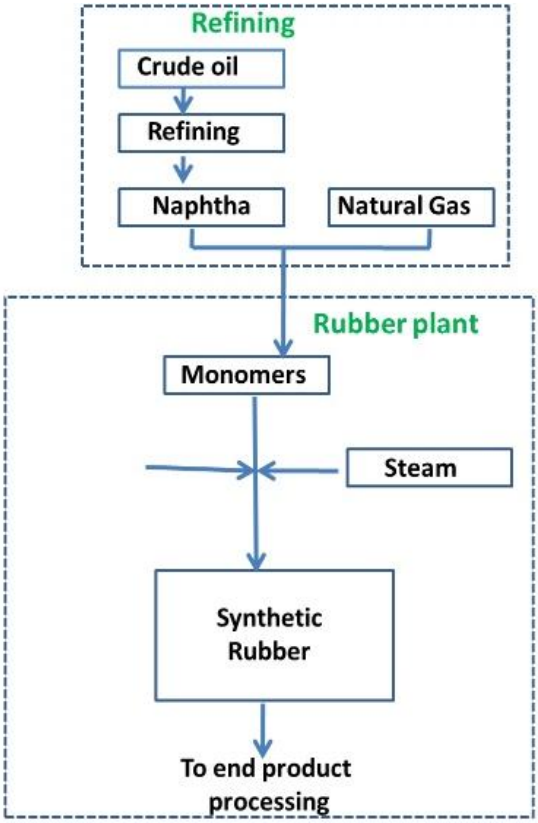


Figure 5: Block diagram of synthetic rubber [7]

1.3.5 Neoprene (chloroprene):

Neoprene rubber is produced synthetically; its properties are closed to natural rubber. [8]

Uses:

Better resistance to oil, solvent, flame and weather.

Not used in concentrated acid and alkalis.

1.3.6 Styrene butadiene (SBR)*:*

Styrene butadiene (SBR) is produced synthetically, which have low cost to substitute for natural rubber. [8]

Uses:

Good water and abrasion resistance.

Not recommended for oil, solvent, acid and alkalis.

1.3.7 Butyl rubber:

Butyl rubber is produced synthetically, have very good resistance to most of gases including air. [8]

Uses:

Good for concentrated acids, alkalis and abrasion resistance.

1.3.8 Nitrile Rubber:

Nitrile rubber also known as acrylonitrile butadiene rubber (NBR) NBR can be synthesized by copolymer of acrylonitrile (ACN) and butadiene.

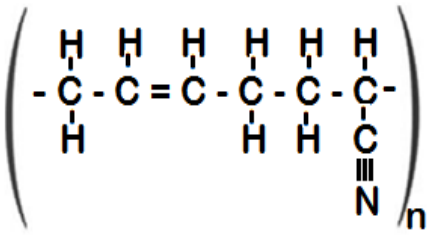


Figure 6: Chemical formula of NBR

The family of (NBR) is unsaturated copolymer of 2-propenenitrle and various butadiene monomers such as 1, 2 butadiene and 1, 3 butadiene. [8]

1.3.8.1 1, 3Butadiene:

From ethyl alcohol:

$$CH_3CH_2OH + CH_3CHO \rightarrow CH_2=CH-CH=CH_2 + H_2O$$

The reaction is carried out in the presence of Silica gel/ Ta_2O_3 act as a catalyst at a temperature of 325^0C and 1atm pressure.

1.3.8.2 Acrylonitrile:

Acrylonitrile is produced by the sohio process that reacts with propylene with ammonia and air in a catalytic reactor.

$$CH_3CH=CH_2 + NH_3 + air \rightarrow CH_2=CHCN$$

The properties of Nitrile rubber is depending on the composition of polymer of nitrile. The amount of acrylonitrile is form 15 to 50 percent present in the final copolymer. To increase the amount of acrylonitrile is content to increase its strength, lower permeability to gases and greater resistance to swelling by hydrocarbon oils. NBR'S have ability to withstand a temperature range from 40 to 180 ^{0}C(40 TO 250 ^{0}F) makes it an ideal material for many applications such as tank lining, gaskets, wire insulation and sealants or other items subject to contact with no oil etc.

Uses:

Good resistance to oil, solvent, concentrated acid and alkalis. Good abrasion resistance and compression set.

1.4 Rubber compounding:

The rubber compounding is a process in which addition of additives into the raw rubber to make a compound of desire properties. The process of compounding is carried out in internal rubber mixer. [9]

1.4.1 Banbury mixer (internal mixer):

Banbury mixer is 2 rotors-counters rotating within a mixer chamber, each has two or four blades which is mixed by smearing the materials against the chamber wall and a weighted ram is placed to keep the mix in place inside the chamber.

Figure 7: Banbury Internal rubber mixers [10]

1.4.2 Forming process (shaping):

After mixing all of its ingredients to form compounded black stock is tacky and thermoplastics, in this stock ,condition of polymer compound can be shaped by the application of force.

This can be accomplished by:

- Calendaring
- Coating
- Extruding
- Molding and casting

1.4.3 Calendaring process:

The process of calendaring, rubber is passed through a three to five roll calendar either to produce a controlled thickness sheet or to force the rubber into close contact with metal cord. Rubber compound is passed through a series of gaps of decreasing size of rotating rolls, the thickness of rubber determined by final roll gap.

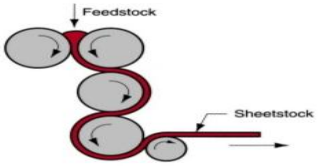


Figure 8: Calendaring followed by roller [11]

1.5 Filler system:

They are composed of two types:

a. Reinforcing filler
b. Semi and non-reinforcing filler

1.5.1 A) Reinforcing filler:

They are typically used as:

- Carbon Black
- Precipitated Silica
- Fumed Silica

1.5.2 B) Semi and non-reinforcing fillers:

These filler are used due to the following factors:

- Reduce Cost
- Increase Hardness
- Improve Processing
- Tensile Strength
- Tear Resistance

1.5.3 Filler:

For many standards NBR compounds, typically carbon black is used. Carbon black is produced during the combustion is controlled to create various sizes of particles which gives reinforcing properties in a rubber compound of varying levels. Higher level of reinforcement of rubber compound required lower particle size (N110, N330) of carbon black which can provide higher physical properties. For use of larger particle size (N990) gives lower physical properties but much better compression set. Typical NBR compound uses N550 and N774 combination of both these. [9]

Figure 9: Carbon black (N-774)

The amount of carbon black can change the hardness or durometer of the final compound. Some non-black fillers such as silica, clay and mica are used for compounds that need to be colored. Each filler has different level of reinforcement and properties like carbon black have different particle sizes and structure.

1.6 Protection system:

They are composed of three types:

- Anti-oxidant
- Anti-ozonants
- Initiators or Promoters

All polymer based product are subject to degradation on exposure to degradative environment such as UV light (weather) ,storage aging, heat, presence of heavy metal ions cased catalytic degradation, fatigue etc. These factors can degrades rubber and rubber products causing substantial changes in the properties lead to the result of failure during service or reduce its service life in the absence of antioxidants.[9] [10]

NBR compound are needed antioxidant to prevent unsaturated polymer backbone degradation caused by high temperature amine and phenolic antioxidants are used in NBR compound which can help scavenge up free radicals that can cause polymer chains to break and increase cross linking and making the compound more harder. Phenols and aryl amine are used as antiozonant which create a barrier to protect the polymer chain like wax. They also can use to gain scavenge free radical. [10]

1.7 Anti-oxidant (PBN):

PBN also known as N-phenyl-2-naphtylamine:

Figure10: N-phenyl-2-naphtylamine (PBN) powders

Chemical structure:

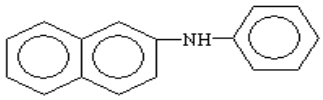


Figure 11: Chemical structure of PBN

It is widely used in all kind of synthetic and natural rubber. It has good preventing performance caused by oxidizing, heat and wind.

1.8 Process aids:

For rubber industries high productivity is very important because it is usual to large variation of raw materials. To improve the production process adds processing aid for flow rate, tackiness, homogeneity. This product range includes homogenizers, chemicals dispersing agent, lubricant, flow promoter and dop oil. [9]

1.9 DOP oil (dioctyl phthalates) (plasticizer):

Plasticizer is used in the mixing of the compound to incorporate all the ingredients in the formulation and also help the processing of the final compound. Physical properties of final compound can be modified and also change the properties such as lower hardness, lower temperature performance changing antistatic and swell tendency and improved flex.

Figure 12: DOP oil

Plasticizer properties are dependent on the polarity of oil, for NBR picking the correct polarity is very important because higher CAN or higher polarity can cause oils to bleed out.

Di (2-ethylhexyl) phthalate (DEHP) or Dioctyl phthalates (DOP) are commonly used in NBR compound, many of the regulations that restrict the use of low molecular weight phthalates because they can be extracted easier and cause reproductive issues. [12]

1.10 Curing system:

They are categorized into three types:

a. Curing Agent
b. Activators
c. Accelerators

Curing agent:

For curing the rubber you the following conditions must be followed:

1) Heat or energy (mostly used thermal energy)

2) Curing agents

- ❖ Sulfur
- ❖ Organic Oxides
- ❖ Metallic Oxides (zinc oxide)

For curing of rubber following two factors are very important:

- ❖ The density of cross linking
- ❖ The nature of cross link

1.10.2 Sulfur curing:

For general purpose or in industries rubber products are used as elemental sulfur for curing agent.

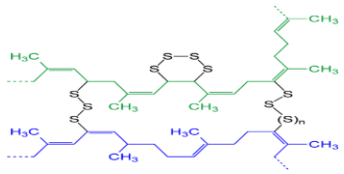


Figure 13: Chemical structure of sulfur curing [13]

Sulfur curing agent is used in combination with one or more accelerators and an activator system such as zinc oxide and stearic acid. An accelerator can determine the rate of curing, whereas the sulfur to the ratio decides the efficiency of curing, and in turn, thermal stability of the resulting curing product.

1.10.3 Curing with peroxide:

Cross linking of elastomer can be carried out by the means of peroxide as well. The same procedure can be adopted in the case of diene and saturated (ethylene-propylene, silicon etc) rubbers. Dicumyl peroxide can perform cross linking of NR, nitrate rubber resulting product which has good cold and aging resistance. By comparison with the sulfur is curing agent and accelerators, peroxide provides a lower reaction rate and resulting product have lower tensile strength. [13]

1.10.4 Zinc oxide:

Zinc oxide can be used in the synthetic and natural rubber compounds as part of the cure system activation. It can also enhance the properties of the vulcanized rubber such as heat aging. For curing of sulfur can consumed too much time and energy for curing that way sulfur along with zinc oxide are used to reduce curing time such as 15-20 minutes. [13]

1.10.5 Rubber Grade Stearic Acid:

It is a tallow- based rubber grade stearic acid can be used as a plasticizer, lubricant, dispersing and activators in rubber compounding. It can also be used as viscosity depressant in PVC processing and external lubricant. [13]

1.11 Adhesive used:

1.11.1 Methyl ethyl ketone (MEK):

MEK act as a solvent and provide more solid content compared to formulation made with lower volatile organic compound solvent. MEK has high solvency power and is compatible with most of rubber compound used as an adhesive. [15]

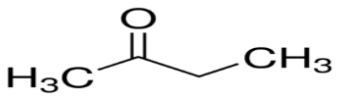


Figure 14: Chemical Structure of MEK [15]

MEK can be used in rubber-based industrial cement as it has fast evaporation make it popular for rubber-based adhesive. In our research work MEK used as an adhesive for metal rubber bonding**.**

1.12 Electrochemical Impedance Spectroscopy:

Electrochemical impedance spectroscopy (EIS) is an AC technique which is used to characterize the constant potential of an electrochemical interface.

A small signal 10 mV AC potential excitation is applied on electrochemical cell. The varied excitation signals are measured as the response of interface and frequency. EIS study is very helpful for coated metal for corrosion resistance, electrochemistry, batteries, and electrode kinetics and industrials electrolysis.

1.12.1 Basic Technique used in EIS:

- Potentiostatic EIS
- Galvanostatic EIS
- Hybrid EIS
- Mott-Schottky Plot

1.12.2 EIS Cell Setup:

Following figure is showing complete setup used to run an EIS test with all the components involved.

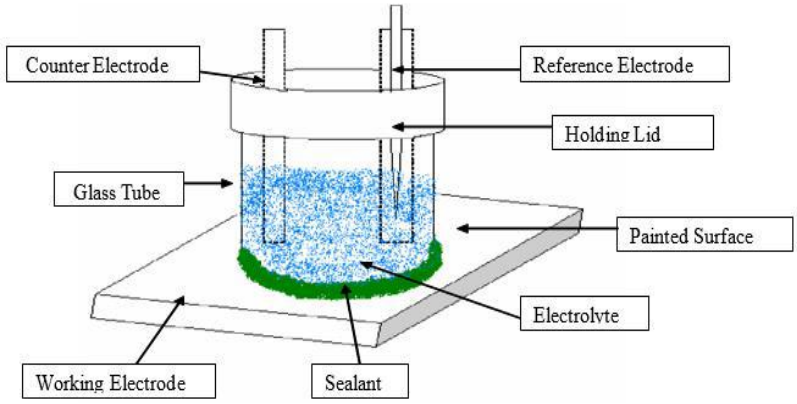


Figure 15: Experimental cell setup of EIS [16]

1.12.3 EIS Data Representation:

The data obtained from EIS experiment comes either in the form of Bode plot in which Impedance magnitude and phase plotted versus frequency or in the form of Nyquist plot in which imaginary impedance plotted versus real impedance.

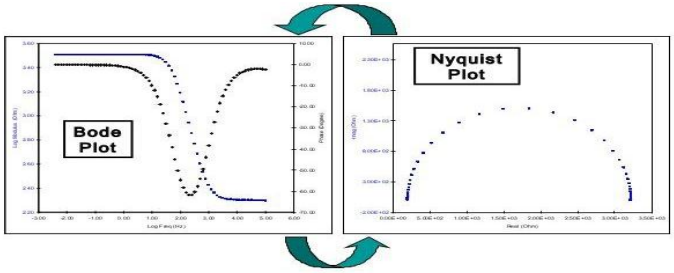


Figure 16: Typical Bode and Nyquist Plot

1.14.4 EIS Output Information:

By analyzing the data obtained and using different fitting model according to the condition or sample used we can get following information from EIS [16]

- Double Layer Capacitance
- Polarization Resistance
- Solution Resistance
- Coating Defect Parameters
- Mechanistic and Kinetic Information

Chapter 2

Literature Review:

In practical world, corrosion had been most important issue. Because it keeps effecting material's life, serviceability, money and time, since the knowing of behavior of corrosion researchers are working to understand its chemistry, reasons of corrosion and ways to protect material from it. Therefor they were studying effect of different environments on material. Protection using electrochemistry and rubber lining or coating, some of their findings and method of investigation is summarized here.

S. Krakowiak, K. Darowicki in 2002 studied bromobutyl rubber lining was performed under field condition and stability lining was determined by the electrochemical impedance spectroscopy (EIS). By the using of brasher-Kingsbury equation to determined moisture contact the results obtained which are compared to the results of destructive tests which are performed in the same location inside the absorber. The capacitance of lining was determined to be the best indication of the condition of the corrosion protection lining. Conformity of both tests was stated, allowing application of EIS and the presented computational procedure in the monitoring of the condition of rubber lining. The results obtained by both these method and the results obtained which can show good agreement of both applied method. [17]

Jui-Ming Yeh, Kung-Chin Chang in 2008 studies the anticorrosion properties of polymer layered silicate (PSL) and their fabrication, characterization and other properties. The measurement of anticorrosion properties of water based and solvent based polymer layered silicates is helpful to find out the gas barrier properties of PSL and structure properties relationship of Nano composite because anticorrosion analysis are strongly influenced by their structure and interfacial characteristics. The Nano composite can be prepared and testing against corrosion protection. The corrosion studies of PSL can be carried out by the measurement of corrosion potential, corrosion current, polarization resistance and impedance spectroscopy. [18]

Stefan Krakowiak∗, Kazimierz Darowicki, Juliusz Orlikowski, Paweł˙Zuchowski in 2014 studies the capacitance of rubber lining which are exposed in the corrosive environment. The rubber lining degradation can be studies in flue gas desulphurization system. The measurement of capacitance of rubber lining in their field condition is good parameter for the assessment of the stability of rubber lining in such condition. The measurement of the stability of rubber lining can be performed Electrochemical Impedance spectroscopy and gravimetric method. The rubber lining degradation can be depending on the corrosive environment allows optimization of protection. [19]

Huang et al. in year 2014 presented a work in which a Nano composite of polyimide/h-boron nitride was synthesized and its anti-corrosive property was reported. Different variation in composition boron nitride in polyamide matrix is made and data was generated where it shows that it is protecting a steel substrate from corrosion. The composite was capable of showing better resistance to water vapor, it was reported that only 5 % h-BN is sufficient in increase the corrosion potential and increase corrosion resistivity.

C.A. Baaha, J.I. Baahb in 2001 studies the 5 different types of rubber specimens and their properties against organic chemical reagent. Immersion test of 5 different type of rubber sampled of Nitrile rubber, neoprene and natural rubber (NR 40, NR 60 and food grade) is immersed in organic reagent of acetaldehyde, acetic anhydride and malic acid for a period of 4 weeks and were examined on weekly basis. After 4 weeks sampled were removed from organic reagent and experiment were performed at room temperature. It was reported that nitrile rubber sample absorbed acetaldehyde and increase its weight and neoprene loss its color in acetaldehyde and acetic anhydride and NR 60 absorbed malic acid. [20]

A. Mostafa *, A. Abouel-Kasem, M.R. Bayoumi, M.G. El-Sebaie in 2009 studies mechanical properties of nitrile butadiene (NBR) and styrene butadiene (SBR) rubber compounds was reinforced with carbon black. It was prepared the 5 different composition of NBR and SBR compounds which was reinforced with carbon black at different level of concentration of carbon black such as 0, 20, 30, 50, and 70 phr and the results are obtained which are compare with the result of without reinforced compounds of carbon black. It was reported that mechanical

properties of both NBR and SBR are enhance compare with without reinforced compounds and swelling behavior was reduce with the increasing of carbon black reinforced and compression set increase in both NBR and SBR reinforced compounds. [21]

Rasha A. Ahmad[123*,] R. A. Farghali[1, 2], A.M. Fekry[1] in 2012 studies the stability and corrosion inhibition of chitosan coating of mild steel alloy in acidic medium. To improve the corrosion protection ability of chitosan coating it was immersed in glutaraldehyde solution for 5 minutes. Chemical cross-linking was confirmed by FTIR spectra of glutaraldehyde and chitosan coating. Electrochemical impedance spectroscopy (EIS) measurement of the stability and resistance of coating to the acidic medium of 0.5M H_2SO_4, Scanning electron microscopy (SEM) and potentiodynamic polarization measurement the coated surface stability and corrosion rate of mild steel of coated and un-coated samples respectively.

The results of EIS show well polarization of chitosan and inhibition efficiency (IE) in 0.5 M H_2SO_4 solution reaches 98.1%.

Chapter 3

Experimental Work:

Sample Preparation:

A mild steel industrial acid storage tank plate was selected as a sample in this research .The importance of this sample is to dip in mix acid for three months to find the corrosion rate by weight loss method and substrate is to provide rubber lining to be placed on and tested against acid solution for corrosion resistance.

3.1.1 Acid storage tanks sheet material: (BS 4360)43A:

43A steel plate with the specification of BS4360 carbon steel plate mainly used various types of steel rivet, steel bolts, steel weld, storage tanks and other structure components.

Table 1: Chemical Composition of mild steel plates

Grade	C	Si	Mn	P	S	Cu
43A	0.25	0.50	1.6	0.05	0.05	0.20 /0.35

Table 2: Mechanical Properties of mild steel Plates

Grade	Thick(mm)	Tensile strength	Minimum yield strength	Minimum elongation
43A	16-40	430-580	265 N/mm^2	22%

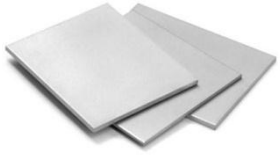


Figure 17: Mild steel tanks plates

Above is the picture of mild steel tanks plates, after which the samples were cut according to the requirement of experiment. The samples were cut by keeping in mind that surface must be sufficient for rubber lining and afterwards that rubber lining sample to be settled easily in EIS cell, by keeping in mind the fact that a container of required electrolyte is to be placed on sample also. So by observing all these fact the samples were made 4x4 $inch^2$ dimension and 1x1 cm^2 dimension. After the preparation of samples the next step was preparation of nitrile rubber lining, the preparation of required rubber composition is discussed below.

3.1.2 Preparation of solution: [23]

Available concentration of H_2SO_4 in lab = 96%

Dilution Formula = $\mathbf{C_1V_1=C_2V_2}$

$\mathbf{C_1}$ = Available concentration in lab

$\mathbf{V_1}$ = Volume will be taken from bottle

$\mathbf{C_2}$ = Required concentration

$\mathbf{V_2}$ = Total volume of prepared solution

$$C_1V_1=C_2V_2$$

$$96*V_1 = 40*200$$

$$V_1 = 83.33 \text{ ml of } H_2SO_4$$

Nitric Acid Concentration in lab = 65%

$$C_1V_1 = C_2V_2$$

$$65*V_1 = 40*200$$

Volume required V_1 = 123.07 ml HNO_3

3.1.3 Sample surface preparation:

Mild steel tank plate's surface which is used for rubber lining is properly cleaned to remove any dust or oily particles from the surface then washed with distilled water and acetone and dried.

Phosphating was done for rubber lining using phosphoric acid (H_2PO_4) 60%weight in distilled water. Sample were treated for 10 to 15 minutes in solution then rinsed in deionized water and dried.

3.2 Nitrile rubber lining:

The method of compounding of rubber to attain required composition was explored from literature review and various industries.

3.2.1 Material used:

The following material and chemical involved in the preparation of NBR lining:

- Nitrile rubber (NBR)
- Carbon black
- Zinc oxide
- Sulfur
- Stearic acid
- Antioxidants
- Accelerators
- Dop oil

3.2.2 Preparation of nitrile rubber lining:

Following are the complete steps for preparation of uncured NBR sheet.

Step 1:

3-5 kgs of raw nitrile rubber which were added in internal mixer which had 50 rpm/mint rotation speed.

Step 2:

Addition of processing oil and stearic acid was added and mixed.

Figure 18: **Raw Nitrile rubbers**

Figure 19: **Processing Oil**

Step 3:

Sufficient amount of carbon black was added and mixed.

Figure 20: Carbon Black

Step 4:

The temperature of internal mixer in all these process was kept constant through water circulation.

Figure 21: **Internal Rubber mixers**

Step 5:

Raw rubber compounded was left down to settle down.

Step 6:

Curing agent (sulfur) and other additives were added and mixed at constant temperature.

Figure 22: **Sulfur Powder**

Step 7:

To obtain the required thickness of rubber sheet, the compounded rubber was passed through two rolling mills.

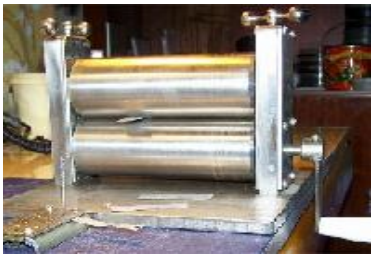


Figure 23: **Rubber Two rolling mill**

Step 8:

The prepared rubber sheet was ready for curing on metal surface.

Figure 24: **Uncured Rubber sheet**

Above chart show various steps for the preparation of uncured nitrile rubber sheet that is initially 3-5 kgs of raw nitrile rubber which are added in internal mixer and uncured filler are added in first stage then the complete mixing is achieved. The color of raw rubber pale brown to black color shows the complete mixing or dispersion of carbon black in raw rubber, the mixing process is carried out constant temperature at 60 ^{0}C. For processing, rubber compound was left to settle down followed by addition of various additives including curing agent (sulfur) and other processing additives. To obtain required thickness of rubber sheet, compound rubber was passing through two rolling mills.

3.2.3 Process of rubber curing on metal surface:

The process of curing of uncured NBR sheet on metal surface is discussed below**.**

Step 1:
Metal surface preparation followed by phosphating for 10 to 15 minutes.

Step 2:
Adhesive applications such as MEK were applied on metal surface.

Step 3:
Assembly of metal and rubber in a mold.

Step 4:
Compression molding was carried out in hydraulic press. Curing of adhesive and rubber were carried out on metal surface.

Step 5:
Production and finishing

Step 6:
Final product

Figure 25: Adhesive MEK

Figure 26: Hydraulic Press machine

Figure 27: NBR cured on metal surface

3.3 Durometer: (Rubber hardness tester)

To determine the hardness of materials such as plastic and rubber, durometer hardness is used. The hardness test is carried out on the surface of hard rubber specimen which is parallel to the surface, indenter for the instrument is pressed on the surface and hardness is read with in one second.

The thickness of specimen required minimum 6.4 mm and used hardness scale such as shore A for soft materials and shore D scale used for harder materials. ASTM D-2240 and ISO-868 standard is used for rubber hardness ranging from 20 to 90 durometer. [24]

Figure 28: Durometer for Hardness tester [24]

Hardness of Un-cured and Cured NBR is as under

Table 3: hardness of Un-cured and Cured NBR

Un-cured NBR Hardness	Cured NBR Hardness
30 durometer hardness	80 durometer hardness

3.4 Electrochemical Impedance Spectroscopy:

After the preparation of rubber compound and applying rubber lining and curing on the mild steel plate, next step is to take the sample for electrochemical test in which firstly EIS was performed.

3.4.1 EIS Cell Setup:

For EIS study Potentiostatic which is actually based on three electrode system manufactured by gamry instrument was used. The figure below shows the cell setup for the experiment is shown

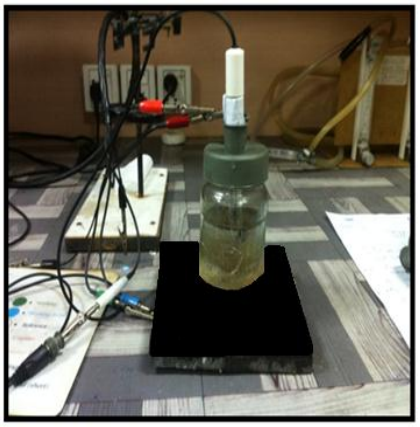


Figure 29: EIS cell setup

3.4.2 Sample (Working Electrode):

Blue and green wire of the cell was connected to the sample which in this setup is acting as a working electrode, electrochemical reaction that we studied occurs on working electrode. It is the sample of the corroding material. [25]

3.4.3 Silver silver chloride (Reference Electrode):

White wire in the setup is attached to the reference electrode which in this setup is saturated calomel electrode (SCE). The purpose of the reference electrode is to measure the potential of the working electrode. [25]

3.4.4 Graphite Electrode (Counter Electrode):

The orange and red wire in the cell were attached to the counter electrode which in this case is graphite electrode ,the counter electrode is generally inert which is a conductor and it is used to complete the circuit . The current that flows in to the solution through working electrode leaves the solution through counter electrode. [25]

Black Wire in the cell was grounded.

3.4.5 EIS Test Run:

After complete cell setup the software of gamry framework and echem analyst provided by gamry instrument was used for electrochemical study. Initially certain data was entered before the test was

started regarding sample information and the frequency on which test have been performed, an example of this is shown below. [25]

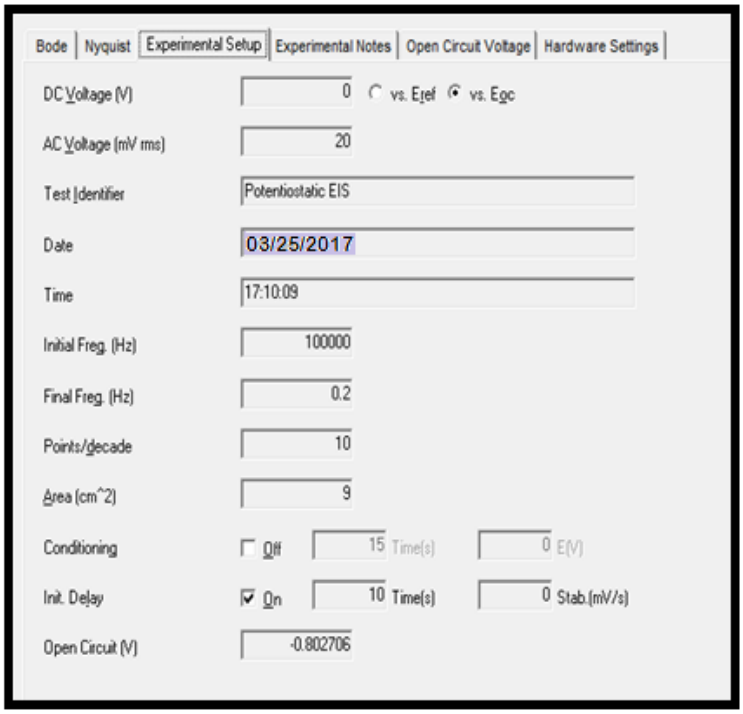


Figure 30: EIS data entry

After data entry the test starts and the data is generated in the following order :

- Open circuit Potential
- Bode Plot
- Nyquist Plot

After the test is completed and all of the three graphs are formed than we apply the appropriate fitting model which will give information on the following properties

R_u = Uncompensated Solution Resistance

R_{coat} = Coating/rubber lining Resistance

C_c = Coating/rubber lining Capacitance

R_{pore} = Pore Resistance

R_p = Polarization Resistance

Cdl = Double Layer Capacitance

3.4.6 Tafel Scan:

It is a DC technique used for the measurement of corrosion rate of a metal in a solution. The cell Current is measured from -250 to +250 mV at a slow sweep of the potential relative to open circuit potential. The data which is obtained from tafel scan is compared to a standard model (Butler-Volmer Model) yield an estimate of Icorr which is used to calculate a corrosion rate.

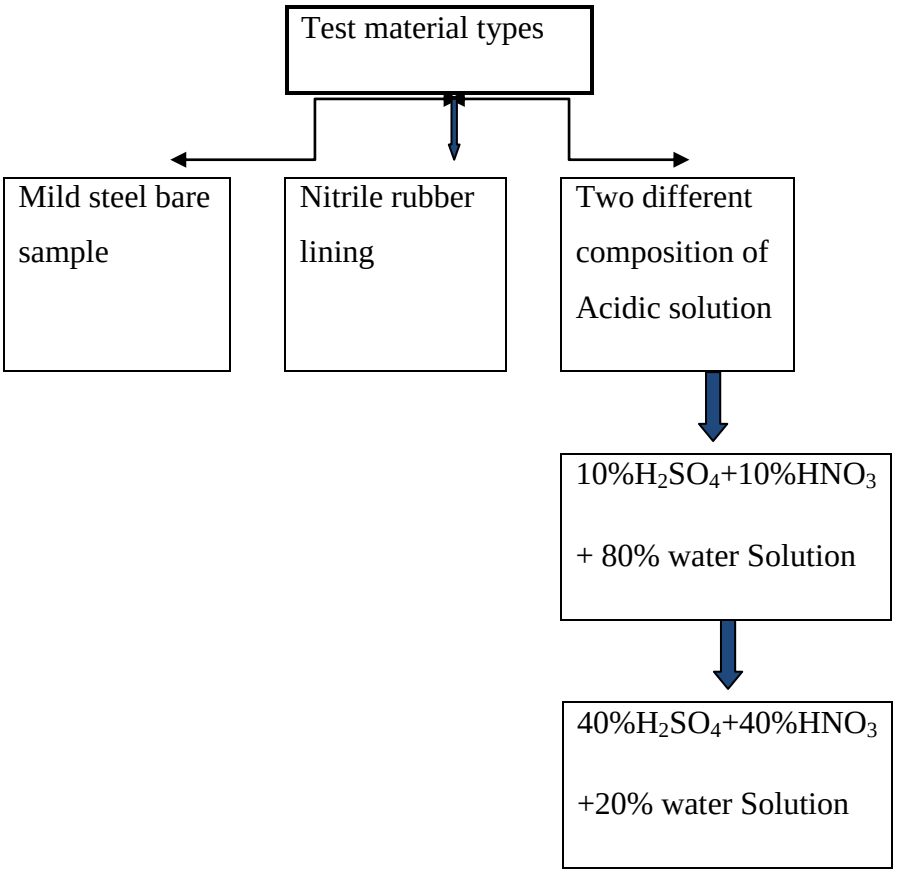
3.5 Scanning Electron Microscopy:

SEM is used for the characterization of the corroded sample, firstly SEM of sample without corrosion is performed and data is obtained on different magnification. After which corroded samples were characterized by using SEM and obtained result was compared with the corroded sample to observe the extent of which rubber lining is degraded or distort due to corrosion.

Chapter 4

Results and discussion:

As discussed there will be nitrile rubber lining and two different compositions of acidic corrosive environment in which the samples were tested, so the research is designed that acidic environment will be selected in which sample of polymer rubber lining along with a bare metal sample is tested for better comparison purpose.



4.1Purely capacitive lining:

Before the result for tested samples it is wise to show the EIS graph for a very strong lining which has the ability to store charges for a very long time without degrading and have very high impedance value. [26]

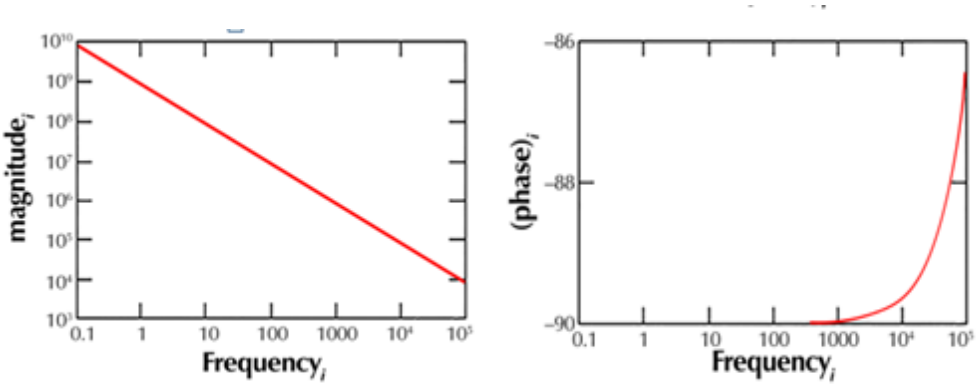


Figure 31: EIS Bode plot of vary strong Lining [26]

Above is shown the bode plot for a very strong lining, it can be observed in the graph of magnitude of impedance that a complete slope of -1 with very high value of impedance can be seen with the graph is increasing throughout. Similar to magnitude graph, the graph of phase Shift also showing highly capacitive behavior of lining tested as it can be seen that graph reaches -90 degree angle and become constant at it. The Nyquist curve of this lining is shown below:

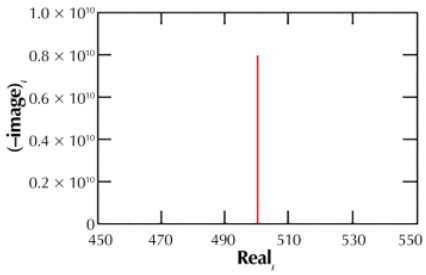


Figure 32: EIS Nyquist Plot of vary strong Lining [25]

The Nyquist plot shows a straight line at 90 degree from the real axis with continuous increase, this shows that the impedance is continuously increasing and lining is not degraded, as for the case of degradation this line increases till a certain point and then started to decrease gradually forming a semi-circle. [26]

4.2 Qualitative Analysis – SEM:

The scanning electron microscopy is a method of analysis of the surface of material and fine detail can be measured and assessed via image analysis. The most important factor of SEM is high magnification and greater depth of field up to 100 times that of light microscopy. [27]

Figure 33: SEM Chamber [27]

a) Bare Metal b) After 3 months c) After 8 months

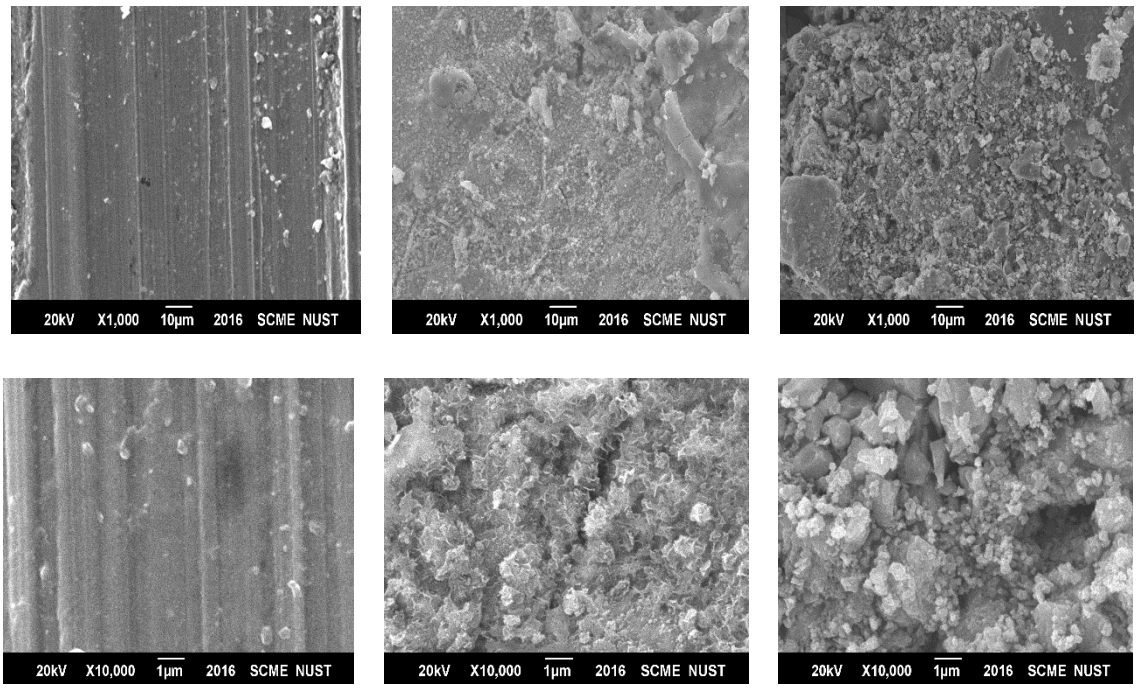


Figure 34: SEM Image of Bare Metal

Surface morphology of mild steel was studied by scanning electron microscopy before immersion and after 3 months or 8 months immersion in Concentrated mixed acid solution. Figure (a) shows the SEM obtained of bare mild steel without being exposed to the corrosive environment and it is clear that the mild steel sample before immersion seems smooth and shows some abrading scratches on the surface while, Figure (b) (c) shows strongly damage on mild steel surface due to the formation of corrosion products after immersion in concentrated

mixed acid solution. And shows that an aggressive attack of the corroding medium on the mild steel surface.

4.3 Immersion test:

ASTM stander G31 provides a simple and straightforward method of determining the rate of corrosion in aqueous solution. Immersion test measure the progress of corrosion damages obtained from the metal is immersed for a period of 24 hours to several months depending on the material/ alloy for corrosive environment as well as the factors which that can accelerate the corrosion rate.[28]

Figure 35: Matel sample dip in Acid

Mild steel sample 1.2*1.2 cm^2 dimensions was immersed in concentrated acidic solution for 9 days and weight of sample before and after immersion can be measured to find the corrosion rate by weight loss method.

4.3.1 Corrosion Rate by Weight loss Method: [28]

Formula of Weight loss in mpy = 534W/DAT
Where W is weight loss in mg
D is density in g/cc
A is surface area in inch2
T is time in hours
W = initial weight of sample – final weight of sample
13418.5 – 13231.0 = 187.5 mg
mpy = 534 * 187.5 / 7.85 * 1.7598 * 216
Corrosion rate = 33.19 mpy

4.4 FTIR spectral Analysis:

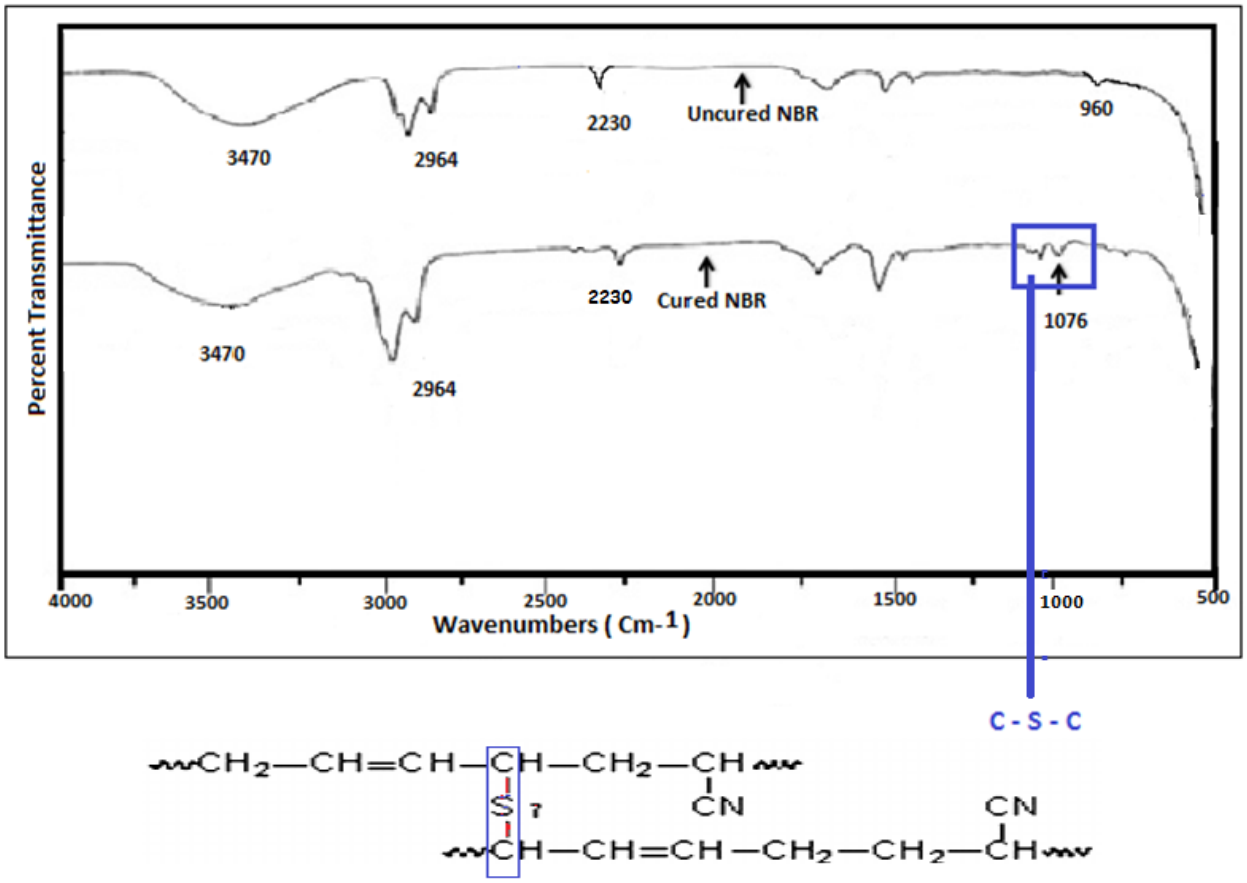


Figure 36: FTIR Spectra of Uncured and Cured NBR

It is noted that the band at 1076 cm−1 is absent in uncured NBR whereas it is present in cured NBR. This band is mainly attributed to the symmetric C–S–C group stretching vibrations in the two C–S bonds. Since during vulcanization the addition of sulfur breaks the Hydrogen bonds of the carbon atoms and the sulfur atoms bridge the gaps between the two chains i.e. they establish cross-links between the chains.

4.5 EIS of bare metal:

4.5.1 EIS of bare metal in dilute mixed acid solution: (Mixed acid of $10\%H_2SO_4+10\%HNO_3+80\%\ H_2O$)

Firstly bare metal samples were tested using gamry Potentiostats and data was obtained using EIS technique whose result is shown below. Left vertical axis is Impedance magnitude whereas right vertical axis is phase shift. Horizontal axis shows frequency. Capacitive and Impedance

behavior shown here is because of Helmots Double Layer which is formed because of surface Metal elements and water molecules. This surface film is not protective especially in conductive electrolyte like acidic solution.

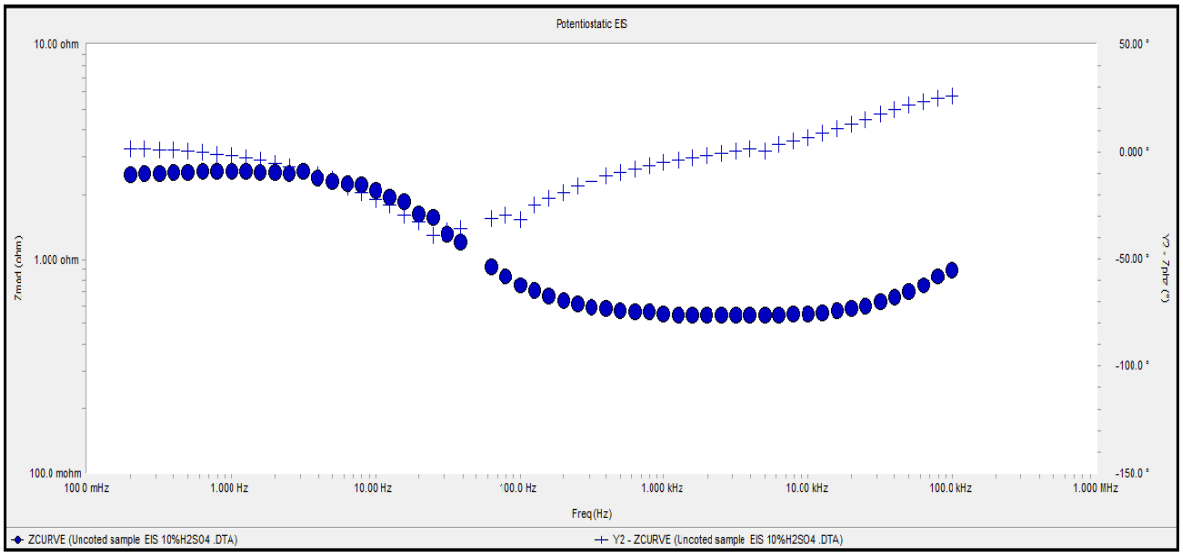


Figure 37: Bode plot of bare metal in dilute mixed acid solution

Bode plot for the bare metal sample is shown above where it can be seen that in case of impedance value is 3 ohm. While in case of phase shift the graph just reached -30 degree showing capacitive behavior till this point and after that again starts moving upward which represents that charge storage is halt at this point making sample behavior resistive.

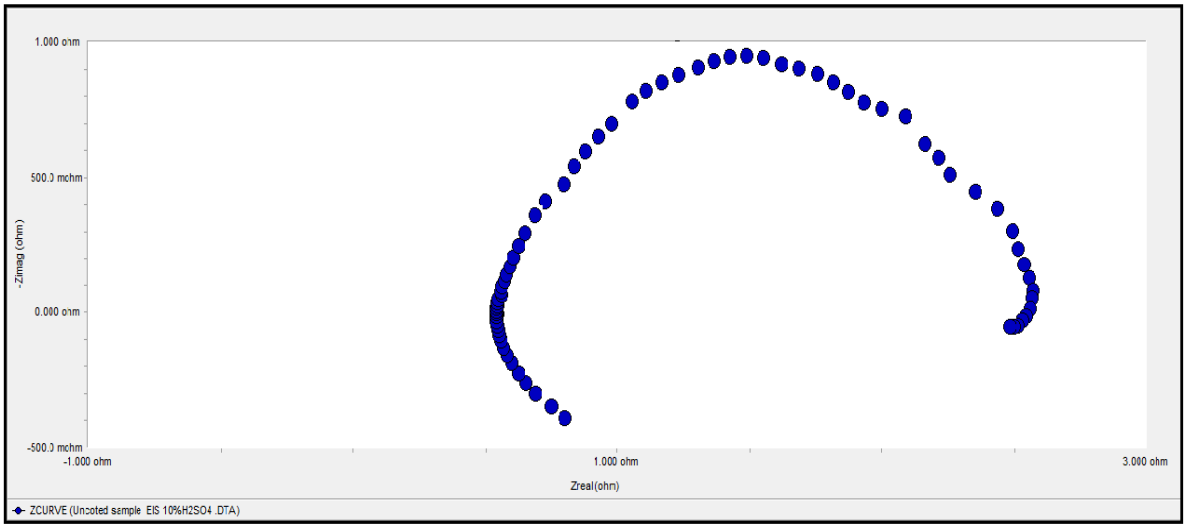


Figure 38 : Nyquist Plot of bare metal in dilute mixed acid solution

Above is the Nyquist plot for the bare metal sample immersed in acidic solution is compared from the graph shown for a very strong lining above that here the graph increased till a certain point after which it become constant at about 1 ohm and if the path is followed ,we may observe that it will start to descend after some point. The graph here shows that after some time the capacitive behavior started to decrease showing that now charges have been started interacting with the sample.

4.6 Mechanism for Bare Metal EIS:

There are predefined electrical models that are present and explain electrical circuit of our electrochemical cell setup. In this cell setup physical component are also shown which are connected according to cell at different manners.

Randel cell is used to explain a bare metal sample corroding is shown below:

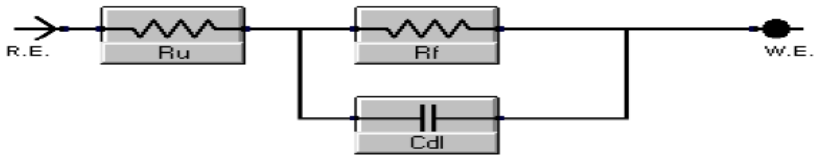


Figure 39: Randel Circuit model for bare metal [29]

Where R.E shows the reference electrode and W.E shows the working electrode and in between these two electrodes this cell is generated. This must be clear that by looking circuit it does not mean that our cell is made from resistor and capacitor but it shows that is circuit which can be made from parts available at electronic shop, for an electrochemical system it can be made from electrodes and electrolyte both behave in the same manner when voltage is applied. As shown and discussed in the test result of bare metal that although the sample is uncoated i.e. bare sample still certain capacitive behavior although very low but still behavior is present can be explained by looking at the circuit element Cdl which means double layer capacitance. The capacitor element here is generated between the metal/electrolyte surfaces generating a very thin single layer of solvent molecules which act as a dielectric, which explains why bare metal sample also shows capacitive behavior.

4.7 Tafel Scan:

After the bode plot and nyquist plot we get the impedance and phase shift values of sample is observed, Tafel scan is run in the same cell setup to obtain the value of corrosion potential (E_{corr}), corrosion current (I_{corr}) and corrosion rate (CR). E log I Fit is the method here which is used to get direct values of E_{corr}, I_{corr} and corrosion rate.

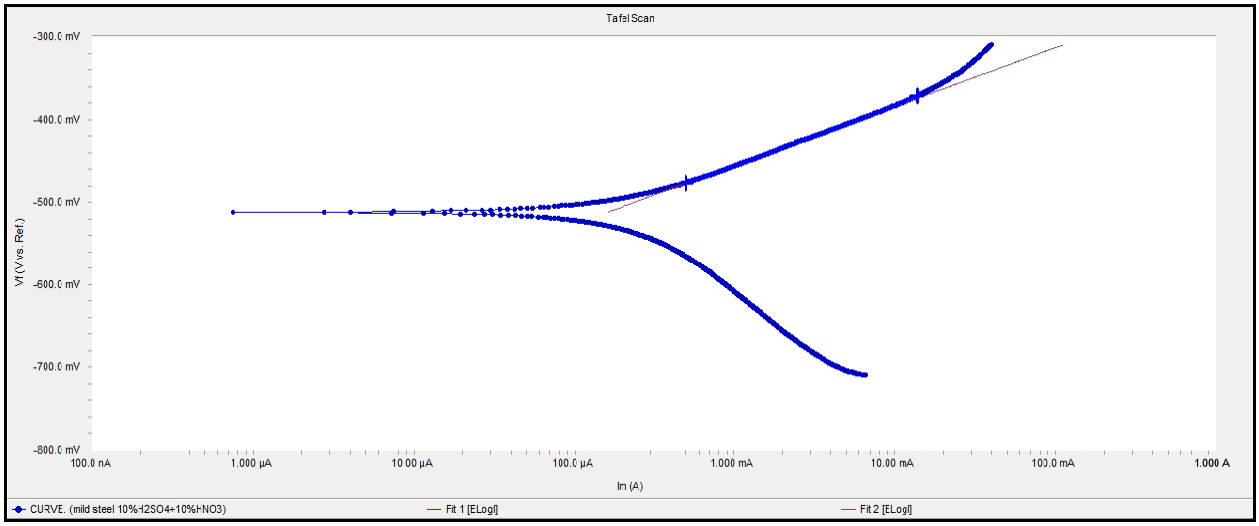


Figure 40: Tafel scan of bare metal in dilute acidic solution

The values obtained from tafel plot are given below:

Parameter	**Values**
Beta	72.43e-3 V/decade
E_{corr}	-511.7 mV
I_{corr}	169.2 µA
Corrosion rate	73.72 mpy

4.8 EIS of bare metal in concentrated mixed acid solution: (Mixed acid of 40% H_2SO_4+40%HNO_3+20%H_2O)

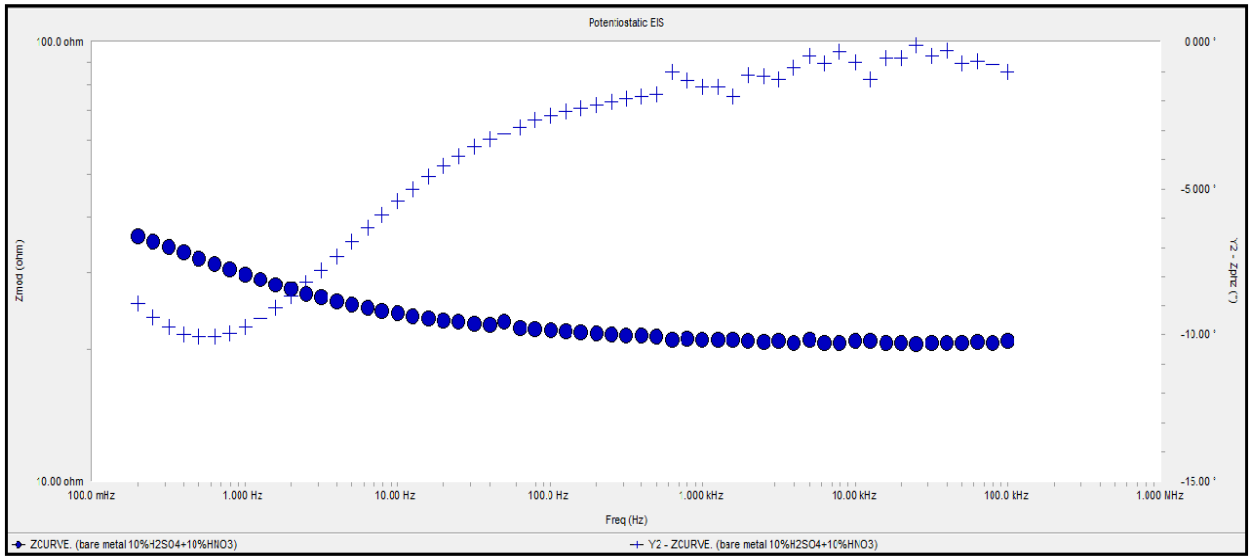


Figure 41: Bode plot of bare metal in concentrated Mixed Acid solution

Bode plot for the bare metal sample is shown above where it can be seen that in case of impedance value of 10 ohm is crossed but it is far more below from 100 ohm. While in case of phase shift the graph just reached -10 degree showing capacitive behavior till this point and after that again starts moving upward which represents that charge storage is halt at this point making sample behavior resistive.

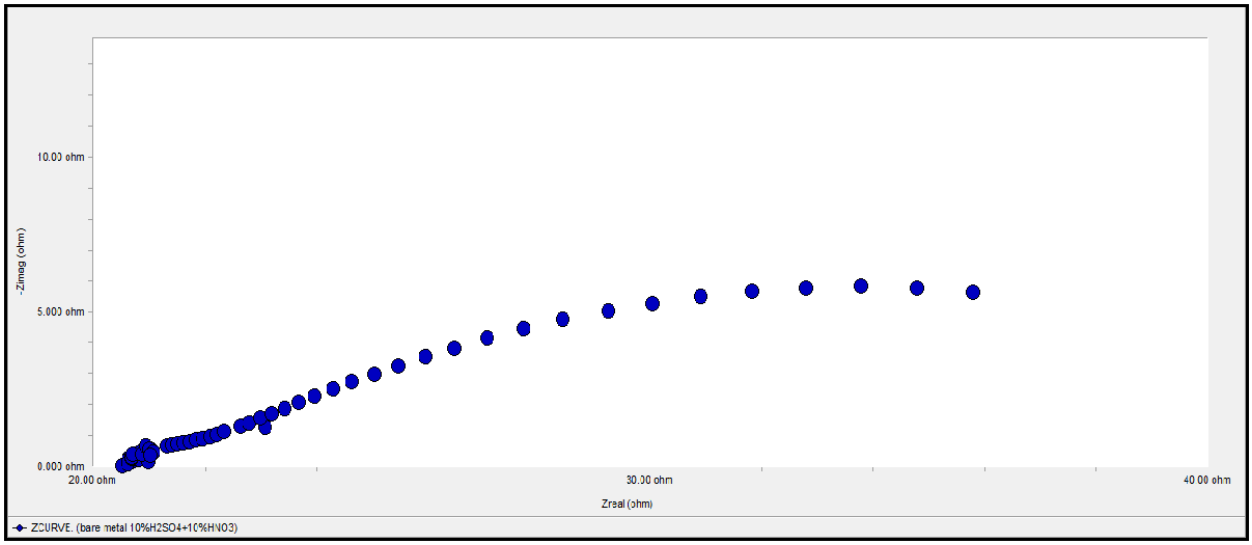


Figure 42: Nyquist Plot of bare metal in concentrated Mixed Acid solution

Above is the Nyquist plot for the bare metal sample immersed in concentrated Mixed acid solution compared from the graph shown for a very strong lining above that here the graph increased till a certain point after which it become constant at about 5 ohm and if the path is followed we may observe that it will start to descend after some point. The graph here shows that after some time the capacitive behavior started to decrease showing that charges are now start interacting with the sample.

4.9 Tafel scans of bare metal in concentrated mixed Acid solution:

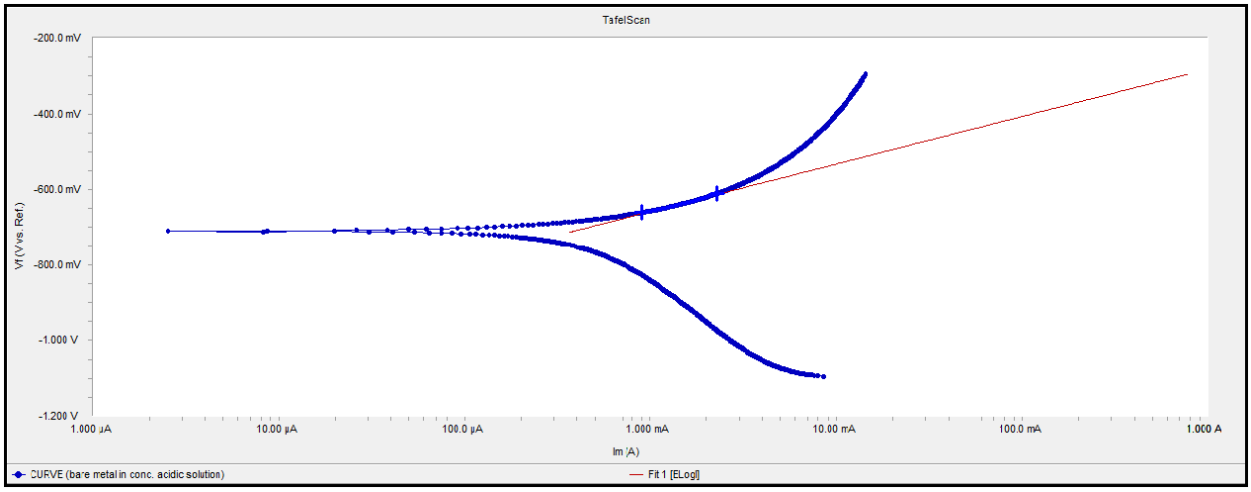


Figure 43: Tafel scan of bare metal in concentrated mixed Acid solution

The values obtained from tafel scan are given below:

Parameter	**Value**
Beta	125.4e-3 V/decade
E_{corr}	-708.1 mV
I_{corr}	396.0 µA
Corrosion Rate	30.19 mpy

4.10 Mechanism of Steel Corrosion:

Mechanism of steel corrosion in Chloride aqueous environment has been explained in a book

"Corrosion Engineering" by M. G. Fontana. There are several Oxidation and Reduction reactions Involved in steel corrosion. [29]These reactions which result rust formation are shown below:

$$Fe \rightarrow Fe^{2+} + 2e^-$$

$$Fe^{2+} \rightarrow Fe^{3+} + 1e^-$$

$$O_2\,(g) + 2H_2O + 4e^- \rightarrow 4OH^-$$

$$2Fe^{2+}\,(aq) + O_2\,(g) + 2H_2O \rightarrow 2FeOOH + 2H^+$$

This rust doesn't have good stability on steel surface beneath it. Also, it has porosity which causes electrolyte penetration to steel. All these pores and holes cause special type of corrosion called as Crevice corrosion. Solution remains stagnant in these sites. In Sea water (Chloride environment) general dissolution of metal and reduction of oxygen occurs as shown below for metal as M.

Oxidation $M \rightarrow M^+ + e$

Reduction $O_2 + 2H_2O + 4e \rightarrow 4OH^-$

Initially dissolution is same on surface and crevices but after certain time there is depletion of Oxygen in crevices. With passage of time this effect gets severe by increasing Metal positive ions in crevices and to neutralize this effect Chloride ions from solution migrate into crevices. This effect even increases corrosion rate inside the crevices. [30]

$$M^+Cl^- + H_2O = MOH\downarrow + H^+Cl^-$$

Following is pictorial representation of this reaction.

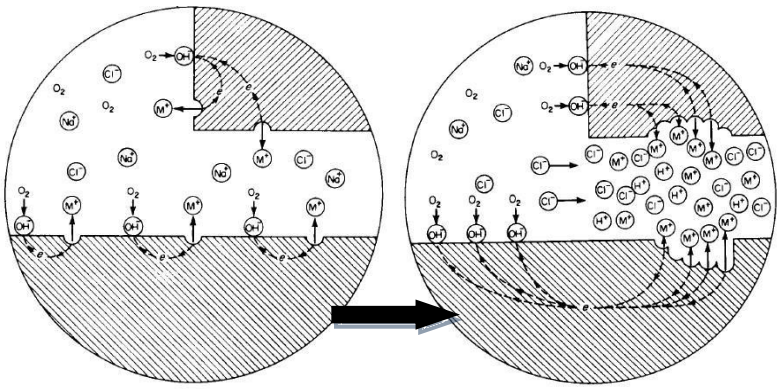


Figure 44: Pictorial Presentation of Crevice corrosions [30]

4.11 EIS of NBR lining in dilute mixed acid solution:

EIS graphs for NBR lining sample immersed in 10%H_2SO_4+10%HNO_3 + 80% H_2O dilute mixed acid solution are given below:

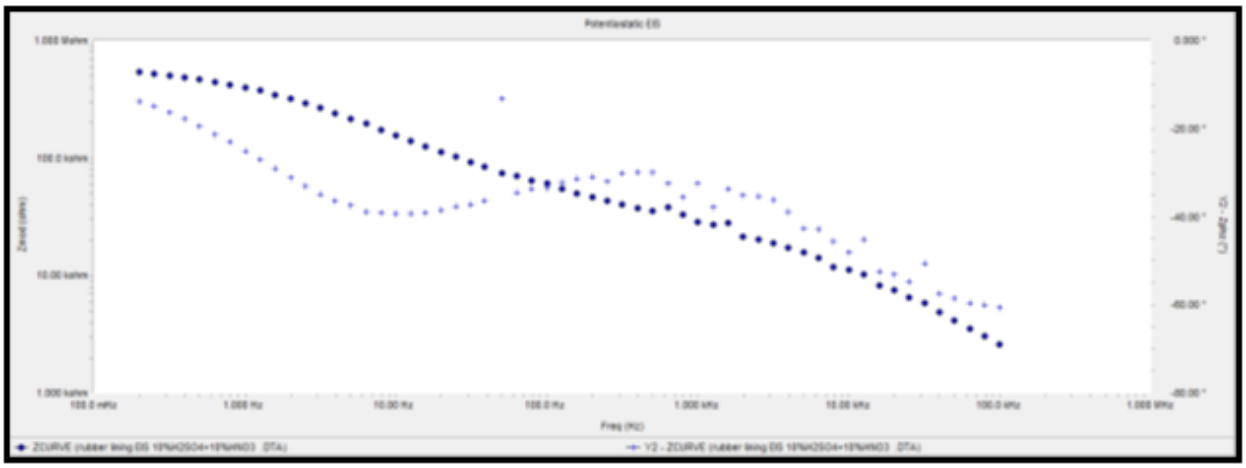


Figure 45: Bode plot of NBR lining in dilute mixed acid solution

Bode plot for this rubber lining is shown above and the increase in capacitance behavior of graph is clearly visible by the increase in the -1 slope compare to the bare steel sample and the increase in phase shift -70^0also support the fact that this rubber lining can capable of storing more charge before degrading, if clearly observe one can also witness the higher value of impedance showing rubber lining strength. For more convenient comparison all these graphs will be compared shortly. Nyquist graph of this rubber lining is shown below which will further support the above observation.

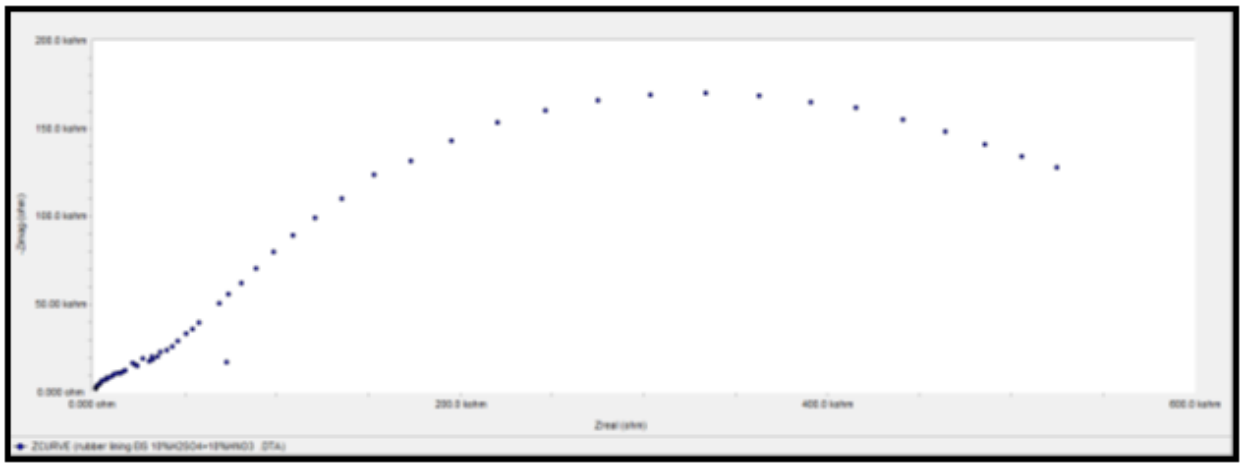


Figure 46: Nyquist plot of NBR lining in dilute mixed acid solution

Nyquist plot for NBR rubber lining, a comparative better impedance value 180 Kohm from the bare sample is shown which is supporting the fact this rubber lining is storing more charges and provides lesser path to the charge to reach sample surface which cause sample. As in the case of bare sample here it is observed that after reaching a certain value it starts to decrease again which shows that after this point rubber lining start to degrade slowly and lining loses its capacitive behavior.

4.11.1 EIS of NBR lining in concentrated mixed acid solution:

EIS graphs for NBR lining sample immersed in 40%H_2SO_4+40%HNO_3 and 20% H_2O mixed acid solution are given below.

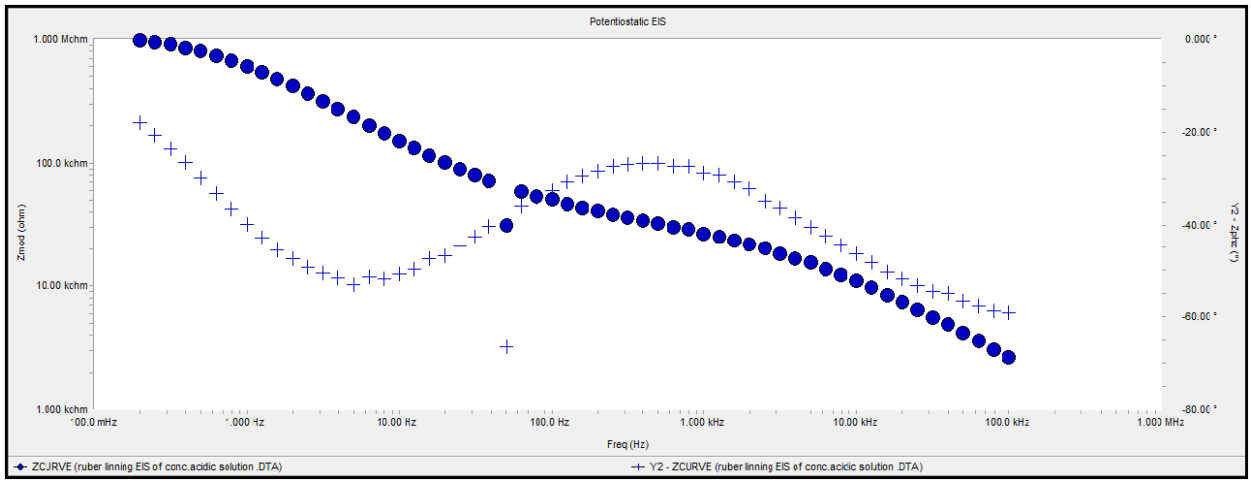


Figure 47: Bode plot of NBR lining in concentrated mixed Acid solution

Bode plot for this rubber lining is shown above and the increase in capacitance behavior of graph is clearly visible by the increase in the -1 slope compare to the bare steel sample and the increase in phase shift -72^0also support the fact that this rubber lining can capable of storing more charge before degrading, if clearly observe one can also witness the higher value of impedance showing rubber lining strength. For more convenient comparison all these graphs will be compared shortly.

Nyquist graph of this rubber lining is shown below which will further support the above observation.

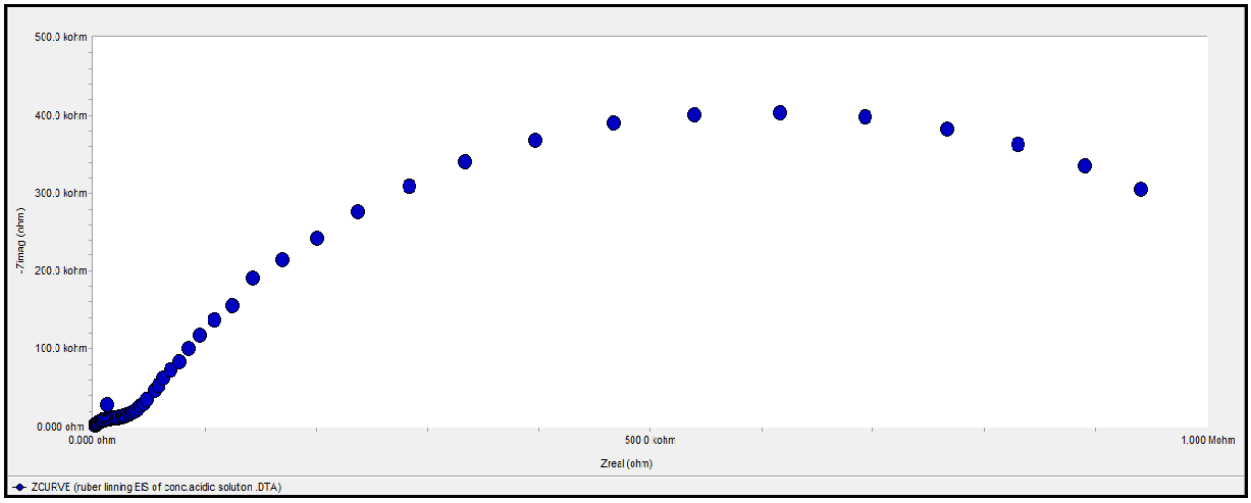


Figure 48: Nyquist plot of NBR lining in concentrated mixed Acid solution

Nyquist plot for NBR rubber lining, a comparative better impedance value 480 Kohm from the bare sample is shown which is supporting the fact this rubber lining is storing more charges and provides lesser path to the charge to reach sample surface which cause sample. As in the case of bare sample here it is observed that after reaching a certain value it starts to decrease again which shows that after this point rubber lining start to degrade vary slowly and lining loses its capacitive behavior.

4.12 Dilute and Concentrated Mixed Acid – Nyquist Plot Comparison:

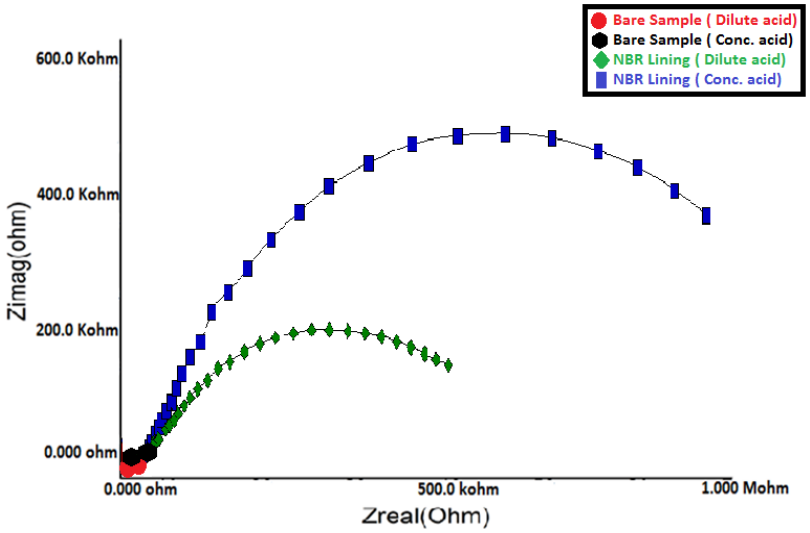


Figure 49: Comparison of Nyquist Plot of bare metal and NBR lining in concentrated and dilute mixed acid solution

Figure shows Comparison of Nyquist plot of Dilute and concentrated mixed acid solution presentation of EIS. Result shows that impedance of bare metal is 12 ohm, 25 ohms in dilute and concentrated mixed acid solution respectively and in case of NBR lining sample impedance is increased to value of 180 Kohm in dilute mixed acid solution and 480 Kohm in concentrated mixed acid solution. This means that NBR lining in concentrated mixed solution have higher value of impedance.

4.13 Equivalent Circuit Modeling for NBR lining on MS:

As discussed earlier an electrical circuit can represent EIS behavior of a metal. Randel model showed this behavior of bare metal but for a NBR lining it won't be that simple. Following circuit diagram shows and Electric circuit responding like a coating.

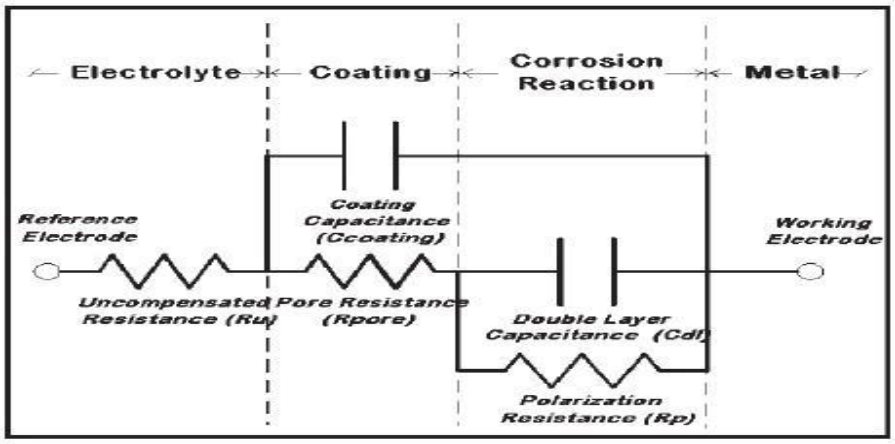


Figure 50: Circuit model representation of Coating [30]

For the case of coated metal a complex circuit is used compare to bare metal and combination of resistors and capacitors are present. The circuit is setup between reference and electrode, each portion of the cell is clearly mention i.e. which part of circuit represent which part of electrochemical cell. Now as this research deals with the coating strength so that area will be the area of interest here in which R_p (Pore resistance) and C_c (Coating capacitance) will be the features whose values will give us information regarding coating stability in corrosive environment. Now to obtain values for R_p and C_c there are number of different fitting models present which are used for curve fitting, in gamry instrument these fitting models are already present with that there is a feature namely EIS model editor which can be used to form numerous

complex circuit according to the requirement of our electrochemical cell. So using the required fitting model one can obtain value of these components and with these values behavior of the graphs can be explained. For a coated metal as in this case also REAP2CPE model is selected for both of our graph and values are generated. The curve fitting graphs are shown below.

4.14 Curve fitting for NBR in dilutes mixed acid solution:

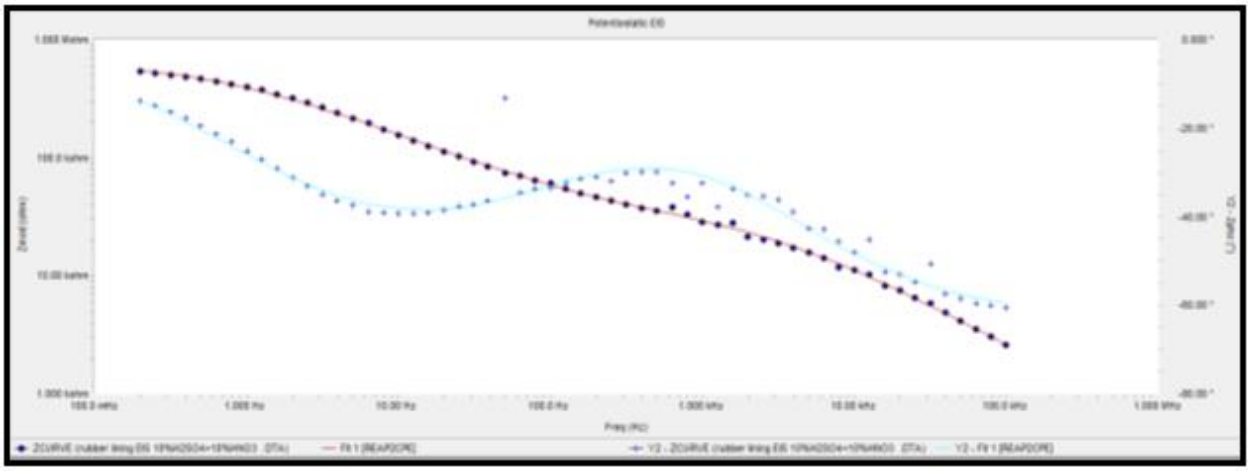


Figure 51: Curve fitting of NBR lining in dilute mixed acid solution

The values obtained are given below

Parameter	Values
R_{solu}	$163.9e^{-12}$ ohms
R_{corr}	$648.0e^{3}$ ohms
R_{pa}	$36.41e^{3}$ohms
C_{corr}	$481.5e^{-9}$ S*s^a
n	$606.9e^{-3}$
C_c	$31.84e^{-9}$ S*s^a
m	$701.1e^{-3}$

Fitted curve of NBR lining in dilute mixed acid solution with Values

The fitted curve for this coating is shown above along with the values that were calculated from the fit model.

4.15 Curve fitting For NBR in concentrated mixed Acidic solution:

Curve fitting model for the NBR lining is shown below.

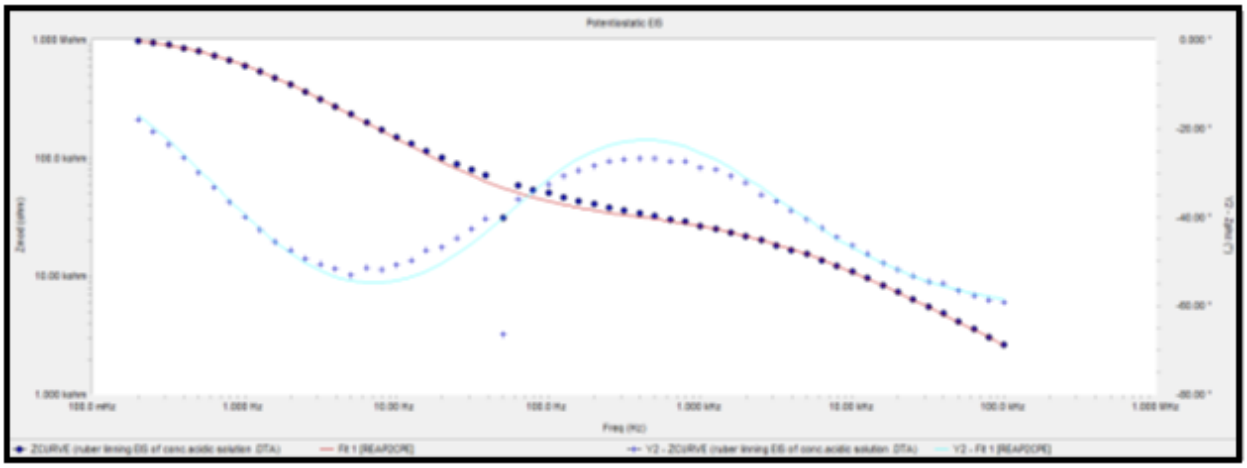


Figure 52: Curve fitting of NBR lining in concentrated mixed Acid solution

The values obtained are given below

Parameter	Values
R_{solu}	$14.81e^{-12}$ ohms
R_{cor}	$1.116e^{6}$ ohms
R_{pa}	$35.77e^{3}$ ohms
C_{cor}	$244.0e^{-9}$ S*s^a
n	$801.0e^{-3}$
C_c	$36.36e^{-9}$ S*s^a
m	$691.2e^{-3}$

The fitted curve for this NBR lining is shown above along with the values that were calculated from the fit model.

Comparison of values:

Table 4 shows the comparison of EIS fit model values of bare metal and NBR lining in concentrated and dilute mixed acid solution.

Table 4: Comparison of Values of EIS fit model for dilute and concentrated mixed Acid solution.

Electrode	R_{solu} (ohms)	R_{cor} (ohms)	R_p (ohms)	C_{cor} (S*s^a)	n	C_c (S*s^a)	M
Bare Mild Steel (Dilute Mixed acid)	126.7	$193.2e^{-3}$	$489.5e^{-3}$	$1.954e^{-6}$	$936.8e^{-3}$	$240.9e^{-9}$	$961.4e^{-3}$
Bare mild steel (Conc. Mixed acid)	14.60	1.452	6.678	2.314	$358.2e^{-3}$	$145.3e^{-9}$	$904.1e^{-3}$
NBR Lining Sample(Dilute Mixed acid)	$163.9e^{-12}$	$648.0e^{3}$	$36.41e^{3}$	$481.5e^{-9}$	$606.9e^{-3}$	$31.84e^{-9}$	$701.1e^{-3}$
NBR Lining Sample(Conc. Mixed acid)	$14.81e^{-12}$	$1.116e^{6}$	$35.77e^{3}$	$244.0e^{-9}$	$801.0e^{-3}$	$36.36e^{-9}$	$691.2e^{-3}$

The higher value of pore resistance NBR lining in dilute mixed acid solution compare to other one explains the fact that why this lining showing better stability, due to higher values of pore resistance it is attributed that there were lesser percentage of pores that were generated when it came in contact with the electrolyte due to which low fraction of area of the metal sample get exposed to acidic solution therefore the reaction of corrosion is suppressed in this case for considerably more time and the exact opposite happened for the case of polymeric coating. Pores play a vital role in increasing or decreasing the corrosion reaction, the complete mechanism of how pores enhance the corrosion reaction will be shortly explained but for now on this statement should be crystal clear that in giving better stability to the ceramic coating pore resistance plays the major role. For the case of C_c it can be observed that polymeric coating showing more coating capacitance compare to other one, which very well explained the fact that why polymeric coating shows less impedance by looking at the following formula

$Z = 1/2\pi fC$

Where Z = impedance

f= frequency

C= capacitance

As the value of capacitance increase impedance value comes down as both are inversely proportional. So we can explain the phenomenon, as polymeric coating have more capacitance means it can capable of more storing more charges so increase in the charge rate degraded this coating more rapidly compare to the one which is showing lesser coating capacitance value.[30]

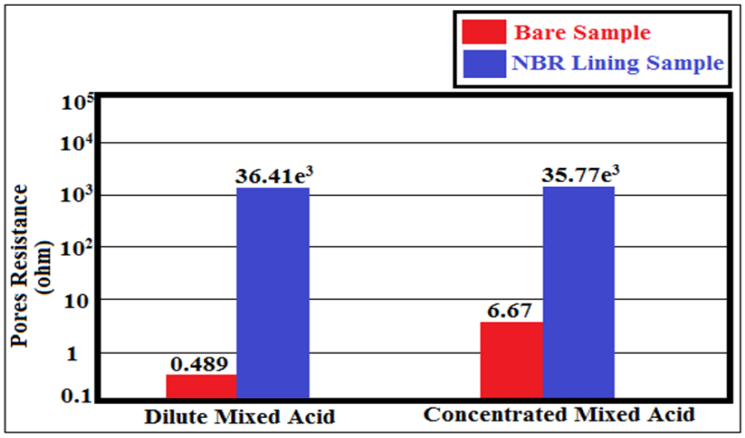


Figure 53: Dilute and Concentrated Mixed Acid-Comparison of EIS Fit Model Values in Graph

4.16 Tafel Scan:

Now when complete information regarding lining stability and the resistance it is providing to our sample is gathered from EIS, in the end to get a definite numeric value of corrosion rate we perform Tafel scan on our sample which using DC technique will provide us with a graph and by using E log I fit important values were obtained**.**

4.16.1 Tafel plot of NBR lining in dilute mixed acid solution:

Tafel plot of NBR lining in dilute mixed acid solution is shown below

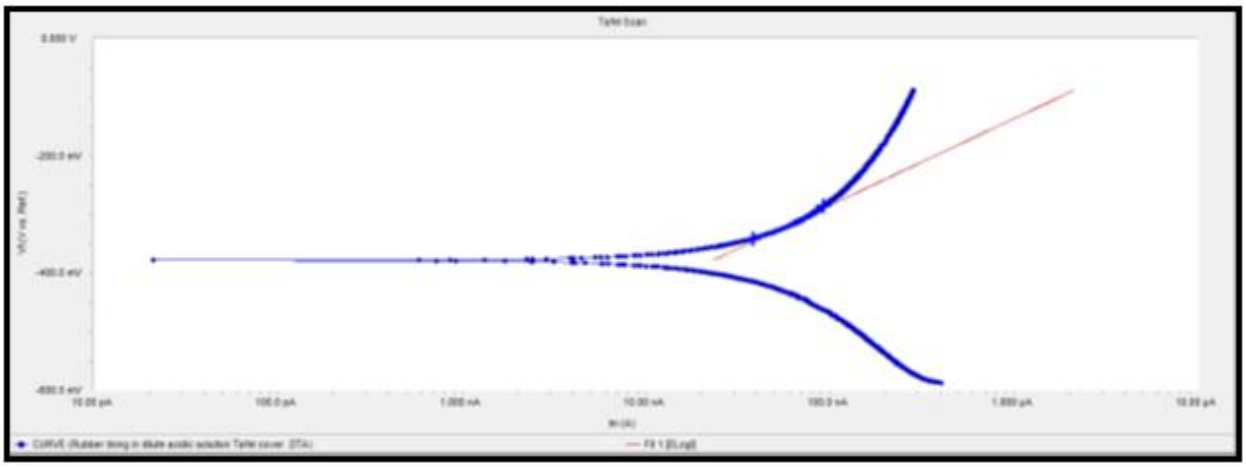


Figure 54: Tafel Plot of NBR lining in dilute mixed acid solution

The values obtained from Tafel plot is given below

Parameter	**Values**
Beta	147.8e-3 V/decade
E_{corr}	-378.3 mV
I_{corr}	23.10 nA
Corrosion rate	274.7e-6 mpy

The tafel plot and its corrosion rate and other values are shows above.

4.16.2 Tafel plot of NBR lining in concentrated mixed Acid solution:

Tafel plot of NBR lining in concentrated mixed acid solution is shown below

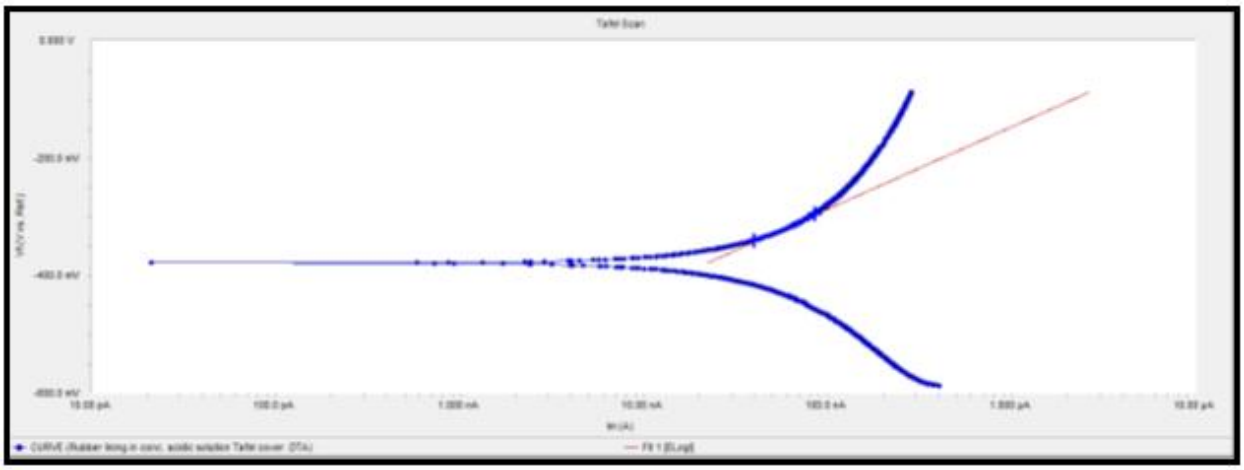


Figure 55: Tafel plot of NBR lining in concentrated mixed acid solution

The values obtained from Tafel plot is given below

Parameter	Values
Beta	140.0e-3 V/decade
E_{corr}	-378.3 mV
I_{corr}	22.13 nA
Corrosion rate	263.1e-6 mpy

Tafel plot and there corrosion rate and other values are shows above.

4.16.3 Comparison of Tafel plot of NBR lining and bare metal in dilute mixed Acid solution

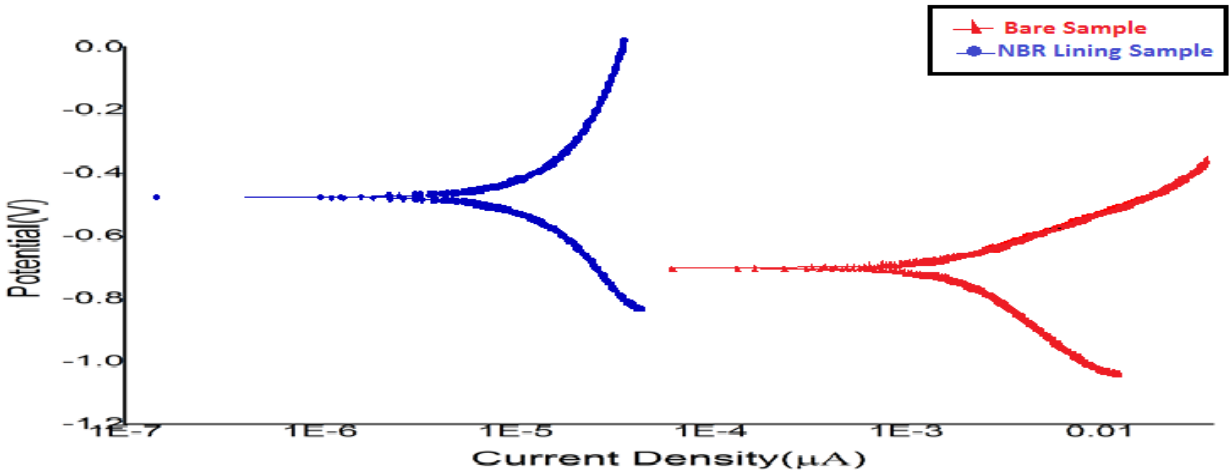


Figure 56: Compared the Tafel plot of NBR lining and bare sample in concentrated mixed Acid solution

Table 5: Comparison of Tafel plot Values

NBR Lining Sample	
Parameter	Values
Ecorr	-378.3 mV
Icorr	23.10 µA
Corrosion rate	274.7e^{-6} mpy

Bare Metal Sample	
Parameter	Values
Ecorr	-511.7 mV
Icorr	169.2 µA
Corrosion rate	73.72 mpy

4.16.4 Comparison of Tafel plot of NBR lining and bare metal in Concentrated mixed Acid solution:

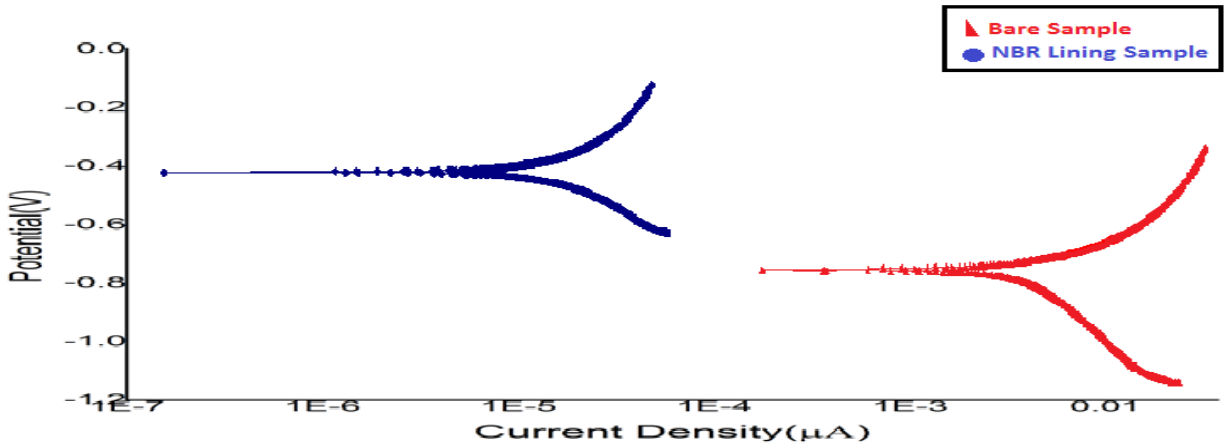


Figure 57: Compared the Tafel plot of NBR lining and bare sample in concentrated mixed Acid solution

Tafel plot compared value is as under:

Table 6: Comparison of Tafel plot Values

NBR Lining Sample	
Parameter	Values
Ecorr	-378.3 mV
Icorr	22.13 µA
Corrosion rate	263.1e^{-6} mpy

Bare Metal Sample	
Parameter	Values
Ecorr	-708.1 mV
Icorr	396.0 µA
Corrosion rate	30.19 mpy

Dilute and Concentrated Mixed Acid-Comparison of Tafel Scan is shown in Graph are as below:

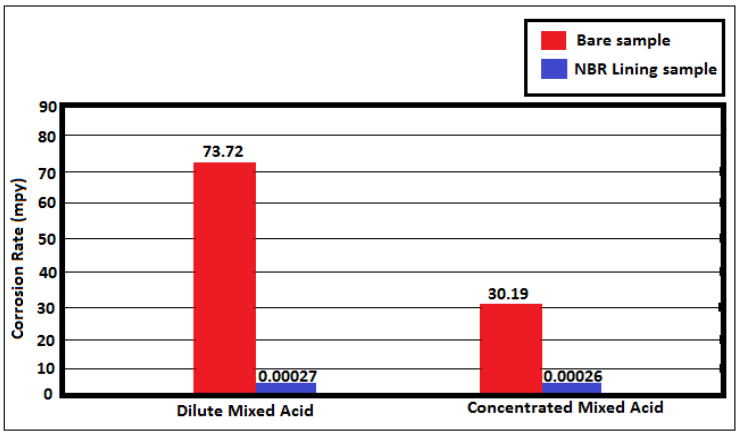


Figure 58: Dilute and Concentrated Mixed Acid-Comparison of Tafel Scan in Graph

4.17 Surface Morphological Analysis of NBR lining(SEM) :

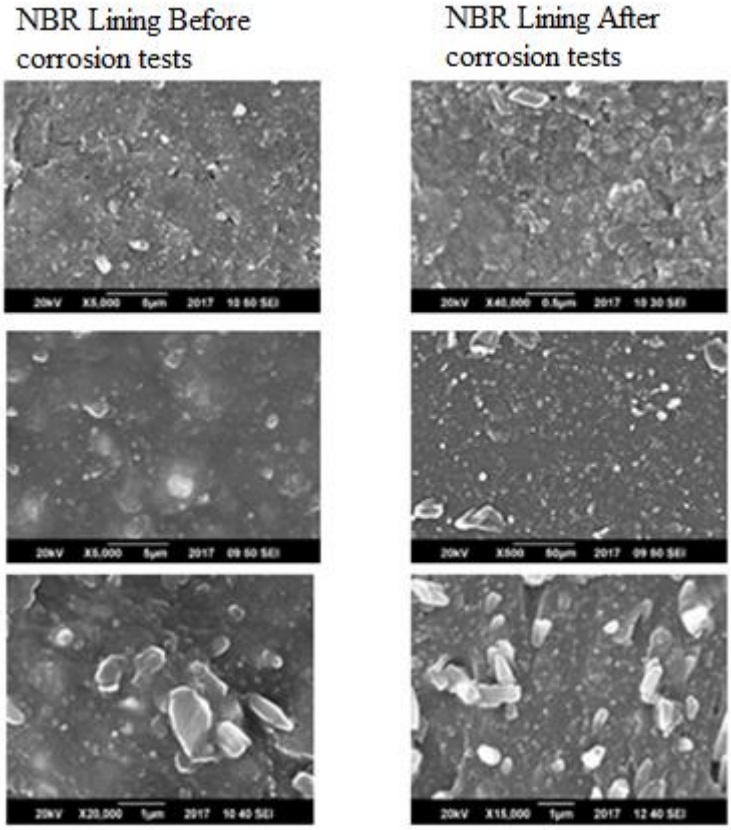


Figure 59: SEM- NBR lining before and after corrosion tests

Surface morphology of NBR lining was studied by scanning electron microscopy before corrosion test and after corrosion test in concentrated mixed acid solution. Figure showed the SEM obtained of NBR lining before and after corrosion test seem smooth and cleared which means that NBR lining surface is not damage in concentrated mixed acid solution.

Chapter 5

Conclusions:

Now here as final discussion, we see that a mild steel acid tank storage sample was selected as a substrate, now applying a nitrile butadiene rubber (NBR) lining on substrate, lining is applied on metal surface in hydraulic press machine.

Series of electrochemical tests were performed on this sample in different acidic environment which are dilute mixed acid solution (10% sulfuric acid, 10% nitric acid and remaining 80% water) and concentrated mixed acid solution (40% sulfuric acid, 40% nitric acid and remaining 20%water).

Development of NBR Lining:

Successful development of NBR processing to obtain lining with desirable characterization such as:

Anticorrosion, thickness, adhesion and shore hardness

Anti-corrosion EIS Data for Mixed Acid Storage Tank:

- NBR lining shows higher strength in concentrated mixed acid solution.
- Higher values of impedance and phase shift
- It has higher value of R_p and low value of C_c
- Corrosion rate percentage reduction was **86% (dilute)** and **94 % (concentrated)** compare to bare mild steel sample.

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