11-24-2015

Evaluation of External Coating Performance on Buried Pipelines in the Oil and Gas Industry

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DOI: 10.25148/etd.FIDC000143

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FLORIDA INTERNATIONAL UNIVERSITY

Miami, Florida

EVALUATION OF EXTERNAL COATING PERFORMANCE ON BURIED
PIPELINES IN THE OIL AND GAS INDUSTRY

A thesis submitted in partial fulfillment of

the requirements for the degree of

MASTER OF SCIENCE

in

MATERIAL SCIENCE AND ENGINEERING

by

Mohammed Alrudayni

2015

To: Interim Dean Ranu Jung
College of Engineering and Computing

This thesis, written by Mohammed Alrundayni, and entitled Evaluation of External Coating Performance on Buried Pipelines in the Oil and Gas Industry, having been approved in respect to style and intellectual content, is referred to you for judgment.

We have read this thesis and recommend that it be approved.

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The thesis of Mohammed Alrundayni is approved.

Interim Dean Ranu Jung
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Florida International University, 2015

DEDICATION

This thesis is dedicated to my mother, Amal AlSehli, Father, Adnan AlRudayni, Father in law, Talal Jahlan, and my wife, Elaf Jahlan, my brothers and sisters, family and friends. Without their patience, understanding, support, and most of all love, the completion of this work would not have been possible.

ACKNOWLEDGMENTS

Praise and thanks be to Almighty Allah for his limitless help and guidance; and peace and prayers be upon his Prophet.

I wish to express my sincere appreciation to the Material Science and Engineering department at Florida International University for providing facilities, AMERI, Prof. Munroe corrosion lab and Prof. Lau corrosion lab at Civil Engineering department to me during the course of this investigation.

My expression of thanks to Prof. Norman Munroe and Prof. Kingsley Lau does not arise from convention. Rather, from my heart-felt gratitude for their constant counsel, matchless patience and extraordinary attentiveness.

I am deeply indebted to my supervisor prof. Benjamin Bosel and Prof. Zhe Cheng, the other two committee members, for their cooperation and valuable suggestions.

I would further express my thanks to Mr. Jad Nasser and Mr. Paek for providing the coated steel panels needed for this work.

It would be a form of unforgivable negligence if I do not mention my parents and my wife. These persons sacrificed their time, efforts, and education and devoted their support for me.

ABSTRACT OF THE THESIS

EVALUATION OF EXTERNAL COATING PERFORMANCE ON BURIED
PIPELINES IN THE OIL AND GAS INDUSTRY

by

Mohammed Alrudayni

Florida International University, 2015

Miami, Florida

Professor Norman Munroe, Major Professor

Protective coatings is used to enhance the corrosion resistance of buried pipelines. However, the effectiveness of epoxy-coatings may be compromised due to inadvertent presence of surface damage and coating disbondment. Additionally, the disbonded coated panels is expected to be less effective than that of scratched or un-defected panels. This research was designed to evaluate the coating performance of FBE and hybrid epoxy in simulated Arabian Gulf water and simulated soils conditions (Sabkha). The influence of coating damage and disbondment on corrosion resistance was also investigated.

Results of this research indicated a reduction in the adhesion bond between the coatings and substrate. The electrochemical impedance measurements demonstrated the need for an appropriate interpretation of results when this technique is used. The corrosion current density measurements indicated that both media are corrosive. Protective coatings under investigation did not show any blistering effect or color change under test conditions, thus reflecting their excellent corrosion resistance property.

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CHAPTER 1 - INTRODUCTION

For centuries, pipelines offered the safest, most efficient, and reliable method for transporting oil and gas. Mostly, these pipelines are installed underground to protect them from damage and to minimize the threat to the environment from spillage, which can result in an ecological disaster. In the US, there are more than 3.7 million kilometers of pipelines that transport natural gas and hazardous liquid. The global demand for a sustainable supply of oil and gas dictates an effective pipeline system. Therefore, economical and effective techniques to minimize the deteriorating effects such as corrosion and coating failure are critical for the lifetime of pipeline systems. Corrosion is considered the major reason behind most pipeline failure. Actually, over the years, corrosion has been the cause for many incidents including pipeline and tank explosions, bridge collapses, and material systems failures [1, 3].

Corrosion is defined as the chemical or electrochemical reaction of a material with its surrounding environment such as air, water, chemical products, and pollutants [1-3]. A recent review suggested that the corrosion cost for US oil and gas companies is more than half of the total cost (\$170 billion per year) [18]. Approximately one-third of this amount could be reduced if precautions are taken to select the appropriate materials and adopt the right techniques. For that reason, corrosion protection is required to maintain the integrity of buried pipelines system in order to prevent leaks, production disruption, and costly maintenance [1, 4].

For corrosion to occur, three elements are essential: an anode, a cathode, and an electrolyte. Oxidation occurs at the anodic site, where metal ions dissociate from the metal

surface into the electrolyte, which is the soil moisture. The electrolyte serves as the chemical medium that enables the transfer of dissolved ions to and from the anodic and cathodic sites. Electrons are lost at the anodic site through the circuit or metal to the cathodic site, where they are consumed by a reduction reaction. Many pipelines are buried underground and are exposed to soil, which is the surrounding environment. There are many factors that contribute to soil corrosivity. In fact, the corrosion of buried pipeline is influenced by the soil's moisture content, temperature, pH, and salt concentration. Moreover, the aggressiveness of the soil depends on the proportion of dissimilar soil type, differential aeration, dissimilar metals, new and old steel pipe, moisture content, ground water table, soil resistivity, soluble ions content, soil pH, oxidation–reduction potential, and the presence of microbes in the soil [2, 4].

The methods used to mitigate the external corrosion of pipelines are usage of protective coatings and cathodic protection. While in the soil environment, coatings are the primary protection of a buried pipeline as it helps to prevent external corrosion and to reduce power consumption in cathodic systems. Hence, in order to serve as an effective protection system, the coating should exhibit certain characteristic in terms of corrosion protection, such as limited water permeability, ionic resistance, good adhesion, and certain mechanical properties. Also, the coating needs to withstand severe weather including extreme temperatures [2, 4]. Occasionally, the aggressiveness of the soil can compromise the performance of the cathodic system [38]. Hence, the electrical conductivity of the soil determines the effectiveness of the cathodic system design. Therefore, a poor design or an increase in soil resistivity can lead to a loss of effective protection of the buried pipeline. Also, if the coating is exposed to high temperatures or excessive cathodic potential, it can

weaken the coating adhesion and cause cathodic disbondment of the coating. Furthermore, high temperatures can accelerate coating deterioration, which results in higher water permeability through the coating to the steel surface.

In this thesis, test panels coated with fusion bonded epoxy (FBE) and hybrid epoxy were immersed in synthetic Arabian Gulf water and synthetic water that represent Saudi Arabia's soil environment (called Sabkha) to study the coating performance including (adhesion, corrosion resistance, and coating degradation). The present work aims at studying two types of coatings assigned for the protection of the pipelines against corrosion, which are practically utilized in the oil and gas industry.

The main objectives of the present work are (1) evaluation of various pipeline coatings at different temperatures and simulated media by electrochemical techniques and (2) investigation of the performance of the coatings in the presence of different types of defects such as cathodic disbondment and scratch.

In the literature, there was no consensus in the specifications list, coating types, the thickness of those coatings, the lab and/or field tests that were utilized, the duration of those tests, or the method by which coating defects were created and assessed, or when coating failure was determined. Furthermore, there was no study on hybrid epoxy in a severe environment.

CHAPTER 2- BACKGROUND AND LITERATURE REVIEW

2.1. Corrosion Process of Metals in Soil

Most metals tend to corrode by reacting with their environments. The thermodynamics and kinetics are dependent on the type of metal and the environment. In this chapter, the concept of corrosion and some relevant aspects are described.

For corrosion to occur, three elements are essential: an anode, a cathode, and an electrolyte. The anode is the oxidation site where, metal M goes into the solution as an ion, leaving behind an electron.

An example of an anodic reaction: steel, which is mainly composed of the element iron, reacts to produce ferrous ions.

The released electrons move instantaneously through the metal, which is an excellent electrical conductor to a cathodic site, where reduction reactions occur. There are three possible reduction reactions that can occur at the cathodic site depending on the type of soil and corrosion conditions, as explained below [1, 3]:

2.1.1. Alkaline and Neutral Soils

Under alkaline or neutral conditions, water reduction occurs where the electrons released from the anodic sites are consumed.

The hydroxide ions (OH^-) migrate through the soil moisture toward the positive anodic sites to react with ions of the opposite charge ions to produce solid corrosion products according to equation (4) that tend to adhere on to the metal surface. Furthermore, this product provides some protection to the underlying steel by retarding the diffusion of corrosive ions as well as corrosion products.

The final product is known as rust, as described by equation (5)

2.1.2. Acidic Soil

Under acidic conditions oxygen reduction occurs as shown in equation (6).

No protective product is produced in this case. The third reaction occurs in the absence of oxygen and is referred to as hydrogen reduction.

Other reduction reactions are possible if there are dissolved ions such as Sn^{4+} , Fe^{3+} and Cu^{2+} , where they are consumed electrons and are reduced to lower oxidation states such as Sn^{2+} , Fe^{2+} and Cu .

2.2. Buried pipelines

For a buried pipeline, corrosion involves local electrochemical processes where water acts as an electrolyte at the pipeline surface. Usually, soil characteristics enable the

access of atmospheric oxygen to the pipeline surface, fostering biological activity microbial, induced corrosion (mic) which alter the chemical composition of the water phase in contact with the pipeline. Additionally, Sulfate-reducing bacterial sometimes influences corrosion whereby soluble sulfates present in the soil are reduced to sulfides [42, 44].

Figure 2.1 shows a situation where the buried pipeline is protected from the soil by a protective coating. If the protective coating remains intact and is impervious, corrosion will not occur. However, if water reaches the metal surface, corrosion is initiated on the pipeline, and this reaction is autogenous as described below. In this particular situation and due to the corrosion processes at the pipeline surface, change in composition can alter the chemistry of the trapped water.

Figure 2.1: Protective coating can enable water to reach the pipeline

An impressed current cathodic system is frequently used to protect buried pipelines. This system uses an external source of DC power (rectified AC) to impress a negative electrical current from an external anode onto the cathode surface.

Clay and silt soil types, which have fine texture and high water-holding capacity, result in poor aeration and poor drainage. These soil types are known to be more corrosive than soils of coarse characteristics, such as sand and gravel, where there is greater

circulation of air. As mentioned, buried pipelines corrode significantly by means of differential aeration and sometimes by bacterial action [30, 44, 53].

Buried pipeline exhibits differential aeration corrosion, which is similar to a concentration cell corrosion. In this situation, the difference in oxygen concentration results in a potential difference, which causes the current to flow. This type of cell is usually located at crevices formed at junction of pipes and is referred to a crevice corrosion. The areas of lower oxygen concentration (inside the crevice) become the anode, while the areas of higher oxygen concentration (outside crevice) become the cathode [2, 44]. Furthermore, differential aeration corrosion can cause pitting damage under rust at the water–air interface. The amount of oxygen reaching the steel surface having a permeable coating or no coating is greater than the amount that contacts other location that are covered by rust or other insoluble products, as shown in Figure 2.2 [2,4].

Figure 2.2: Buried pipeline exhibiting differential aeration corrosion [4]

Even though many chemical elements and their compounds are present in soil, only a limited number has a significant effect on corrosion. For example, in high-rainfall areas, the leaching of soluble salts and other compounds could result in the soil becoming acidic. In contrast, in arid areas, soluble salts are carried to the upper soil layers through capillary

action and evaporative processes, making these soils generally alkaline [42, 44]. Generally, the most corrosive soils contain high concentrations of soluble salts, especially sulfates, chlorides, and bicarbonates and can either be acidic (low pH) or alkaline (high pH) [41, 44].

2.3. Effect of Soluble Salts on Corrosion

Soluble salts may have the ability to degrade a coating on steel by causing osmotic blistering on low permeable coatings or at defect, thus accelerating corrosion. Yet, in some locations, salts are not a significant problem, while in others, salts may be very detrimental.

The amount of soluble inorganic solutes (anions and cations) in water or soil has a direct impact on the solution electrolytic conductivity. An increase in soluble ion content can decrease soil resistivity, which in turn will increase the corrosion rate in unprotected metals. On the other hand, some ions may have the opposite effect, e.g., calcium and magnesium ions tend to form insoluble carbonate deposits on the metal surface, causing a reduction in the corrosion rate [42, 44, 47].

Chlorides, sulfates, and sulfides ions have been recognized as being the primary agents in promoting corrosion. Locations with a high concentration of those ions have very low resistivity and can be potentially very aggressive with respect to metallic corrosion on unprotected steel surfaces. Therefore, accurate determination of chloride, sulfate, and sulfide concentration of the total salt content is an important element in determining corrosivity.

2.3.1. Effect of Chloride Ion on Corrosion

Chloride minerals are very soluble and thus ionize in aqueous solutions according to the following reactions.

Malik et al. [14] reported that the majority of FBE coating failure of rebar in soil was due to the permeability of chloride ions from low-resistivity soil and the subsequent attack of the iron bar. The corrosion and mechanical behavior of FBE have been investigated in aqueous media including water, distilled water, and saline water. The mechanical properties of the coating included adhesion, bending, and cathodic disbondment. While the corrosion testing included immersion under different conditions, the results indicated chemical inertness of the FBE coating and good adhesion and suggested that FBE was a promising material for internal coating of buried pipelines.

2.3.2. Effect of Sulfate Ion on Corrosion

The extraction and quantification of soil sulfur is a more complex problem compared to chloride. Sulfate is present in soil in different forms: the inorganic sulfate may occur as water soluble (i.e., sodium sulfate), sparingly soluble (i.e., gypsum), or insoluble (i.e., jarosite) minerals. The solubility of sulfate is also restricted in some soils by absorption to clays and oxides or by co-precipitation with carbonates. Usually, the soluble

sulfate will not represent the total sulfate in all soils. However, it is a good way to quantify the soil solution activity with respect to corrosion potential [39, 44].

Altayyib et al. investigated the role of sulfate ions on reinforced steel corrosion at 22°C and 50°C by using linear polarization resistance (LPR) and electrochemical impedance spectroscopy (EIS) techniques. They found that an active corrosion results from a buildup of sulfate film, which is less protective than iron oxide film. Also, at high temperature, a 7-fold increase in corrosion rate occurs compared to chloride ions at normal temperature [47, 48].

In 2005, the European Commission investigated the effect of soluble salt contamination on steel surfaces and the durability of subsequently applied coatings [42]. They found that the effect of sulfate, especially under immersion and cathodic protection conditions, was very harmful and corrosive either when present alone or in combination with chloride. Furthermore, the two systems (FBE and glass flake epoxy (GFE)) evaluated under cathodic protection were both very sensitive to ion contamination. The FBE appeared sensitive to chloride but not sulfate, while a single coating of GFE was sensitive to both ions [42].

2.4. Soil type

The Canadian best practice to mitigate external corrosion on buried pipelines summarized the effect of different soil types/resistivity on bare steel with no cathodic protection on external corrosion rates. As shown in Table 2.1 [68], low soil resistivity and wet conditions produce very high corrosion of > 1.0 mm/yr. Whereas high resistivity and dry conditions result in non-corrosive rate < 0.2 mm/yr.

Table 2.1: Soil Resistivity Effect on Corrosion Rates [68]

Soil Resistivity (Ohm-cm)	Soil Type	Moisture	Corrosion (mm/yr)
<500	Muskeg/sloughs/free water accumulation	Always wet	Very corrosive >1.0
500–2000	Loams/clays	Mainly wet	Corrosive to moderately corrosive 0.5–1.0
2000–10000	Gravels, sandy	Mainly dry	Mildly corrosive 0.2–0.5
>10000	Arid, sandy	Always dry	Noncorrosive <0.2

2.4.1. Soil (Sabkha)

Sabkha is located on the western coast of the Arabian Gulf, Saudi Arabia, and characterized as a siliciclastic-dominated soil, with minor bioclasts and surrounded by tertiary carbonates as shown in Figure 2.3. It is wet most of the time, as the ground water table is shallow (<120 cm in depth). Basyoni and Mousa [32] studied brine samples of Sabkha soil and found that the majority of groundwater in Sabkha soil is composed of chlorides ($MgCl_2$ and $CaCl_2$). Also, due to capillary rise phenomena, evaporation resulted in the deposition of minerals in the Sabkha by the “ascending-brine” mechanism. Table 2.2 shows the chemical composition of the Sabkha soil. It should be noted that the concentration of sulfate is high (5552 mg/l), which is close to the Arabian Gulf side [32].

Figure 2.3: The surface of the bare Sabkha zone [32]

Table 2.2: Chemical Analysis of the Major Elements (mg/l) in the Brine Samples of Sabkha [32]

Samples No.	Temperature (°C)	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl	HCO ₃ ⁻	SO ₄ ²⁻	T.D.S.	Cond. µs/cm.	pH
Gulf water	22.0	473	1770	15270	486	24126	151.00	1123	49000	63300	8.00
I. 1	22.5	750	12258	115320	3334	211000	91.20	5552	295200	231000	6.80
I. 2	30.4	969	11528	122550	1701	208000	89.10	3680	318000	234000	6.80
I. 3	32.4	959	9716	110780	2937	203500	73.00	3090	302600	234000	6.85
II. 1	33.8	2131	7900	82340	1610	150000	49.60	1443	237400	216000	6.84
II. 2	24.0	590	9690	119480	2935	235000	122.40	1904	313200	238000	6.90
II. 3	29.5	1564	11972	140925	2888	226000	169.00	3668	298600	236000	6.70
II. 4	28.7	631	9272	124340	2502	257000	23.10	3440	305000	237000	6.66
II. 5	29.3	1711	6664	99060	1524	190000	34.10	3452	253800	224000	6.64
III. 1	32.5	812	10916	128540	4166	230000	33.60	1400	339200	243000	6.50
III. 2	33.6	902	8976	117310	1833	189500	114.00	1400	282800	234000	6.70
III. 3	34.7	2100	10180	114180	1927	188500	50.00	2832	303600	240000	6.66
III. 4	30.0	1854	7300	79260	2280	131500	78.20	4460	209400	202000	6.80
IV. 1	31.5	3329	9800	137800	3141	289000	17.60	2220	329800	244000	6.50
IV. 2	33.1	2157	9192	136075	3209	260500	26.00	2070	324200	246000	6.67
IV. 3	29.5	3145	8640	111380	2439	184000	64.90	2158	273800	229000	6.64
IV. 4	30.9	938	8228	117080	2089	191000	45.00	2028	277600	231000	6.66
IV. 5	29.2	719	9464	118680	2393	192000	119.00	2104	287600	235000	6.70
IV. 6	30.1	599	1813	54480	319	59689	73.20	3360	94200	116600	7.30
V. 1	28.0	1819	5924	125280	1771	178000	16.40	2898	307570	207000	4.50
V. 2	35.6	1586	5348	121180	2595	186000	28.70	2714	311880	206000	5.60
V. 3	30.1	1894	5904	121080	2949	209500	46.00	2550	261184	204000	5.70
V. 4	34.1	1453	4692	107520	2822	170000	50.30	3250	201372	202000	6.50
V. 5	36.5	1931	6134	118020	2051	183500	47.90	2470	302176	207000	6.50
V. 6	31.1	1591	4054	84920	1374	148000	34.70	4440	231194	187700	6.60
VI. 1	31.9	1624	1834	6366	618	47040	93.30	804	93224	95000	7.52
VI. 2	30.8	1480	5002	81600	1129	139000	30.60	3334	217570	180200	6.50
VI. 3	31.0	1329	1902	26970	597	50563	166.10	3404	87058	85100	7.00
VI. 4	29.8	1204	1260	11660	226	20247	157.00	2996	38392	44200	7.00
VI. 5	31.1	1091	1592	31995	556	32305	129.40	720	58850	63300	7.40
VII. 1	34.1	1447	3236	68565	901	88212	61.80	2676	145308	143800	7.70
VII. 2	35.5	1545	4104	64220	1217	113800	48.90	3288	201800	173500	6.90
VII. 3	33.5	1449	4728	107260	1529	198000	33.80	2780	256356	198000	6.50

Basyoni and Mousa [32], in their report, provided climatic data for 10 years from 1991 to 2000, which indicated that the Sabkha is characterized by hot and humid summer months (July–September). The average maximum temperature is 35.8°C (in July) and the average minimum temperature is 15.5°C (in January). The maximum average relative humidity is 70.32% (in December), while the average minimum relative humidity is 34.7% (in June) [32].

Table 2.3 summarized two different investigations by Al-Amoudi [49] and Al-Saaran [50], who studied the different soluble ion concentrations of the Sabkha brine near the Arabian Gulf area of significance is the high concentration of salts and Cl⁻. It can therefore be concluded, that the Sabkha environment is very aggressive for buried pipelines due to high salt concentration and a shallow water table.

Table 2.3: Chemical Analysis of Sabkha & Arabian Gulf Water [49, 50]

Parameter	Sabkha [50]	Sabkha Brine [49]	Gulf water [50]
Na ⁺ (ppm)	73,300	78,800	20,700
Mg ²⁺ (ppm)	7,400	10,320	2,300
K ⁺ (ppm)	3,260	3,060	730
Ca ²⁺ (ppm)	4,900	1,450	760
Sr ²⁺ (ppm)	-	29	13
Cl ⁻ (ppm)	151,800	157,200	36,900
SO ₄ ²⁻ (ppm)	2,700	5,450	5,120
HCO ₃ ⁻ (ppm)	30	87	128
Br ⁻ (ppm)	-	490	121
pH	6.9–8.0	6.9	8.3
Resistivity (Ohm-cm)	5	4.8	25
Total dissolved solids (ppm)	80,000–310,000	-	35,000

Malik et al. [11] evaluated a type of coating called Souplethane rebar concrete sample. Uncoated, scribed coated, and coated panels were used and exposed to 5% NaCl, splash zone in Arabian Gulf water, salt fog, atmosphere, and Sabkha soil. The results for the uncoated samples indicated the following corrosion trend (in decreasing order);

5% NaCl > Sabkha > splash zone > salt fog > atmosphere.

However, the corrosion trend for the scribed sample appeared to follow the sequence:

5% NaCl > splash zone > Sabkha soil > atmosphere.

2.5. Corrosion Protection

In order to prevent or mitigate corrosion of metals, many techniques are employed. In the oil and gas industry, a combination of protective coating and cathodic protection is often used to protect pipelines depending of the environment.

2.5.1. Protective Coating

Coatings are the first line of defense against corrosion. Coatings are known to prevent corrosion by four primary means. Firstly, by barrier resistance through which the coating film prevents the corrosive elements from coming in contact with the metallic substrate; secondly, by the electrical resistance that the coating offers, restricts electrical conductivity in the corrosion circuits; thirdly, cathodic protection where an electrical current counteracts the corrosion current and fourthly, through anodic or cathodic chemical inhibition of the corrosion process [30, 38].

Coatings are defined as films applied to the surfaces of structures, piping, tanks, and offshore structures. Although there are numerous types of coatings, they are similar in composition, consisting of four principal components: 1) Vehicle or binder, 2) solvents, 3) pigments, and 4) additives. Vehicle is the most important component that forms the film and provides the necessary integrity to prevent corrosion. It provides basic physical properties such as resistance to water, hydrocarbons, and other chemicals and to weather. Typical vehicles include epoxy, phenolic, alkyd, vinyl, and acrylic which are polymers. Solvents are the key to any coating's success because they provide viscosity, drying properties, and flow control. Solvents are used to dissolve the vehicle so that the coating may be uniformly applied to the surface. Pigments are solid materials that deliver

atmospheric resistance, corrosion resistance, color, and toughness. Additives are small amounts of liquid or solid that control the drying and curing of the coatings, flow, and wetting.

The required properties of pipeline coatings are as follows [68]:

- 1) Coating should have a high electrical resistance in order to isolate the external surface of the piping from the environment.
- 2) Coating should be an effective moisture barrier.
- 3) Coating should have good ductility to resist cracking.
- 4) Coating should have sufficient strength and adhesion to mitigate soil stress and normal handling.
- 5) Coating should be compatible with cathodic protection to prevent shielding.
- 6) Coating should be resistant to chemical and physical damage or degradation during service.
- 7) The use of the coating should not impart or pose any environmental or health risks.

Pipeline coatings have been in constant development and in use for more than 80 years. In addition to the selection of the proper coating, other variables affect coating performance and long-term durability. These variables are as follows:

2.5.1.1. Environment

The environmental conditions in which a surface coating system is exposed can have a significant effect on the performance and durability of the coating.

2.5.1.2. Surface preparation

Surface preparation is the most important factor that can affect coating performance. Perhaps more than 70% of coating failures result from inadequate surface preparation. In most cases, surface preparation can account for as much as 40%–50% of the total cost. Usually, the quality of proper surface preparation is controlled by accessibility.

2.5.1.3. Application

Protective coating can be applied using a brush, roller, or spray equipment. Mostly, coatings are shop applied, but it can also be field applied. Shop application is much faster and usually can be controlled more easily.

2.5.1.4. Inspection

Inspection of coatings is an important step to ensure high quality and long life of the protective coating. In general, the inspection should be more detailed when the coating system is more sophisticated. Rapid failures of protective coatings is a result of not performing inspection. These failures may occur quickly, causing shutdown of critical equipment units, facilities, or vessels for long periods of time, which can cause huge losses.

For over 60 years, the oil and gas industry has used several types of coatings for buried pipeline, including asphalt, coal tar, epoxy, FBE, polyethylene, and urethane coatings.

Coatings are usually classified based on the resin binder, which provides protective properties and resistance to degradation. Different coating resin types exhibit different

properties such as good adhesion to substrate. According to the coating's formulation, they can be used as primers or top coats.

2.5.1.5. Protective Coatings generic type

2.5.1.5.1. Fusion Bonded Epoxy Coatings

FBE is widely recognized as the most used pipeline protective coating system. This type of coating is dielectric, meaning it cannot conduct current and therefore isolate the path for galvanic currents to flow, which breaks and terminates the corrosion process [38, 68].

FBE is known to be hard and durable to withstand abrasion under normal construction conditions and have strong mechanical as well as chemical properties that help in bonding to the substrate to ensure long-term integrity. Also, it does not shield the cathodic protection of the pipelines [28, 29].

Moreover, FBE coatings have low permeability to gases and moisture and free of microscopically thin gaps at the substrate–coating interface.

The disadvantage of FBE is that it requires more surface preparation and application techniques than most plant-applied coatings, therefore requiring more attention during the coating process. Higher temperatures may cause more water to permeate through the coatings and cause cathodic disbondment, especially if surface contaminants are present. When stored outside, UV rays can cause the FBE to become chalky and grainy [38, 68].

2.5.1.5.2. Hybrid Epoxy

Hybrid epoxy is an advanced 100% solid, two component epoxy. It is designed to protect the external of the pipeline. It has much less cure temperature (around 4°C), which allow quick quality control and backfill times. There is not much research in the literature regarding its performance with cathodic protection. Hence, it is mentioned that it should have an excellent cathodic protection and provide a superior adhesion to steel over FBE.

2.5.2. Cathodic Protection

Corrosion requires direct contact between electrolyte “moisture” and metal; hence, coating this metal, which is completely waterproof and absolutely holiday free, would not prevent the metal from all forms of attack. Protective coating is the primary method to resist underground corrosion. However, “coatings are never perfect,” deterioration, soil stress, environmental factors, and external damage would cause some coating areas to fail. Therefore, cathodic protection provides additional protection at holiday or soil damaged areas of the coating. Thus, protective coating and cathodic protection work together to protect the buried pipeline.

Cathodic protection is an electrochemical process that reduces the corrosion rate on a metal surface by decreasing its corrosion potential, bringing the galvanic potential of the metal to the immune state level to be protected. If not applied properly, cathodic protection can have a negative effect on coating as it may cause blistering or cathodic disbondment of the coating. Loss of adhesion between the coating and substrate consequently leave a void on the metal. The level of cathodic protection varies for each type of coating. The required electrical strength of a coating is often defined as the resistance per square foot

unit of coating. The effective current density measurement is related to coating capacitance [4, 38].

Some coating properties can act as an electrical insulator to the external layer, such as polyolefin tape coating, which can prohibit the cathodic protection from reaching the pipe surface in disbanded areas.

2.6. Mechanisms of Coating Degradations

Damage such as macroscopic and microscopic defects including pinholes, voids and mechanical scrapes, and scratches, which will allow access of the environment to the substrate metal to the external surface of pipelines is almost unavoidable. Wood [10] suggested that pure epoxy coatings on carbon steel showed brittle erosion behavior, while FBE showed mixed ductile and brittle behavior. But glass fiber reinforced epoxy showed strong ductile behavior. Darwin et al. [19] studied FBE coating behavior in poor-quality concrete and exposed the samples to cyclic wet/dry environment over a period of 12 months using 3.5% NaCl or demineralized water. After the end of the test, the bars were removed for visual inspection and assessed for corrosion rate in terms of weight loss. He also examined the presence of coating holiday and chromate conversion, and concluded that FBE provided excellent corrosion resistance, which was further enhanced by the presence of chromate conversion coating.

Elleithy et al. [20] evaluated the effect of holidays and damage to FBE on reinforcement corrosion in chloride contaminated concrete. Corrosion potential and corrosion current density measurement were utilized to evaluate the effect of the corrosion of FBE coated bars. The results showed that surface damage to FBE coating was more

critical compared to holidays. Also, they found that at 2% wt. chloride in the concrete specimens FBE bars were passivated.

Holub et al. [63] investigated the performance of coatings under different standard cathodic disbondment test conditions, and found major issues in test reproducibility as well as inconsistency in the results. These discrepancies were attributed to different parameters and procedures that were utilized in test standards. For example, some cathodic disbondment test standards utilize different test temperatures, electrolyte, concentrations, and test durations.

Alamilla et al. [9] presented a failure analysis of FBE-coated buried pipelines. The reasons suggested for external corrosion were characterized by two corrosion mechanisms involving iron oxides and iron sulfides. Furthermore, the ductile type failure was attributed to leakage. In this study, an environmental analysis that included soil chemical analysis was carried out. The high Cl^- ions present in the system, inhibited the formation of passive films on the steel. The soil was observed to have low resistivity of 182 Ohm-cm, which may have contributed to the corrosion rate 0.7 mm/year. A scanning electronic microscope (SEM) was used to characterize the steel coating. The results indicated good adhesion between the FBE and the substrate and an adequate coating thickness of 470 to 480 μm .

2.7. Preparation of Synthetic Water

In this study, synthetic saline water was prepared based on the chemical analysis of the Sabkha soil. The procedure described by Lyman and Fleming was adopted for the preparation of Sabkha water with adjustment for high salinity [70]. For example, to prepare 1 liter of saline water, two major steps were taken. The first step required preparation of a

stock solution by mixing 100 ml distilled water with 6 g potassium chloride (KCl), 90 mg strontium chloride ($\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$), 150 mg sodium bicarbonate (NaHCO_3) and 8.25 g sodium sulfate (Na_2SO_4). After that, the 100 ml stock solution was again mixed with 1 liter of distilled water, followed by mixing with the following dry chemicals: 5.5 g calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$), 200 g sodium chloride (NaCl) and 87.5 g magnesium chloride ($\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$). Then, the sample was subjected to chemical analysis. The chemical composition of the prepared synthetic water based on both calculated and measured values is shown in Table 2.4. This saline water is expected to be a representative of the Sabkha soil environment existing in Saudi Arabia [36].

The same procedure was also adopted to prepare Arabian Gulf water, but with different salt concentrations. The results are shown in Table 2.5.

Table 2.4: Chemical Composition of Synthetic Sabkha Water.

<u>Parameters</u> <u>(ppm)</u>	<u>Local</u>	<u>Calculated</u>	<u>Measured</u>
HCO_3^-	30–87	87	46
Cl^-	151,800–157,200	151,000	140,000
SO_4^{2-}	2,700–5,450	5,500	4,900
Ca^{2+}	1,450–4,900	1,450	1,100
Mg^{2+}	7,400–10,320	10,320	8,700
Na^+	73,300–78,800	81,578	79,000
K^+	3,060–3,260	3,060	3,300
Sr^{2+}	29	29	
PH	6.9–8.0		6.95

Table 2.5: Chemical Composition of Synthetic Arabian Gulf Water.

<u>Parameters</u> <u>(ppm)</u>	<u>Local</u>	<u>Calculated</u>	<u>Measured</u>
HCO ₃ ⁻	128–151	128	100
Cl ⁻	24,000–36,900	35,000	34,000
SO ₄ ²⁻	1,120–5,100	3,300	2,800
Ca ²⁺	420–473	420	350
Mg ²⁺	1,550–1,770	1,550	1,400
Na ⁺	15,270–20,650	20,540	21,000
K ⁺	486–730	660	760
PH	8–8.3		7.69

2.8. Barrier Property Detection of Coating Deterioration

Protective coatings are often used to protect pipelines and steel structures against corrosion. Hence, coatings act as a barrier to slow down the ingress of aggressive ions to the metal/coatings interface. Usually, the protective coating possesses very high electrical resistance, which restricts the movement of ions between the anodic and cathodic areas. Therefore, Electrochemical Impedance Spectroscopy (EIS) technique is useful to assess the protective ability of a coating system since it provides a measurement of the impedance which indicated material degradation. A coating absorbs water, causes the substrate to corrode. Dielectric or chemical changes to the metal/coating interface are time dependent as the ingress of aqueous solutions take place which can be represented on a Bode plot with a slope of magnitude slightly less than 1 [17, 65]. Most researchers measure EIS spectra by starting at the high frequency and progress toward low frequency with the objective of

measuring the maximum number of data points before the system changes, since measurements at low frequencies take much longer or are not always possible [17, 62, 67].

EIS spectra are analyzed under the assumptions of linear behavior and steady state equilibrium, which is important if an “equivalent circuit” technique is to be utilized.

2.8.1. Coating Adhesion

A good adhesion between the coatings and the substrate is recommended to inhibit corrosion and prevent delamination. However, corrosion protection and adhesion of the film are inter-related. It is not clear if loss of adhesion is a direct consequence of the corrosion process or vice versa, but the relationship between adhesion and corrosion remains a subject open to discussion. Nevertheless, polymer–metal bonding exhibits low surface energy, which normally translate in poor adhesion to the metal substrate [38].

The strength and stability of the coating adhesion to the substrate is a critical factor in the long-term epoxy performance. There is abundant information and practical evidence that epoxy coating adhesion to metal substrate is partially or totally lost when it is exposed to water or high humidity. Such exposure may quickly lead to coating delamination. This phenomenon of wet-adhesion loss has been investigated by many scientists. It can be described as the penetration of water through the coating down to the polymer/metal interface or to bonding compounds as a result of electrochemical decomposition of water at this interface. In both cases, the bond between the hydroxyl or other polar groups from the resin and the metal oxide layer on the substrate is destabilized [29, 30].

Understanding the adhesion of protective coatings to metal substrates is crucial for the prediction of coating performance. There are some methods to measure the adhesion of

thin coatings, but experimental measurements of polymer adhesion are qualitative or problematic. However, pull-off tests described in ASTM D4541, provide a quantitative assessment of adhesion.

Samimi et al. [15] reported that polyurethane coatings exhibit excellent properties such as good adhesion, high temperature tolerance corrosion resistance and compare it with FBE coating. It was concluded that polyurethane coating is suitable for external pipeline for oil and gas transportation.

Mobin et al. [37] investigated the performance of FBE coatings under water transmission lines. Adhesion tests were performed between the coating and pull stub interface. During the test, the pull stub was detached at the coating/ pull stub interface. This confirm that the bonding between the metal substrate and the coating was better than the coating and pull stub. Also, this showed that that the strength of epoxy adhesive was not sufficient to pull off the coatings from the metal substrate.

2.8.2. Role of Temperature

Angeles et al. [51] evaluated epoxy coatings with iron oxide pigment at temperatures of 25, 65, 85, and 100°C based on the degradation parameters measured by EIS. The results showed that there was no damage in their protective capacity over time at 25°C. As temperature increases, the plots do not show the same behavior, which is evidence of the thermal effect each sample encountered. This was concluded by Angeles et al. from the Bode plots because in the original sample (at 25°C), an impedance value of the order of 10^7 Ohm-cm² and more than one time constant can be observed. Conversely, the sample aged at 85°C showed a capacitive behavior with impedance range of 10^{10} Ohm-cm² and

phase angles close to 90° . Therefore, the high impedance was attributed to the oxides on the metal/paint interface, which blocked the pores and prevented electrolyte permeability. However, the sample aged at 100°C showed a performance different to that expected for an insulated coating, although the impedance value was 10^7 Ohm-cm^2 , the phase angle showed at least two time-constants.

Rezaei et al. [24] studied the influence of temperature on the impedance of polyurethane coating immersed in 3.5% wt NaCl. The results showed a significant decrease in the diffusion behavior and coating resistance at 75°C compared to the results at 25°C . The study concluded that the impedance spectra of some coatings are sensitive to temperature; however, some high impedance coatings exhibit little change in the impedance over a temperature range of $25\text{--}80^\circ\text{C}$. Generally, degree of the coating protection decreases at higher temperatures due to the increase in diffusivity of the electrolyte.

In summary, the coating barrier properties decrease at higher temperatures due to the increase of the electrolyte diffusion rate through the coating film. Furthermore, the film ages, the rate of corrosion increases at the coating/metal interface. In addition, the loss of this barrier property is more significant in the presence of ions.

2.9. Cathodic Disbondment

Huichao et al. [16] found that the cathodic disbondment of epoxy coating in 3.5% NaCl was similar for both the semi- and fully immersed conditions.

Lee et al. [13] evaluated polyethylene coating in synthetic ground water. A variety of electrochemical techniques was used including EIS, potentiodynamic, and potentiostatic polarization tests and morphology analysis using SEM. Those tests were employed to accelerate and evaluate the coating degradation. Resistance values oxide resistance (R_{oxide}), charge transfer resistance (R_{ct}) and pore resistance (R_p) after anodic, cathodic and pulsed potentiostatic polarization tests showed that the coating delamination was accelerated effectively by the pulsed potentiostatic polarization test. Therefore, the pulse potentiostatic technique accelerated both anodic and cathodic reactions and generated the coating degradation mechanisms: cathodic disbondment and oxide lifting.

Wang et al. [12] studied the effect of cathodic protection on corrosion with disbonded coating. Various measurements were recorded, including pH, polarization potential, current density, and dissolved oxygen concentration. The result of this work revealed that cathodic protection system could not reach the crevice bottom, which reduced the effectiveness of corrosion protection. This effectiveness depends on the crevice geometry and could be improved with the increase of crevice length and decrease of its mouth size.

Amadi et al. [23] evaluated the performance of three types of coating: FBE, polyethylene, and polyurethane. A variety of tests was conducted, including cathodic disbondment, exposed to salt fog, and pull-off adhesion. This research illustrated the usefulness of anticorrosion agents in improving the rate of reducing corrosion effect on materials.

2.10. Electrochemical Impedance Spectroscopy Test

EIS has been widely recognized as an ideal technique to study corrosion resistance of organic coatings. Also, it has been used to investigate the degradation of organic coated metals because it can measure high impedance systems and provide information. Advantages of this technique over DC and conventional techniques include the absence of any significant perturbation to the system and its applicability for assessment of low-conductivity media such as polymers. Moreover, this method is nondestructive and can reveal early signs of coating degradation [17].

Enos et al. [31] conducted a comparative study of cathodically disbonded coated panels using EIS followed by corrosion analysis. An FBE-coated panel was compared to a modified FBE-coated panels. They found that the damaged FBE coating healed and recovered much of its properties.

Bierwagen et al. [22, 61] studied FBE coating at different temperatures using EIS measurements and plotted Bode and Nyquist plots to interpret the data. During the test, the coating was immersed in 3% wt NaCl electrolyte at 25°C, and the results showed a decrease in coating resistance and an increase in its capacitance with temperature. At higher temperature, a further decrease in resistance and higher capacitance were noted. Thermal effects on FBE coated steel immersed in NaCl solutions were also studied by EIS, noise resistance (R_n), and direct current resistance (RDC) at temperatures 28°C–95°C. The Nyquist plot, revealed a significant decrease in impedance as the temperature increased. Whereas, the Bode plot, indicated that $|Z|$ remained constant at low-frequency and decreased drastically as the temperature increased. In fact, the logarithm of all three

measurements (R_{DC} , R_n , and $|Z|_{\text{low frequency}}$) of the resistance properties of the coating indicated that they were following an Arrhenius relationship of temperature dependence where the log (property) is linear in $1/T$, as shown in Figures 2–4.

Figure 2.4: R_n , Z , and R_{DC} at 3%wt NaCl for FBE coating vs. $1000/T(K)$ [22]

Oliveira et al. [25, 26] used EIS measurement to rank different coating systems according to their susceptibility to degradation when immersed in 3% wt NaCl at different temperatures. Yet, the detection of coating degradation enabled an assessment of interaction between specific regions of the organic coating with the environment.

Jadoon et al. [8] conducted a field study for FBE coating for ultrahigh strength steel. The following tests were conducted on the coating: adhesion, water immersion at 50°C for 28 days, cathodic disbondment, impact, flexibility, strain polarization resistance, and

coating porosity. An EIS analysis was performed to assess the corrosion protection associated with FBE coating. Using the Bode plot, a slope of -0.93 was found before the immersion, which indicated that the coating film was behaving as a capacitor. After 28 days of immersion, a slope of -0.86 was recorded, which indicated less resistance, but yet retained the capacitive nature. The Nyquist plot showed an increase in curvature as the immersion time increased, which was an indication of ionic species ingress from the portable water through the coating film, as shown in Figure 2.5.

Figure 2.5: Nyquist and Bode plots after water soak tests [8]

Thu et al. [6] examine the degradation kinetics of four thick organic coating under cathodic protection in seawater using EIS. It was not possible to examine the experimental data through EIS spectra using two models: classical equivalent circuits and dipolar relaxation of polymer layer; however, modified equivalent circuits were used. The results showed that a solvent-free coating exhibits the best compatibility with cathodic protection.

2.11. Scope and Objectives

The objective of this research was to assess the coating performance including (adhesion, corrosion resistance, and coating degradation) for the two coatings, namely, FBE and hybrid epoxy, in the simulated soil environment (Sabkha and Arabian Gulf water). To meet the objectives, the work was subdivided into the following specific goals:

- 1) Synthesize the actual Saudi Arabia's severe soil environment (Sabkha) and Arabian Gulf water.
- 2) Characterize the coatings' degradation.
- 3) Evaluation of FBE and hybrid epoxy coatings using various electrochemical techniques such as EIS, LPR, and open-circuit potential (OCP) at different temperatures.
- 4) Elucidate the coating degradation that led to corrosion.
- 5) Verify the electrochemical equivalent circuit to enhance the measurement of the coating properties.
- 6) Investigate the performance of protective coatings in the presence of different defects, coating disbondment, and scratches.

Hypothesis

In order to evaluate the thesis objectives, the following hypothesis has been postulated.

- Cathodic disbondment has a detrimental effect on coating degradation and corrosion resistance of FBE and hybrid epoxy coated pipelines.

CHAPTER 3- METHODOLOGY AND EXPERIMENTAL PROCEDURE

In this chapter, the experimental methods of the acceleration corrosion, evaluation of the effectiveness of organic coating, and characterization of the coating degradation are described. An optical microscope and SEM were utilized to describe the degradation of the coating. LPR was used to evaluate the corrosion behavior of the substrate and protective coating. EIS is a state-of-the-art technique used for evaluating the protective efficiency of the coatings in industrial field. Protective coating with high impedance implies low permeability to the corrosive fluid, and therefore provides more protection to the steel.

3.1. Testing Materials

Two types of organic coating, FBE and hybrid epoxy, were provided by the manufacturing company.

Coated test panels with a dimension of 150 mm $\times$ 50 mm with 5 mm thickness carbon steel substrate, as shown in Figure 3.1 were used in this investigation. These testing specimens were prepared by the supplier by blasting the substrate to achieve a profile of (2–4) mils and (2.5–4.5) mils for FBE and hybrid epoxy, respectively. The thickness of the FBE and hybrid epoxy coating was 13–21 mils and 25–35 mils, respectively.

Figure 3.1: Example of FBE and hybrid epoxy coated panels received from manufacturers.

3.1.1. Testing Cell

The corrosion testing cell consisted of a customized cylinder vessel with three electrodes, as shown in Figure 3.2. An acrylic cylinder (diameter = 1.5 inch) was mounted directly on a coated test panel using silicon glue. A saturated calomel reference electrode (SCE) with a potential of $0.241 \text{ V}_{\text{SHE}}$ was employed and titanium was utilized as the counter electrode (CE). The steel substrate served as the working electrode (WE). When the defective panels were being tested, titanium with a constant potential of -0.110 and $-0.170 \text{ V}_{\text{SCE}}$ in Gulf water and Sabkha respectively were utilized as the reference electrode.

Figure 3.2: Corrosion testing cell for coated substrate

3.1.2. Electrolyte

Two media (Arabian Gulf water and Sabkha) were used as the electrolyte in all electrochemical tests. The electrolyte was assumed to simulate the actual environment in Saudi Arabia. The electrolyte solutions were prepared as previously mentioned in chapter 2.6.

A volume of 75 ml of Sabkha and Arabian Gulf water were used for each corrosion test in this investigation.

3.2. Schematic of the Research Plan

The flowchart in Figure 3.3 illustrates the research plan involved in studying the effect of cathodic disbondment and scratch tests for FBE and hybrid epoxy coated panels in terms of protectiveness and corrosion resistance.

Figure 3.3: Schematic of the research plan

3.3. Material Characterization

The analytical techniques used in this research include SEM and optical microscopy analysis. A cross section from the coating and metal substrate was embedded in two-component epoxy resin using a mold. Then, it was repeatedly wet grinded using 300, 400, and 600 grit silicon carbide abrasive paper to achieve smooth and scratch-free surface, as shown in Figure 3.4. After that, the specimens were polished using alpha alumina 0.5 and 1 μm , and then washed with distilled water.

Figure 3.4: Grinder and polisher apparatus

3.3.1. Scanning Electron Microscopy

A JEOL JSM-6330F low-vacuum SEM with EDS was used in this test. The degradation of the coating was examined using SEM using different working distances, beam energies, and magnifications in order to get high-magnification image.

3.4. Pull-Off Adhesion

There are three types of coating failures: adhesive, cohesive, and substrate. In an adhesive failure, the coating is separated from the metal substrate and does not leave any coating attached. In cohesive failure, the coating breaks and leaves a layer of coating on

the substrate. Third, in substrate failure, cohesive occurs when the substrate fail instead of the coating as shown in Figure 3.5. Pull-off adhesion of coating was used to quantify the adhesive strength of the coatings.

Figure 3.5: Types of coating failure: a) adhesive, b) cohesive, and c) Substrate failure [71]

Pull-off adhesion was performed to determine the effect of Sabkha and Arabian Gulf water on the adhesive strength of the coating. The coated panels (before and after immersion) were subjected to pull-off adhesion test at room temperature in accordance

with ASTM-D4541. A portable manual adhesion tester (Elcometer 110 PATTI) was used in this test, as shown in Figure 3.6. In this test, a true axial tensile stress is applied relative to the pull stub axis. The magnitude of the tensile stress was recorded which is indicative of the strength of the bond between the coating and the substrate. The pull-off adhesion test was performed by attaching an aluminum pull stub perpendicular to the coating's surface with an epoxy adhesive. After the adhesive was cured, the pulling piston was attached to the stub. Increasing pressure was applied to the pull stub until it detached from the surface. The tester gave the maximum pressure (Psig), and this value was converted to bond strength (pull-off tensile strength in Psi).

Figure 3.6: Pull-off adhesion tester

3.5. Chemical Resistance (Immersion)

Two test media (Arabian Gulf water and Sabkha) were utilized at two operating temperatures (room temperature and 36°C). The high-temperature immersion was carried out by placing test panels inside the incubator, as shown in Figure 3.7.

Figure 3.7: Incubator (temperature-controlled environment)

3.6. Surface Defective Panels

3.6.1. Scratch

Scratch or (defects) is a mode of coating failure that frequently occurs in externally coated pipelines. Therefore, scratch test is a widely used test procedure for evaluation of coatings using (Elcometer 1538), as shown in Figure 3.8.

The linear defect produced was 1 ± 0.1 inch long and 0.02 inch (0.5 mm) wide with an area of about 0.02 in^2 (12.9 mm^2).

Figure 3.8: Scratch-coated panel

3.6.2. Cathodic Disbondment

Cathodic disbondment test method is an accelerated procedure for determining the extent of coating delamination under simulated environment following modified ASTM-G8 & G42. Also, it provides a comparative characteristic of coating systems applied to the external of pipeline for corrosion prevention that may occur in buried service where pipeline is in contact with natural soil and receive cathodic protection.

The coated panels were subjected to a constant potential in a highly alkaline electrolyte. Electrical source (potential) was obtained from an impressed DC system, as shown in Figure 3.9. A multimeter (Hewlett Packard 34401A) was used to measure the current and potential throughout the duration of the test. At the end of the test period, the panels were subjected to sharp knives test and immersion test.

In this test method the coated test panels were subjected to a potential of about -1.43 ± 0.01 V in a highly alkaline electrolyte of pH 10.47, as shown in Figure 3.10. The coated panels (before and after cathodic disbondment) were subjected to EIS and LPR.

Figure 3.9: A multimeter used in the investigation

Figure 3.10: the power supply and CD experimental setup

Figure 3.11: CD test setup

3.6.2.1. General Adhesion

The test involved making two scratches through the coating to the metal substrate, using a utility knife. The scratch formed a 'V' with an angle of intersection of approximately 30°. Adhesion was determined by inserting the blade of the utility knife at the point of intersection of the 'V' and attempting to remove the coating using a levering action.

The adhesion results were rated in accordance with the following guidance, which mirror the rating schemes in the Canadian Standard Z245.20 and the NACE Recommended Practice RP0394-2002.

- Rating 1: The coating pieces removed are the same size as, or smaller than, the size of the inserted knife point.
- Rating 2: Coating can be removed in chips that are slightly larger than the inserted knife point. Coating remains on 50% or more of the scribed 'V-cut' area. In areas where coating has been removed by chipping, partial coating fragments may remain

firmly attached to the steel surface and shall be counted as part of the 50% or more with coating.

- Rating 3: Coating can be removed in chips larger than the inserted knife point. Coating remains on 20% or more of the scribed area. In areas where the coating has been removed by chipping, partial coating fragments may remain firmly attached to the steel surface and shall be counted as part of the 20% or more of coating.
- Rating 4: The coating can be easily removed in strips or large chips considerably larger than the inserted knife point and coating remains on less than 20% of the scribed area.
- Rating 5: The coating can be completely removed as a single piece or in a few large chips with little effort.

3.7. Electrochemical Testing

The instrument used in this study consisted of a voltage power supply. The potentiostat maintaining the potential (E) of the WE at a constant potential or by varying the potentiostat as a function of time with respect to a reference electrode. The magnitude and direction of this current served as a measure of the corrosion rate. The investigation was carried out using a Gamry potentiostat G 750.

3.7.1. Open-Circuit Potential

The OCP of coated steel specimen or the rest potential described as “the potential of the WE relative to the reference electrode measured under virtual open-circuit conditions.” OCP of a metal depends on the substrate morphology and also on the nature of the surrounding environment [54, 55].

A high-resistance multimeter was used to carry out OCP test by recording the potential difference during immersion of the WE in the electrolyte (Sabkha or Gulf water) for 60 s vs. SCE.

3.7.2. Linear Polarization Resistance

The electrochemical technique of polarization resistance was used to measure the corrosion current density and corrosion potential. Polarization resistance test can be done in less than 10 min. Polarization resistance is also referred to as “linear polarization resistance.”

The polarization resistance measurements was performed using the potentiodynamic option by scanning through a potential range very close to the corrosion potential E_{corr} . Measurements were carried out by changing the electrode potential automatically from 0 to -25 mV at a scan rate of $0.05 \text{ mV}\cdot\text{s}^{-1}$. It was observed that the applied current density is approximately linear with potential in this range. The slope of this plot was determined at corrosion potential with a resistance unit known as the R_p polarization resistance. The slope of this plot is $\Delta E/\Delta i$. When determined from a tangent to the $E-i$ curve at E_{corr} , it defines the polarization resistance, as given by equation (1) [4, 53].

$$i_{corr} = \frac{1}{2.3 R_p} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) = \frac{\beta}{R_p}, \quad (1)$$

Where β_a and β_c are the anodic and cathodic Tafel parameters, respectively, and i_{corr} is the corrosion current density.

3.7.3. Electrochemical impedance spectroscopy (EIS)

EIS is a technique that has been used for decades to measure and monitor the degradation of protective coatings. EIS provides a powerful tool to quantitatively measure the resistances and capacitances of coated electrodes in an electrochemical cell [65, 67].

The impedance data can be represented in two ways:

- Nyquist plot: $-Z_{im}$ as a function of Z_{re}
- Bode plot: $\log |Z|$ and phase angle ϕ as a function of $\log f$

The Nyquist plots of coated panels provide a characteristic behavior that is dependent on the state of the coating; therefore, it follows that the penetration of an electrolyte into the coating and to detect the initiation of corrosion at the substrate/coating interface. Hence, the electrolyte permeates through the coating to reach the metal substrate.

In order to analyze the impedance data and determine the resistances and capacitances of the coated panels in an electrochemical cell, an appropriate equivalent circuit was used to help with the interpretation of the impedance data. Each element of the equivalent circuit provides a defined function of the electrode/electrolyte interface. This procedure leads us to determine the electrochemical properties of the coated pipeline.

An OCP test followed by potentiostatic EIS tests was done on both coatings (FBE and hybrid epoxy) in the temperature range of room temperature to 36°C. The impedance measurements was performed over large frequencies ranges, typically from 300 kHz to 10 mHz using amplitude signal voltage in the range of 10 mV to 25 mV rms. For the as-received coated panels, a value of 25 mV rms was chosen to characterize intact coatings and direct current of $-0.6 V_{SCE}$. On the other hand, for EIS measurement on defected

panels, the response of the exposed metal being dominant, a perturbation of 10 mV rms was used. Titanium was used as the reference electrode and a titanium mesh was used as a CE on a temperature-controlled chamber.

3.7.4. Equivalent Circuit of Coating

The interpretation of impedance data was based on the use of electrical equivalent circuits that represent the electrochemical processes occurring at the metal/coating interface. These circuits were built from the appropriate combination of simple electrical elements (capacitors, resistors, etc.).

The as-received coated panels behave as a dielectric and can be represented by a capacitor. When the coating gets in contact with an electrolyte, it starts to absorb water and the electrolyte penetrates through the pores of the coating. The electrical equivalent circuit describing this system is shown in Figure 3.12. While penetrating through the pores, the electrolyte results in a decrease in the pore resistance R_p .

Figure 3.12: Equivalent circuit model for analysis of EIS data

In case of artificial defected coating, once the corrosion reactions start at the substrate under the coating or at the pores, a coating electrical element that is related to the metal/coating interface was included in the equivalent circuit, as shown in Figure 3.13.

This circuit consists of a double-layer capacitance and charge transfer resistance, which describe the electrochemical reactions at the metal/electrolyte interface.

Figure 3.13: Equivalent circuits proposed for analyzing the data collected from coated panels

The fitting of the impedance data to the circuits of Figures 3.12 and 3.13 provides the following electrical parameters that describe the coating:

- C_c , the coating capacitance defined by

$$C_c = \frac{\epsilon_0 \epsilon_r A}{d}, \quad (2)$$

where ϵ_0 is the vacuum permittivity or the permittivity of free space, ϵ_r is the relative permittivity or coating dielectric constant, A is the coating surface area, and d is the coating thickness.

- R_p , the pore resistance defined as

$$R_p = \frac{\rho d}{A_p}, \quad (3)$$

where ρ is the electrolyte resistivity in the pores, d is the pore length (approximately equal to the coating thickness), and A_p is the total pore surface area.

It is worth noting that R_p decreases as the electrolyte penetrates the coating and fills the pores. This reduction in R_p with time may be caused by an increase in A_p , which is related to the number of filled pores or an increase of their area in case of delamination [17, 67].

Most of the time, the measured impedance differs from the ideal or theoretical behavior. Nyquist plots do not demonstrate that the two perfect semi-circle shaped account for the loops (or time constants). This nonideal behavior may be caused by coating heterogeneities as roughness and inhomogeneous composition. In this particular case, the coating cannot be described by a simple capacitor. Therefore, it was replaced by a constant phase element (CPE) whose impedance is given by equation (4):

$$Z_{CPE} = \frac{1}{Y_0} (i\omega)^{-n}, \quad (4)$$

where n denotes nonideal behavior. When $n = 1$, the CPE is a pure capacitance, and when $n = 0$, the CPE is a pure resistance.

Based on many investigators, it is sometimes better to restrict the data interpretation to simple parameters such as the total resistance of the coated panels represented by the low frequency impedance modulus ($|Z|_{0.01\text{Hz}} \sim R_s + R_p + R_{ct}$), while the coating capacitance values are obtained from the high frequency impedance modulus. The coating capacitance was determined from the impedance modulus at a fixed frequency (10 kHz) and calculated by equation (5) [67]:

$$C_c = \frac{1}{2 \pi 10^4 |Z|_{10\text{kHz}}}. \quad (5)$$

CHAPTER 4 - RESULTS AND DISCUSSION

4.1. Pull-Off adhesion

In this test, the adhesion strength of FBE and hybrid epoxy coated panels was conducted as per ASTM-D4541. As can be seen from Figure 4.1, an adhesive glue failure occurred for all panels. In this regard, if the bond between the dolly and the coating is weaker than the bond between the coating and steel substrate, the test dolly would be pulled off without measuring the coating bond strength. This indicated that the strength of epoxy adhesive glue was not sufficient to pull off the coatings from the metal substrate.

Figure 4.1: Example of pull-off adhesion strength dollies on a FBE and hybrid epoxy coated panels

As can be seen from Figure 4.2, the adhesion strength of FBE and hybrid epoxy coated panels show a glue failure for both Sabkha and Gulf media. All of the available FBE and hybrid epoxy sections did not show any signs of deterioration, as evidenced by the extremely high adhesion strength values.

Figure 4.2: Pull-off adhesion results for as received coated panels

Similarly, the scratched FBE and hybrid epoxy coated panels also indicated a glue failure for both Sabkha and Gulf, as shown in Figure 4.3. Furthermore, the adhesion strength of intact FBE coatings was systematically above the maximum strength of the adhesive used to attach the dollies to the steel substrate, indicating that adhesion between the steel substrate and the coating was not degraded. However, the total strength was more than 1000 psi, which indicated that both coatings have an excellent adhesion to the substrate. On the other hand, the pull-off at areas affected by cathodic disbondment on the FBE and hybrid epoxy coatings could not be tested due to the disbonded regions was smaller than dolly size, as shown in Figure 4.4.

Figure 4.3: Pull-off adhesion results for scratched coated panels

Figure 4.4: Pull-off adhesion results for cathodic disbonded coated panels

4.2. Knife Test

In this test, adhesion is determined by inserting the blade of a utility knife at the point of intersection of the 'V' with an angle of intersection of approximately 30°, as shown in Figure 4.5.

Figure 4.5: Example of knife test on a hybrid epoxy and FBE coated panels and pull-off test

If the coating fails adhesion (rating 4 or 5) at any test interval within the 28 days, it is deemed to have failed the test. Figure 4.6 indicated that the hybrid epoxy removed area was higher in Gulf with rating 2, in accordance with NACE best practice as mentioned in chapter 3.6.2.1. Also, FBE coated panels that were exposed to the Gulf environment were peeled more easily than in Sabkha, especially at high temperature.

Figure 4.6: Knife test results for cathodic disbonded coated panels

The scratch FBE and hybrid epoxy showed a very strong adhesion to the metal substrate, and there was no peeled off coating, as shown in Figure 4.7. Similarly, the as received panels for both coatings showed a strong adhesion to the substrate, as shown in Figure 4.8.

Figure 4.7: Knife test result for as received coated panels

Figure 4.8: Knife test result for scratch coated panels

4.3. Visual observations

After the knife test, the removed substrate of the removed FBE coating showed a corrosion product growth on the disbonded area. On the other hand, hybrid epoxy showed a very clean substrate with no visual corrosion product as shown in Figure 4.5.

4.4. Electrochemical testing

In this section, electrochemical testing techniques have been used to study the corrosion protection performance of the FBE and hybrid epoxy coated panels at 23 and 36°C under two simulated conditions, namely, Sabkha and Arabian Gulf water. This temperature was chosen to compare the externally coated buried pipeline with actual environment.

4.4.1. Linear Polarization Resistance (LPR)

In this test, the applied potential of the coated panels was varied from 0 to -25 mV, and the resulting current was recorded by electrochemical software (Gamry). Then, the current potential curves were conducted by the same system for each run.

From each curve, the polarization resistance was obtained and recorded. The polarization resistance (R_p) is the direct slope of the potential – current lines, while the corrosion current (required for calculation of the corrosion rate) is usually obtained from R_p according to the following simple relation, as mentioned in Chapter 3.7.2.

$$i_{corr} = \frac{1}{2.3 R_p} \left(\frac{\beta_a \beta_c}{\beta_a + \beta_c} \right) = \frac{\beta}{R_p} \quad (1)$$

After the end of each linear polarization runs, an EIS test run was started on the same panels and in the same environment.

4.4.1.1. As Received Coated Panels

There was no sign of corrosion for FBE coating under both Sabkha and Gulf media at 23 and 36°C. This reflects that the FBE coating has a strong corrosion resistance and efficient performance towards corrosion protection during the immersion time.

Similarly, hybrid epoxy coating in the Sabkha environment at 23 and 36°C showed a strong corrosion resistance and efficient performance to protect the pipeline from corrosion during the immersion time. On the other hand, hybrid epoxy in the Gulf environment showed an increase in corrosion current by increasing the residence time of the coated panels, as shown in Figure 4.9. The hybrid epoxy performance is expected due to partial degradation of the epoxy coating and the possible permeation of some moisture or saline water at the surface of the epoxy coating.

Figure 4.9: Icorr result for FBE and hybrid epoxy at 36°C

4.4.1.2. Scratch Coated Panels

The scratch FBE coated samples showed a corrosion product growth, as shown in Figure 4.10, which indicated that both environments are corrosive. Furthermore, potentiodynamic polarization curves representing FBE scribed coated panels exposed to different environments are shown in Figure 4.11. It is clear from the results of these runs, shown in Figures 4.12 and 4.13, that the corrosion current was high for the exposed period of 21 days in both environments. However, the FBE coating exposed to the Gulf media showed a higher value in corrosion current than the Sabkha environment, probably due to dissolved oxygen. Baboian et al. [57] mentioned that at near neutral pH values, chloride has less effect than dissolved oxygen. Also, Malik et al. [11] showed that the corrosion trend for scribed coated panels in Arabian Gulf water was higher than in Sabkha soil. Scribed panels exposed to Gulf showed maximum corrosion current ($7.82 \mu\text{A}\cdot\text{cm}^{-2}$), and the one exposed to Sabkha showed minimum corrosion current ($5.00 \mu\text{A}\cdot\text{cm}^{-2}$). Moreover,

the results showed that the temperature was not very sensitive to the corrosion current for both coatings.

Figure 4.10: Examples of scratched FBE and hybrid epoxy under Sabkha and Gulf

Figure 4.11: Icorr result for FBE and hybrid epoxy at 36 and 23°C

Figure 4.12: icorr result for scratch coated panels in Sabkha

Figure 4.13: icorr result for scratch coated panels in Gulf

The scribed hybrid epoxy coated panels showed a corrosion product growth, as shown in Figure 4.10. Moreover, corrosion current and corrosion current densities curves representing hybrid epoxy scribed coated panels exposed to different environments are shown in Figure 4.11. Figures 4.12 and 4.13 show that the corrosion current was high for the exposed period of 21 days. Also, hybrid epoxy corrosion current was smaller than FBE for both media. Scribed panels exposed to Gulf showed maximum corrosion current ($6.68 \mu\text{A}.\text{cm}^{-2}$) and the one exposed to Sabkha showed minimum corrosion current ($4.31 \mu\text{A}.\text{cm}^{-2}$).

4.4.1.3. Cathodic Disbondment Panels

Due to the observed strong corrosion resistance of the present investigated coatings, an accelerated test was recommended to account for the actual performance and evaluation of these coatings. This test was selected from the literature and is known as The Cathodic Disbonding Test. More details of this test are given in the literature ASTM G 8 and G 42, and also explained in the experimental part.

Figure 4.14: Examples of CD FBE and hybrid epoxy under Sabkha and Gulf

After exposure for 21 days, the cathodic disbondment for both FBE and hybrid epoxy coated panels showed a corrosion product growth, as shown in Figure 4.14. As shown in Figure 4.15, the corrosion current (I_{corr}) for Gulf was higher than Sabkha, probably due to higher dissolved oxygen in Gulf than dissolved oxygen in Sabkha. Also, at high temperature (36°C), the corrosion current density was higher for both media. After exposure for 21 days, hybrid epoxy at high temperature had less cumulative corrosion current density than FBE, as shown in Figures 4.18 and 4.19. On the other hand, FBE had a higher corrosion current density at lower temperature (23°C), which may indicate that hybrid epoxy had a better performance when cathodic disbondment is initiated.

Figure 4.15: I_{corr} result for FBE and hybrid epoxy at 36 and 23°C

Figure 4.16: icorr result for cathodic disbondment coated panels in Sabkha

Figure 4.17: icorr results for cathodic disbondment coated panels in Gulf

Figure 4.18: Cumulative icorr result for cathodic disbondment coated panels in Sabkha

Figure 4.19: Cumulative icorr result for cathodic disbondment coated panels in Gulf

4.4.2. Electrochemical Impedance Spectroscopy (EIS)

To further analyze the results, an electrical equivalent circuit (EEC) technique was employed to characterize the coatings at different temperature under two test media based on the EIS results. Figure 4.21 shows the model used, and Figure 4.20 shows the physical representation of that model. Using the Gamry Echem Analyst software, a fit was performed where a simplex algorithm was used to calculate values of the model elements that score minimum value of goodness of fit. It was possible to develop an electric circuit model, as shown in Figure 4.21, which represents both systems.

Figure 4.20: Physical representation of the EEC used to represent the coating systems [62]

Figure 4.21: EEC used to represent coatings FBE and hybrid epoxy

4.4.2.1. As Received Coated Panels

At the start of these experimental runs on the actual coated pipes, the equilibrium potential i.e., open circuit potential of these coated pipes versus the calomel reference electrode was not stable, and its value jumped to large unstable values. Hence, to avoid this problem, and to be able to conduct the required electrochemical tests, a reasonable value similar to the previous equilibrium potential of the previous test runs was considered, i.e., a value of -600 mV was given to the software of the electrochemical tests as the E_{corr} value.

Different shapes of impedance plots were observed, which corresponded to the initiation and propagation of corrosion species permeation with time. At the initial immersion period, all FBE coatings exhibited capacitive behaviors, indicating excellent protective properties for the pipes.

The total impedance results collected during the 21-day runs revealed the values of the three significant elements (C_c , R_{po} , $Z_{10\text{mHz}}$), as shown in Figures 4.22- 4.24. For studies of organic coatings, simulated solution was very low (6 – 15 ohm.cm) and can be ignored.

It is clear from the EIS results in Figures 4.23 and 4.24 that the FBE coating capacitance and pore resistance for both Sabkha and Gulf was almost constant. This indicated that the coating did not degrade for the 21 days of exposure. Also, the other element $Z_{10\text{mHz}}$ was linear in some intervals, which indicates an energy dependence and can be described as an Arrhenius-type system. Nevertheless, the slope of $Z_{\theta=45}$ was almost constant, so it was not sensitive enough to reflect the coating degradation for this period of time. Therefore, at the immersion period, all FBE coatings exhibited capacitive behaviors, indicating excellent protective properties for the pipes.

On the other hand, Figure 4.23 showed the hybrid epoxy coating capacitance C_c , which increased from 2.63×10^{-10} to 2.87×10^{-10} F and 2.73×10^{-10} to 3.01×10^{-10} F for Sabkha and Gulf, respectively, which indicates a detectable decrease in the coating impedance, indicating the degradation of coating with time. Also, water ingress into coating pathways may be the reason for that increase. Moreover, the pore resistance for hybrid epoxy in the Gulf start low and degrade with time, as shown in Figures 4.25 and 4.26. Furthermore, $Z_{10\text{mHz}}$, decreased drastically with time, which is further evidence of the decreasing the impedance of the coating system, indicating the degradation of the coating over time.

Figure 4.22: Impedance for as received FBE and hybrid epoxy at 36°C

Figure 4.23: Coating capacitance for as received FBE and hybrid epoxy at 36°C

Figure 4.24: Pore resistance for as received FBE and hybrid epoxy at 36°C

Figure 4.25: Pore resistance for as received FBE and hybrid epoxy in Sabkha at 36°C

Figure 4.26: Pore resistance for as received FBE and hybrid epoxy in Gulf at 36°C

Figure 4.27: Bode plot for as received FBE in Gulf at 36°C

Figure 4.28: Nyquist plot for as received FBE in Gulf at 36°C

Figure 4.29: Bode plot for as received hybrid epoxy in Gulf at 36°C

Figure 4.30: Nyquist plot for as received hybrid epoxy in Gulf at 36°C

4.4.2.2. Scratch Coated Panels

To measure the impedance of FBE and hybrid epoxy coatings in Sabkha and Gulf electrolytes under temperatures of 23 and 36°C, an EIS technique was employed. The EIS was performed on duplicate panels to insure the reproducibility of the results, as shown in Figures 4.31 to 4.33 for FBE and hybrid epoxy. The impedance in Figure 4.31 indicates that the FBE of scratch coated panels in Gulf water was lower than in the Sabkha environment at both temperatures. On the other hand, the impedance measurement $Z_{10\text{mHz}}$ was sensitive enough to both environments to describe the hybrid epoxy coating performance in presence of coating damage. This result indicated that hybrid epoxy in the Gulf and Sabkha did not change during the exposure period. However, the impedance of hybrid epoxy in Gulf media was lower than in the impedance in Sabkha environment, which indicates that the Gulf is more severe than the Sabkha environment.

Figure 4.31: Impedance for scratch FBE and hybrid epoxy

Figure 4.32: Impedance trend for scratch FBE and hybrid epoxy in Sabkha

Figure 4.33: Impedance trend for scratch FBE and hybrid epoxy in Gulf

In order to fit the depressed semicircles, the double layer capacitance was substituted with a constant phase element (CPE). The non-ideal capacitance behavior is usually attributed to microscopic roughness from scratches or pits on the surface which leads to coupling of the solution resistance with the surface capacitance.

It should be noted that although the CPE is useful in facilitating the EIS data analysis by avoiding difficulties associated with the fitting of non-ideal EIS data, the physical meaning of CPE is not well-defined. The exact relationship between CPE and surface heterogeneity is unknown, and, therefore, CPE analysis is not sufficient for determining coating defect because the measurement of coating disbondment requires quantitative analysis of surface heterogeneity defined by coating disbonded areas. Therefore, there are other factors that may affect the impedance and the double layer capacitance result, such as the coating thickness and surface preparation.

The results shown in Figure 4.34 indicated that the constant phase element (representative of double layer capacitance), for both FBE and hybrid epoxy increased over the 21 days of exposure in both media. This relationship implies that EIS measurement under coating defects could follow the penetration of the electrolyte through the coating.

Figure 4.34: Constant phase element result for scratch FBE and hybrid epoxy

4.4.2.3. Cathodic Disbondment Panels

The impedance shown in Figures 4.35-4.37 indicated that the FBE cathodic disbondment coated panels in Gulf water was lower than the impedance in Sabkha environment at both temperatures. On the other hand, the impedance measurement $Z_{10\text{mHz}}$ was sensitive enough to both environment to describe the hybrid epoxy coating performance in the presence of cathodic disbondment. The impedance measurement for the hybrid epoxy was higher than FBE, which probably indicates that the hybrid epoxy had a better performance in presence of cathodic disbondment.

Figure 4.35: Impedance for cathodic disbondment FBE and hybrid epoxy

Figure 4.36: Impedance trend for cathodic disbondment FBE and hybrid epoxy in Sabkha

Figure 4.37: Impedance trend for cathodic disbondment FBE and hybrid epoxy in Gulf

Figure 4.38: Constant phase element result for cathodic disbondment FBE and hybrid epoxy

4.5. Coating Degradation

To study the degradation of protective coatings, OM and SEM techniques were utilized. Images from OM and SEM showed both coatings have smooth surfaces with some randomly appeared blisters of different diameter, as shown in Figures 4.39 - 4.42. Generally, metal fillings are commonly used in polymer coatings, but an excess of metal might be the cause of blistering.

4.5.1. As Received Coated Panels

It can be seen that FBE has a lower pore surface area than hybrid epoxy, and the diameter of the pore is smaller than hybrid epoxy, as shown in Figures 4.39 - 4.42. Moreover, this may be the reason why hybrid epoxy degraded with time according to the pore resistance equation:

$$R_p = \frac{\rho d}{A_p} \quad (2)$$

where ρ is the electrolyte resistivity in the pores, d is the pore length (approximately equal to the coating thickness), and A_p is the total pore surface area.

Figure 4.39: SEM for FBE coating pore with a magnification of 190X

Figure 4.40: SEM for FBE coating pore with a magnification of 1,000X

Figure 4.41: SEM for hybrid epoxy coating pore with a magnification of 190X

Figure 4.42: SEM for hybrid epoxy coating pore with a magnification of 1,000X

Therefore, it can be concluded that FBE showed a very good performance indicators, high impedance, high adhesion and high corrosion resistance, on the other hand, hybrid epoxy was not as good as FBE.

4.5.2. Scratch Coated Panels

In the scratch panels, SEM revealed that there was a corrosion creep under FBE coating of approximately 123 μm in one side in the Gulf media, as shown in Figures 4.43 and 4.44. Additionally, there was a corrosion growth in the scratch area, as expected due to the corrosive media. On the other hand, the hybrid epoxy coating had approximately 133 μm of corrosion between the coating and the substrate in both sides in the Gulf media, as shown in Figures 4.47 and 4.48. It is worth mentioning that both FBE and hybrid epoxy coatings exposed to Sabkha media did not show any corrosion creep between the coatings and substrate. However, only the growth of corrosion is shown in Figures 4.45 and 4.49. As mentioned before the corrosion current densities for both Sabkha and Gulf was high.

Figure 4.43: SEM for FBE defect coating in Gulf

Figure 4.44: SEM for FBE defect coating in Gulf

Figure 4.45: SEM for FBE defect coating in Sabkha

Figure 4.46: SEM for FBE defect coating in Sabkha

Figure 4.47: SEM for hybrid epoxy defect coating in Gulf

Figure 4.48: SEM for hybrid epoxy defect coating in Gulf

Figure 4.49: SEM for hybrid epoxy defect coating in Sabkha

Figure 4.50: SEM for hybrid epoxy defect coating in Sabkha

4.5.3. Cathodic Disbondment Panels

Frequently localized corrosion occurs within crevices. This type of attack is usually associated with small volumes of stagnant solution caused by holes, surface deposits, and crevices. The deposit acts as a shield and creates a stagnant condition thereunder. The deposit could also be a permeable corrosion product. To function as a corrosion site, a crevice must be wide enough to permit liquid entry but sufficiently narrow to maintain a stagnant zone. For this reason, crevice corrosion usually occurs at openings a few thousandths of an inch or less in width. Until recently, it was believed that crevice corrosion resulted simply from differences in metal ion or oxygen concentration between the crevice and its environment. The overall reaction involves the dissolution of metal M and reduction of oxygen to hydroxide ions:

Initially, these reactions occur uniformly over the entire surface, including the interior of the crevice. After a short interval, the oxygen within the crevice is depleted because of the restricted convection, and oxygen reduction ceases in this area. After oxygen is depleted, no further oxygen reduction occurs within the crevice, although the dissolution of the metal M continues, as shown in Figure 4.51. This tends to produce an excess of positive charge in the solution (M^+), which is necessarily balanced by the migration of chloride ions into the crevice. This results in an increased concentration of metal chloride ions in the crevice. [53]

Figure 4.51: Left- crevice corrosion- initial stage / Right – crevice corrosion- later stage [53]

Hybrid epoxy showed a corrosion layer in the coating/metal interface, which may indicate that the oxide lifting occurs when anodic corrosion products accumulate under a coating, as shown in Figures 4.52-4.56. Additionally, it may be possible that, after a short

interval, the oxygen within the crevice is depleted because of the restricted convection. On the other hand, FBE coating showed corrosion in many spots in the coating/steel interface, which may indicate that the chloride ions migrate and react with metal ions inside the crevice to produce the corrosion spots shown in Figures 4.56–4.58. It is worth mentioning that FBE in Gulf is very easy to peel, and this may be the cause of the oxide lifting action. Also, this indicates that FBE has a tight crevice that allows more accumulation of corrosion product or more aggressive localized corrosion. Which indeed can be shown in Figure 4.56 where localized pitting corrosion is formed under FBE coating. Where hybrid epoxy allows a bigger crevice less accumulation of corrosion product or large localized anodic spots. Therefore, it can be concluded that FBE had more convection area inside the crevice than hybrid epoxy, and this can be considered to explain the cathodic disbondment process.

Figure 4.52: OM for hybrid epoxy/substrate interface in Sabkha

Figure 4.53: OM for hybrid epoxy/substrate interface in Sabkha

Figure 4.54: OM for hybrid epoxy/substrate interface in Gulf

Figure 4.55: OM for hybrid epoxy/substrate interface in Gulf

Figure 4.56: OM for FBE/substrate interface in Sabkha

Figure 4.57: OM for FBE/substrate interface in Sabkha

Figure 4.58: OM for FBE/substrate interface in Gulf

CHAPTER 5 - CONCLUSIONS

The results from the characterization and electrochemical testing techniques were discussed and the following has been concluded:

- Temperature was not a major factor in short exposure time.
- The results suggest that localized EIS measurements under disbonded coating are necessary to achieve in situ quantitative determination and monitoring of the cathodic disbondment of coatings.
- Excellent performance was observed with the FBE and hybrid epoxy coatings, as they passed the various pass/fail criteria tests.
- As received FBE coatings under the testing media and different temperatures have shown excellent corrosion properties, high impedance, and good adhesion properties, and these properties qualify them as a suitable choice for external coating for buried pipelines. On the other hand, hybrid epoxy was less efficient than FBE, especially in the Gulf water environment.
- The protective coatings under investigation did not show any blistering effect, loss of adhesion, or color change under the test conditions, thus reflecting their excellent corrosion resistance property.
- The effect of residual chloride concentration on the corrosion property of the coatings appears to be insignificant.
- The results of the adhesion test carried out on the FBE and hybrid epoxy coatings showed that the strength of epoxy adhesive was not sufficient to pull off the coatings from the metal substrate.

- In the presence of scratch damage, both coatings performed the same, exhibiting an excellent adhesion to the metal substrate, whereas, under cathodic disbondment, hybrid epoxy performed slightly better than FBE, as indicated by both LPR and EIS results.
- At high temperature (36°C) in the Gulf water, the coating disbonded was high for FBE and hybrid epoxy (1.2 and 1.4 cm, respectively). On the other hand, the coating disbonded in the Sabkha environment was low for FBE and hybrid epoxy (0.9 and 0.95 cm, respectively).

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