

**THE EFFECT OF BITUMEN COATINGS ON THE CORROSION OF LOW CARBON STEELS
(API 5L X65)**

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**THE EFFECT OF BITUMEN COATINGS ON THE CORROSION OF LOW CARBON STEELS
PIPES (API 5L X65)**

ATHESIS APPROVED

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ABSTRACT

The corrosion behavior of uncoated and cut-back bitumen coated X65 Steel samples are being investigated in environments of different pH (2, 3, 4 and 7). Immersion tests were carried out on the samples at 25°C. The comparison of the corrosion behavior of uncoated, spray-coated and brush-coated X65 steel samples in the different pH media and temperature were observed using the weight measurements approach and visual examination. With 72 hours intervals in the weight measurement of the samples, the weight loss of the uncoated X65 samples in the pH 2 was more than the pH (3, 4, and 7). This is mostly due to the attack of chloride ions on the surface of the steel. It was also observed that there was different weight gained measurements for both spray-coated and brush-coated samples which is expected to be due to water absorption. The visual examination and weight changes showed that spray-coated samples are more likely to corrode less than brush-coated samples.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Corrosion is the greatest source of deterioration and the degradation of materials that are used in engineering structures and components. It accounts for few hundred billion dollars in losses to the global economy [1,2]. There is therefore a need to explore different approaches to the reduction of the economic losses due to corrosion. Although several definitions of corrosion have been proposed [3], corrosion has been defined by Fontana [4] to be the deterioration of materials as a result of reactions with the environment. It is nature's way of reducing metals to its original states (Andrew et al., 2007) [5]. Despite different definitions, it can be observed that corrosion is the interaction of materials and their environment. It is a natural and costly process of destruction. However, corrosion can be prevented or at least controlled by the use of protective coatings [6] and cathodic protection [7].

In the case of the oil and gas industry where pipelines, refineries and offshore structures are used to transport liquid and gaseous fuels, the reactions between these fuels and the carbon steels result in corrosion [8]. Similarly, the environments that surround pipelines (soil, oceans and humid environments) can react with the carbon steels that are often used to fabricate pipelines, offshore structures and refineries. There is therefore a need to develop improved methods for the environmental protection of structures that are used in the oil and gas industry.

In the case of pipelines, corrosion can be reduced by the use of corrosion resistant materials, chemical treatment, electrochemical protection and protective coatings. The coatings may also be organic, inorganic and metallic coatings. However, the large surface areas that have to be coated have limited the practical application of several lab-scale coatings in the industrial environment. This is due largely to the cost and availability of the coating materials for use in extensive networks of oil and gas pipelines across the world.

1.2 PROBLEM STATEMENT:

Due to the availability and relatively low cost of bitumen, recent efforts have been made to explore the use of bitumen as a coating material for pipelines in the oil and gas industry. However, although some studies of corrosion have been performed on bitumen-coated steels, our fundamental understanding of the swelling and stress induced deformation and interfacial cracking of bitumen-coated steels have not been performed with the required combination of micromechanics and materials characterization. There is also a need to develop a fundamental understanding of substrate corrosion mechanisms in bitumen-coated steels.

1.3 AIMS AND OBJECTIVES OF THE THESIS:

The objective of this thesis is to study the mechanism of corrosion in a bitumen-coated pipeline steel (X65 steel) that is used in the fabrication of steel pipes. The mechanisms of swelling, stress-induced deformation, cracking and corrosion are studied in coated structures exposed to different environments. The failure mechanisms observed during the experiments will be modeled to provide insights into the swelling, interfacial cracking and substrate corrosion. Practical guidelines will then be proposed for the design and maintenance of bitumen-coated pipelines.

1.4 SCOPE OF WORK:

This study will be carried out in the following stages:

- The surface preparation of the X65 steel samples;
- The optical characterization of the uncoated samples;
- The set-up of the different corrosive environments set up;
- The immersion and measurement of weight loss of the uncoated samples in the corrosive environments;

- The spray deposition and brush coating techniques of the bitumen with different thicknesses on the X65 steel substrates. ;
- The immersion and measurement of weight changes of the coated samples in the different corrosive environments;
- The study of water absorption and corrosion behavior of the coated samples in these different environments.
- The development of guidelines for pipeline design and maintenance.

1.5 Outline of Thesis:

Following the introduction (Chapter 1), the relevant literature is reviewed in chapter 2. The experimental methods are described in chapter 3 before presenting the results and the discussion of the results in chapter 4. Salient conclusions arising from this study are presented in chapter 5 along with suggestions for future work.

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CHAPTER 2

BASIC THEORY AND LITERATURE REVIEW

2.1 Definition of corrosion:

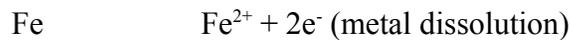
Corrosion may be defined as: “a physicochemical interaction leading to a significant deterioration of the functional properties of either a material, or the environment with which it has interacted, or both of these” [1]. Generally, corrosion can occur in the different classes of materials such as metals,

semiconductors, ceramics, polymers, composites. The corrosion of metallic materials is taken into consideration in this thesis due to its wide range of its applicability in the oil and gas industry. The corrosion of metal embraces all interaction of a metal with its environment. It can be defined as the undesirable deterioration of a metal i.e an interaction of the metal with its environment that adversely affects those properties of the metal that are to be preserved.

2.1.1 Fundamentals of aqueous metallic corrosion:

A corroding system is driven by two spontaneous couple reactions which take place at the interface between the metal and an aqueous environment. The two simultaneous reactions are the oxidation (anodic) reaction and a reduction (or cathodic reaction). The first reaction is when the chemical species from the aqueous environment remove electrons from the metal; the other is a reaction in which metal surface atoms participate to replenish the electron deficiency.

Example of anodic (oxidation, electron-donating) reaction:



While examples of cathodic (reduction, electron-accepting) reactions:



Electron exchange between the two reactions constitute an electronic current at the metal surface and imposing an electric potential on the metal surface of such a value so that the supply and demand for electrons in the two coupled reactions are balanced is an important effect.

The potential imposed on the metal is of much greater significance than simply to balance the complementary reactions which produce it. This is because it is one of the principal factors determining what the reactions will be [2].

Generally at the anodic locations, there is corrosion damage (e.g metal loss), while at the cathodic location, no corrosion damage occurs. The location of anodes and cathodes tends to move randomly over

the surface of the metal for alloys that are subject to general corrosion. However, the location of an anode tends to become strongly localized for corrosion resistant alloys, which are covered by a passive oxide film. This gives rise to localized corrosion damage such as pitting corrosion, stress corrosion cracking and crevice corrosion [3].

2.1.2 Forms of Corrosion:

Corrosion manifests itself in different forms that have certain similarities and can be categorized into specific groups. Many of these forms are not unique but involve mechanisms that have overlapping characteristics that may influence or control initiation or propagation of a specific type of corrosion. The most familiar and often used categorization of corrosion is probably the eight forms presented by Fontana and Greene (1967) such as: uniform attack, galvanic corrosion, crevice corrosion, pitting corrosion, intergranular corrosion, erosion corrosion, selective leaching and stress corrosion [4]. This classification of corrosion was based on visual characteristics of morphology of attack as well as the type of environment to which is exposed. Other prominent corrosion authors such as Uhlig and Evans (1963) have simply discussed the classical types of corrosion as they relate to specific metals and alloys [5,6].

2.2 Corrosion Rates:

Corrosion rates are determined by applying a current to produce a polarization curve (the degree of potential change as a function of the amount of current applied) for the metal surface whose corrosion rate is being determined. When the potential of the metal surface is polarized by the application of the current in a positive direction, it is said to be anodically polarized; a negative direction signifies that is cathodically polarized. The degree of polarization is a measure of how the rates of the anodic and the cathodic reactions are retarded by various environmental (concentration of metal ions) and/or surface

process factors. Hence, polarization measurements can thereby determine the rate of the reactions that are involved in the corrosion process- the corrosion rate. The corrosion rate can be expressed in mil per year [7]. It is given by:

$$\text{Corrosion rate} = \frac{KW}{\rho At}$$

Where K = constant which depends on the system used, W = weight loss after exposure to environment (mg), ρ = Density of the material (g/cm^3), A = Area of the material exposed (square meter), t = time of exposure (hour)

2.3 Corrosive Environments:

The deterioration of material due to corrosion can be caused by a wide variety of environments. Metallic corrosion in aqueous (i.e water-containing) environments with or without dissolved species such as electrolytes (i.e salts) and reactants (e.g dissolved oxygen) [3]. However, every industry such as the food, pharmaceutical, oil and gas e.t.c features a variety of applications encompassing a range of corrosive environments. In the food industry the corrosion environment often involves moderately to highly concentrated chlorides on the process side, often mixed with significant concentrations of organic acids. Process environment for the pharmaceutical industry can include complex organic compounds, strong acids, chloride solutions comparable to seawater. The consideration for this work is mostly focused on the oil and gas industry which have corrosive environment such as the sour and sweet environment from the sour reservoirs (those containing hydrogen sulphide, H_2S) and the sweet reservoirs (containing carbon dioxide, CO_2). The sour environments can result in sulfide stress cracking of susceptible materials [8].

2.4 Corrosion of low Carbon Steels (X65):

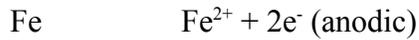
Carbon steel is one of the most widely used engineering materials Nigeria. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, transportation,

chemical processing, petroleum production and refining, pipelines, mining, construction and metal processing equipment. The importance of this material has made different research work to be carried out by several researchers. A recent study of corrosion behavior and Stress corrosion cracking (SCC) of low and medium carbon steels in cassava and cocoa extracts was carried out by A.S Afolabi, 2007 [9]. He found that the medium carbon steel is more susceptible to corrosion than low carbon steel in both media.

Carbon steels are by their nature of limited of limited alloy content, usually less than 2% by weight for total of all additions. At these levels of addition present in low alloy steels, the usual impurities have no significant effect on corrosion rate in the atmosphere, neutral water or soils, only in the case of acid attack is an effect observed. In a recent research work carried out

The corrosion of carbon steel in the atmosphere and in many aqueous environments is best understood from a film formation and breakdown standpoint [10]. It is an inescapable fact that iron in the presence of oxygen and/or water is thermodynamically unstable with respect to its oxides. In the absence of film formation and with a constant environment, one would expect the oxidation rate to be constant. Conversely, if the corrosion product film that forms isolates the steel from the corrosive environment, one would expect a zero corrosion rate after the initial film formation period. A tightly adherent film that permits only diffusion transfer of the reactants would be characterized by a corrosion rate decreases with the square root of the exposure time. These idealizations are rarely encountered in corrosion of carbon steels. The other factors that tend to be operative to disrupt stable film formation can be external such as erosion by wind or rain, or they may be internal to the film itself such as stresses caused by the different specific volumes of metal and oxide. The complexity of these various breakdown processes makes a quantitative prediction of corrosion so difficult.

The corrosion of iron in the atmosphere proceeds by the formation of hydrated oxides. The half-cell reactions can be expressed as:



Further reactions can then occur, such as:

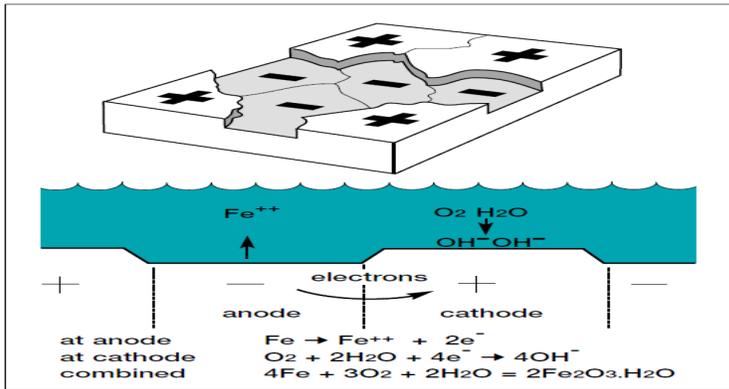
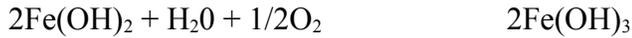
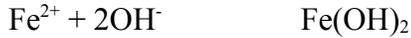


Fig 2.1: Schematic diagram of corrosion mechanisms of iron

The formation of the rust is observed to be formed at a distance from the surface and attack on metal cannot be stifled. This conclusion was firmly established by Evans [6] and co-workers

The various oxide and hydroxides of iron form a rather complicated system of compounds. The compound FeOOH has been to exist in three different crystal forms plus an amorphous form. The occurrence of the various oxide species is dependent on pH, oxygen availability, various atmospheric pollutants, and the composition of the steel [11]. The actual nature of the rust film is important because FeO and FeOOH seem to be more adherent than Fe₃O₄ and Fe₂O₃, and therefore more likely to slow the corrosive attack, but the higher oxides and oxy-hydroxides are more prone to spallation.

2.5 Controlling of Corrosion:

It is generally difficult to prevent corrosion in industrially/commercially important metals (iron, zinc, copper e.t.c) that are used in structures such as pipes. This is due to their inherent instability. Their ionic solutions and their carbonates, hydroxides, oxides and sulfides are more stable than the metal under environmental exposure.

There is therefore a need for practical approaches to the reduction of corrosion rates in pipeline materials. The methods that are used to reduce the corrosion of metals include: the careful selection of materials; the protection by design; the application of inhibitors and cathodic protection [12, 13]. This work will consider the effects of protective coatings that are relevant to oil and gas industry. The goal is to develop a more fundamental understanding that could enhance future applications.

2.5.1 Protective Coatings:

Protective coatings are one of the most widely used products for corrosion control. They are applied to substrate to provide long-term protection under different corrosive conditions, such as chemical processing conditions and atmospheric exposure. The main function of a protective coating is to isolate structural reactive elements from environmental corrosives [14]. A coating must provide a continuous barrier to prevent either chemical compounds or corrosion currents from contacting the substrate, as any imperfection can become the focal point for degradation and corrosion of the substrate [15].

Steel structures, such as underground buried gas pipelines, or over ground pipelines, require the use of protective coatings. Corrosion protections of over-ground and under-ground steel pipes with the help of protective coatings, such as organic coatings is one of the most proven methods. The increase of the electrical resistance of metals by applications of coatings of high resistivity such as bitumen, vinyls, chlorinated rubbers impede the flow of electric current to the metal surface. Hence organic coatings offer the effective methods for corrosion protection and control. The use of coating materials is one of

the first attempts to control steel structures (pipes). This could be seen from the view that if the substrate could be isolated from contact with the surrounding earth, no corrosion could occur. Furthermore, a coating would be completely effective as a means of stopping corrosion, if the coating material is an effective electrical insulator. This can be applied with no breaks whatsoever and will remain so during the backfilling process and constitutes an initially perfect film that will remain so with time.

Although coatings by themselves may not be the one total perfect answer to corrosion control, they are extremely effective when used properly. A properly selected and applied coating will provide all the protection necessary on most of the pipeline surfaces to which it is applied. This properly selected coatings and well coated pipeline along with cathodic protection may result in improved corrosion behavior.

2.5.2 Characteristics of Coatings

NACE Standard provides a comprehensive to characteristics of coatings. This standard lists the following desirable characteristics of coatings such as:

2.5.2.1 Effective electrical insulator and maintenance of constant electrical resistivity with time:

A pipe coating has to stop the current flow by isolating the pipe from its installed environment/electrolyte. To assure high electrical resistance, the coating should have a high dielectric strength. The effective electrical resistance of a coating per average square foot depends on the following: (a) resistivity of the coating material;(b) coating thickness;(c) resistance to moisture absorption; (d) resistance to water vapor transfer;(e) frequency and size of holidays and resistivity of the electrolyte and(f) bond or adhesion of coating.

2.5.2.2 Good adhesion to pipe surface: A pipeline coating needs sufficient adhesion to prevent water migration between the coating and the pipeline and also to resist handling and soil stress. Soil stress is

one of the main causes of pipe coating failure and its effective can be seen on flexible coatings as characteristics wrinkling.

2.5.2.3 *Effective moisture barrier*: Although the absorption of water increases the effectiveness of CP, the transfer of water through coating may cause blistering and will contribute to corrosion by prohibiting isolation.

2.5.2.4 *Applicability*: The application of the coating to the pipe must be possible by a method that will not adversely affect the properties of the pipe and with a minimum of defects.

2.5.2.5 *Ability to withstand normal handling, storage (UV degradation), and installation*: Coating ability to withstand damage is a function of its impact, abrasion, and flexibility properties. Pipe coatings are subjected to numerous handling between application and backfill. Hence these factors need to be evaluated to determine if any special precautionary measures are needed to resist the factors that can cause damage to pipeline coatings. The resistance to ultraviolet is a very important consideration since ultraviolet rays can be very destructive to pipe coatings

2.5.2.6 *Non-toxic interaction with the environment*:

Some coating materials have been modified, restricted because of environmental and health standards. This has been a major influence of change on today's pipe coatings. Other factors to be considered when selecting pipeline coatings are the type of environment, Operating temperature of the pipeline, accessibility of pipeline, pipe surface preparation requirements, ambient temperatures during application, storage and installation, cost.

In the selection of a coating system for a pipeline, a very important characteristic is its stability. This means a coating combination that will have a high electrical resistance after the pipeline has been installed and the backfill stabilized. Such a film should lose the least electrical resistance with passage of time. The selection of the most appropriate system is important. However proper application is the most important consideration [12].

2.5.3 Properties of the Ideal Coating for Aqueous Corrosion Resistance

An ideal coating should have a very hydrophobic surface and should form high barriers to water and electrolytes. Hence there is a need for polymer coatings that are highly cross-linked and that contains silicone or fluorocarbon monomers that promote hydrophobic surfaces. Such coatings should also have controllable gradients in chemical composition to minimize interfacial discontinuities and create a covalent bonded structure from the substrate through to all of the coating layers. Tightly controlled interfacial regions that can be chemically matched to the coating system is another important property in an ideal coating. This provides the basis for water-resistant, adhesion and mechanical property matching with the coating layer to avoid excess stress concentration in the interface, resulting to mechanical delamination [21].

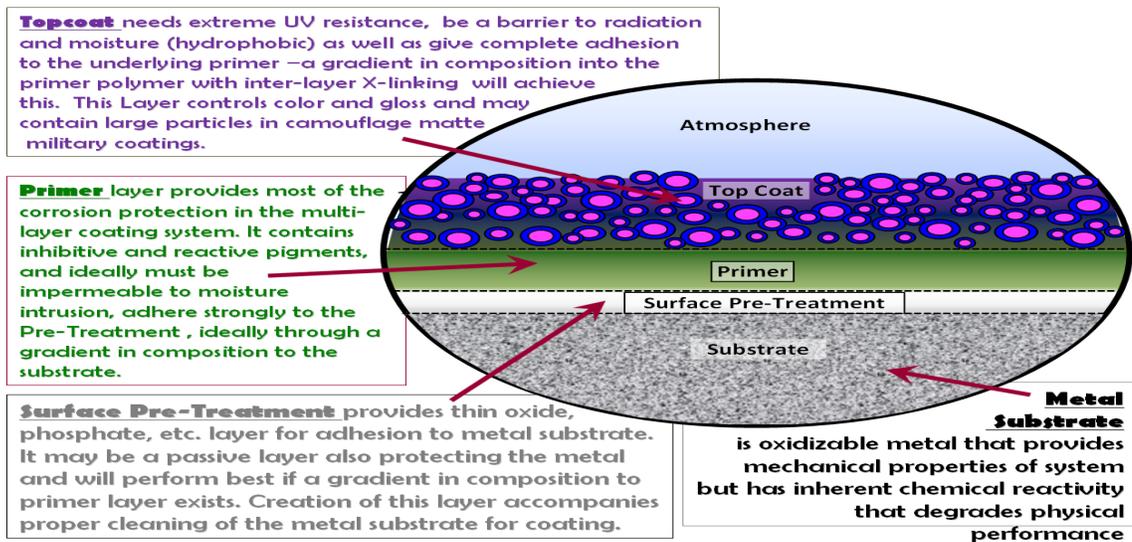


Fig 2.2 The Ideal Coating System [16]

2.5.4 Theory of Adhesion:

Adhesion is one of the most important properties of coatings. The life span of a coating is related to the nature of adhesion. It can be defined as the energy required to separate an interface between the substrate and a coating. Theories like diffusion, chemical bonding can be used to explain the mechanism of adhesion between a coating and its substrate. Reactivity at the interface takes place between a coating and its substrate upon application. It is necessary and desirable that there is surface modification of the substrate to ensure proper adhesion and maximum reactivity at the interface. The modification of the substrate surface could be in terms of removal of grease, dust or mill scale etc. The adhesive strength for anti-corrosion coatings according to DIN 55945, can be defined as the resistance of the coating to mechanical separation from the substrate. The use of adhesion promoters, such as coupling agents is one of the ways of promoting adhesion between a coating and its substrate. Hence there is a need for the careful preparation of the substrate surface since the substrate roughness can have a significant effect on the adhesion of the coating to the substrate.

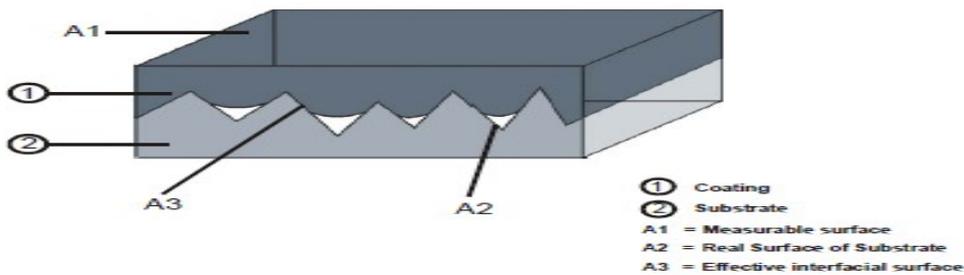


Fig 2.3: Surface effects determining the measurement of adhesion [17]

There are different types of chemical bonds that form when a coating is applied on the substrate. These include primary chemical bonds and polar or the secondary bond. However, adhesion of most coatings occurs mostly by polar bonding. The physical and chemical causes of adhesion of coating with the substrate can be described schematically, as shown in Fig 2.3.

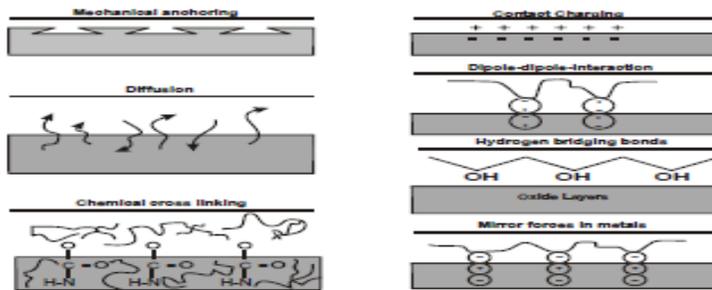


Figure 2.4 Physical/Chemical causes for adhesion of coatings to the substrate [17]

2.5.5 Water Permeation:

Water permeation is one of the major causes coatings failure. This can lead to early disbondment at the coating-substrate interface during the service life. Organic coatings are permeable to water, oxygen and ions. The polymer structure and composition determines the extent of permeability of water. Water is taken up by the coating through pores and micro-cracks. It enters the film in several different ways and can accumulate in various places [18]. The existence of water molecules within the polymer phase is possible because polymers generally contain polar groups that chemisorb water molecules. The chemisorbed water molecules can be the centers for formation within the polymeric phase.

The factors that influence that make water permeation include the concentration gradient, osmosis due to impurities at the coating-substrate interface, and capillary forces in the coating due. These can occur due to improper solvent evaporation, poor interaction between binder and additives or entrapment of air during application. Solubility and diffusion are important factors that influence water permeation. Depending on the values of solubility and diffusion, a coating under immersion can be saturated after a

relatively short time [19-21]. Hence the effect of water uptake can result in coating failure by blistering/adhesion loss and delamination etc.

2.6 Coating Failures:

A coating may fail as a result of large number of potentially adverse conditions. Some of these can be defined as mechanical, e.g when abrasion or impact removes the coating. Alternatively, local damage can occur within the coating and create a corrosion site that will reveal itself in a few months. A common reason protective coatings do not perform well is that they have not been considered as systems. Figure 2.1 shows the distribution of failure mechanism associated with coatings failure [22].

The following list summarizes many of the factors that can cause such failures:

Water absorption, moisture vapor transfer, osmosis, electro-endosmosis, Blistering due to gas inclusion or due to phase separation during film formation, surface contamination, surface defects, soluble components in the film, temperature differential or cold wall effect

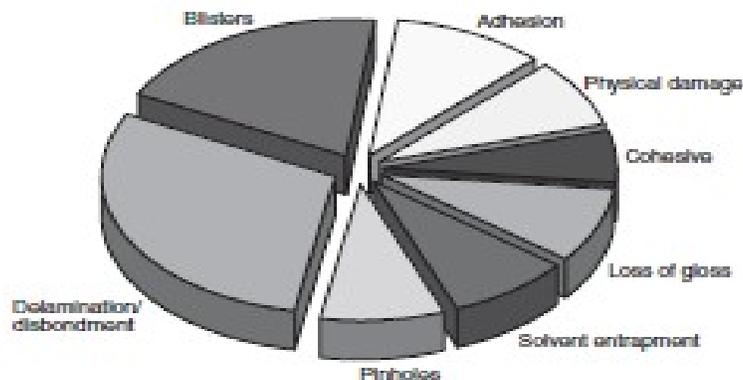


Fig 2.5: Breakdown of the root causes behind 84 coating failures thoroughly investigated.

Modern coatings are mainly of the barrier type, among which organic coatings are being extensively used in oil and gas storage distribution due to their ease of application. They have excellent barrier and fairly quick drying properties, besides being cost effective. The study of water uptake in organic coating easily provides knowledge about the interaction between water molecules and polymer.

2.7 Types of Protective Coatings

The protection of metals against corrosion has been done with several different types of coatings. These include: metallic, inorganic non-metallic and organic coatings. These coatings can be further divided according to method of application and into number of subtypes. The classification of coating types may help in understanding its degradation mechanism and ultimate corrosion underneath coating at an early stage [23].

Metallic coatings: These are thin layer of metals over the surface of the substrate material to be protected. They are mostly applied in situations where it is too expensive or impossible to use the protecting metal in bulk form. The method of application may be used to classify metallic coatings. This can be seen in cladding, which consists of hot rolling of a thin sheet of corrosion resistant metal onto a thick plate of a less resistant one. Other methods of application that are used in classifying metallic coatings are hot dipping, electroplating and metalizing or flame spraying [24]. Metallic coatings are mostly used in protecting mild steel. The most extensively applied are tin, zinc, cadmium, copper and nickel [25].

Inorganic non-metallic coatings: This involves numerous classes of materials that can be produced by chemical action, with or without electrical assistance. They include: clays, glass, carbon, silicates and others. Conversion coatings are inorganic coatings that can be formed by electrochemical reaction of the metal to form insoluble compounds with good adhesion [26]. The different types of conversion coatings

can be obtained by anodizing, phosphatizing [27], chromate filming, nitriding [28, 29] among others. This is discussed fully by Biestek and Weber [26].

2.8 Organic Coatings:

Organic coatings consist of a binder, pigments and additives such as dryers, hardening agents, stabilizing agents, surface activating compounds, and dispersion agents [30, 31, and 32]. Organic coatings are applied on pretreated surfaces. They are the most common and the most effective mode of corrosion protection for metallic object and structures. They are expected to exclude moisture and should retard further corrosion [33]. They can protect metals against corrosion through a barrier function or inhibitive function. The barrier function is achieved by blocking the entrance of water, oxygen and ions towards the substrate, while the inhibitive function is achieved by modification of the aqueous environment, as it moves through the coating film. The purpose of an organic coating is to promote, enhance, and maintain a passive or a protective layer on the reactive metal substrate.

A large variety of organic polymeric materials belonging have been used as external coatings for open air or buried low carbon steel pipelines. Fusion epoxy, coal tar epoxy, extruded polyethylene, multilayer polyolefin, asphalt mastic and asphalt enamel are some of the most widely used organic materials that are used to coat pipelines.

2.8.1 Corrosion Mechanism under Coatings

Adhesion is a very important property, when considering corrosion under coatings. There is loss of adhesion when water molecules permeate the organic coating and reach the substrate-coating interface. The loss of adhesion, due to water, is attributed to chemical disbondment due to chemical interaction of water with covalent, hydrogen or polar bonds and osmotic pressures (Leidheiser and Funke, 1987) [34]. The presence of an aqueous electrolyte, with an electrochemical double layer, a cathodic species

(oxygen) and an anodic species (metal) can initiate a corrosion reaction. The constant supply of cathodic species, such as water and oxygen, facilitates the corrosion reaction (De Wit, 1995) [35].

An example of corrosion under coatings is the formation of a blister due to cathodic delamination. A complex oxide and hydroxide will be produced after the local corrosion reaction. This will precipitate beneath the polymer, and allows the permeation of water but not of oxygen. This results in the separation of the cathodic and anodic sites. The location of the anodic area is under the precipitate, while the cathodic reaction moves to the edge of the blister, where oxygen may still permeate the coating. The cathodic reaction will increase the pH value at the edge which causes delamination and further growth of the blister.

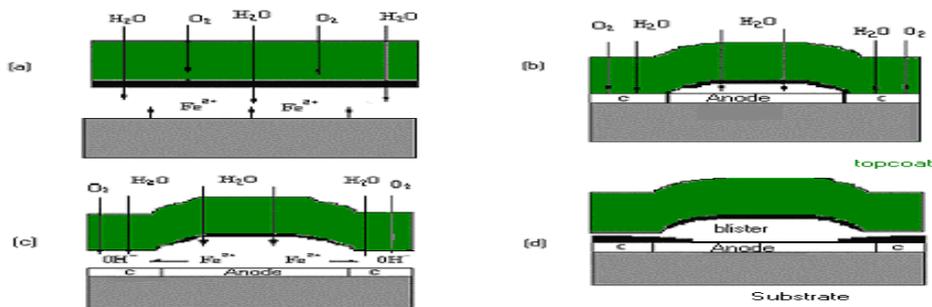


Fig 2.6 Initiation and propagation of a blister due to cathodic delamination under and intact organiccoating (De Wit, 1995). (a) Initiation of local corrosion due to permeation of water and oxygen; (b) separation of anodic and cathodic sites; (c) propagation of the blister due to the high pH at the edge; (d) formation of a blister under the coating.

2.9 Bitumen Constitution:

Bitumens are the residues from the distillation of crude oil. They are non-crystalline viscous materials, black or dark brown, which are substantially soluble in carbon disulphide, possessing adhesive and water proofing qualities. The abundance reserves of natural bitumen resources in Nigeria is up to the tune of over 14.86 billion barrels located in Ondo, Lagos, Edo, Enugu and Oyo states. The sustained production of some of these bitumens from suitable crudes is done at the Kaduna Refining and

Petrochemical Company (KRPC). Rich bitumen deposits can be found in Ondo State around the region of Okitipupa, Foriku and Agbabu e.t.c [47].

Bitumen consists of complex mixture of hydrocarbons of carbon number C_{25} and above, the remainder being oxygen, sulphur, nitrogen and traces of various metals. The average bitumen molecular structures are gotten from molecular weight, elemental analysis and nuclear magnetic resonance data. It consists of one or two, 3, 4-ring condensed aromatic systems with several aliphatic side chains and alicyclic systems attached. Bitumen comprises about 25-35% aromatic, 15-30% alicyclic and 35-60% aliphatic carbon (Herrington et al. 1994, Petersen 2000, Branthaver et al. 1993)[36-38]. The complexity in the hydrocarbon mixture and inter-molecular association can make the measurement of bitumen molecular weight difficult and lead to erroneously high results. The average values are typically 600-700, with the upper range probably in the region of 2000-3000 amu (Moschopedis et al. 1990, Domin et al. 1999)[39, 40].

2.9.1 Properties and Behavior of Bitumen

The stability of bitumen in the environment is thought to be very high. There is no available specific data concerning the transport and distribution of bitumen among environmental transformation, environmental media and degradation, interaction with chemical, physical, biological factors and bioconcentration [41,42]. The constituents of bitumen suggest that they are potentially bioaccumulative [43] as they have high steady state ratio of the solubility of a substance in n-octanol to the solubility of that substance in water. The high molecular weights and low water solubility of bitumen indicate that the bioaccumulation of bitumen is highly unlikely [44]. Some research concerning the leaching characteristics of bitumen or bitumen waste have carried out (Townsend & Brantley 1998, Bowen, de

Groot & Brandt 2000) [45, 46]. Townsend & Brantley found no heavy metals, volatile compounds in the leachate after performing a standard leachate test on asphalt road waste. Bowen et al. (2000) carried out static leaching test and characterized the leaching behavior of PAHs from nine different bitumens. They found that PAH concentration reached a steady state between days 4 and 9. The constituents were majorly naphthalene (n.d.: 371 ng/L) and phenanthrene (3-182 ng/L), which were not considered as a hazard to aquatic environments because these levels are below European limits for surface water. The study of water leaching of bitumen mixed with mineral aggregate (hot mix asphalt) was carried out by Kriech (2000) with the use of the Environmental Protection Agency (EPA) SW846-1311 and SW846-351 Toxic Characteristic Leachability Procedure (TCLP). A range of semi-volatile organics was not observed above detection limits however naphthalene (250 ng/L) was detected [48].

Bitumen is a strong and durable adhesive that binds together with a very wide variety of other materials, without affecting their properties. It is insoluble in water [41] and can act as an effective waterproofing sealant. It also resists action by most acids, alkalis and salts. It is a thermoplastic material which softens and becomes liquid, with the application of heat and hardens as it cools. It can be spread relatively easily in the areas where it is required, because it can readily be liquefied by one of three methods: applying heat; dissolving it in petroleum solvents or dispersing it in water (emulsification).

2.9.2 Chemical Characterization of Bitumen

Elemental composition

The quality and properties of bitumen depend largely on the chemical composition of the bitumen. Bitumen is a complex mixture of molecules of a predominantly hydrocarbon nature, which vary widely in their composition. They contain amongst others minor amounts of heteroatoms containing sulphur, nitrogen and oxygen with trace quantities of metals, such as vanadium, nickel, iron, magnesium and calcium, which occur in the form of inorganic salts and oxides.

The origin of the crude oil and the processes used during bitumen manufacture determines the chemical composition of bitumen. It is not feasible to determine the total analysis of bitumen because of the complexity in its chemical composition associated with large number of molecules with different chemical structures. The elemental composition does not provide all the information of the type of molecular structure available in bitumen. This knowledge is necessary for a fundamental understanding of how the composition of the bitumen affects the physical properties and chemical reactivity.

2.9.3 Fractional composition:

Out of the complex mixture of molecules of bitumen, there are three principal types of molecules found in bitumen: aliphatics (or paraffinics), naphthenics (or cyclic) and aromatics. The various ways of interaction of these compounds affect the physical and chemical behavior of bitumen. These molecules are held together through chemical bonds that are relatively weak and can be broken by heat and/or shear forces.

Generally, bitumen can be divided into two broad chemical groups: asphaltenes and maltenes. The maltenes can be subdivided into saturates, aromatics and resins. These compounds enable comparison bitumen properties with broad composition.

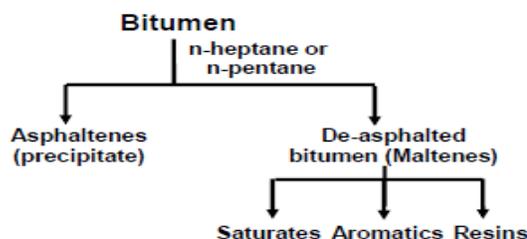


Fig 2.7. Separation of bitumen based on solubility into four classes (SARA fractionation)

In separating bitumen into fractions, various techniques have been developed where chromatographic techniques are the most common methods. There are based on differences in chemical reactivity and polarity. Bitumens can be separated into the four groups with using this technique such as: asphaltenes, resins, aromatics and saturates. The main characteristics of these groups are:

Asphaltenes: They are considered as highly polar, complex aromatic materials with a tendency to interact and associate. They have high molecular weights between 1,000 and 100,000. This is why asphaltene content has large effect on the rheological characteristics. The increase of asphaltene content results in the change in physical properties, such as harder bitumen with lower penetration, higher softening point and consequently higher viscosity. Bitumen contains 10 to 20% asphaltenes [49].

Resins: Resins (polar aromatic) are very polar in nature. This makes them strongly adhesive. They serve as dispersing agents for asphaltenes. The range of their molecular weights is within 500 to 50,000. Bitumen contains 10 to 25% resins.

Aromatics: They are weakly polar in nature and are known as naphthene aromatics. They also act as the dispersion medium for asphaltenes (peptised). They are made of 55 to 70% of the entire bitumen and their average molecular weight is within the range of 300 to 2000.

Saturates: Bitumen can be separated into saturates. Saturates are known as aliphatics and are non-polar viscous oils. This molecular weight range is similar to that of aromatics. They are waxy and non-waxy components. Saturates constitute 5 to 15% of the bitumen.

2.9.4 Bitumen Structure:

The structure of bitumen can be viewed from the perspective of a colloidal model. It is traditionally considered as a colloidal system with high molecular weight asphaltene micelles dispersed or dissolved in a lower molecular weight oily medium (maltenes). The micelles is made up of both asphaltenes together with an absorbed sheath of high molecular weight aromatic resins. These resins act as a

solvating layer and peptise the asphaltenes within the solvent maltenes phase. Bitumens are considered to be of solution or SOL type bitumens when the resins have adequate solvating power to fully peptise the asphaltenes. 'GEL' type bitumen are formed when the aromatic/ resin fraction has insufficient solvating power to fully peptise the asphaltenes. Most bitumens that are used in practice are of intermediate character.

The index of colloidal instability is used to describe the stability of the colloidal structure. The lower the CI, the more stable the colloidal structure. The extent of which asphaltenes are peptised will considerably influence viscosity of the bitumen.

2.9.5 Physical Characterization of Bitumen

The stress response of bitumen depends on loading time and temperature. Bitumen behaves elastic at low temperatures and short loading times while at high temperature and/or long loading times it behaves in a viscous manner. Therefore it can exhibit both viscous and elastic behavior. Different test methods (most of which are empirical) have been developed to characterize bitumen properties. These properties are divided into four groups: performance properties, index properties, control properties, mixing properties. Performance properties are real material properties such as stiffness and strength. The other properties are empirical properties which are related to performance properties.

Specifications of Bitumens: There are different specifications and quality of bitumens. The major and common specifications are: The oxidized bitumen, hard grade bitumen, Penetration grade bitumen and the cutback bitumen. The cutback bitumen is being considered in this work

2.9.6 Cutback bitumen in the Environment:

It is highly unlikely that the bitumen will move through the environment. This is based on the characteristics of kerosene and bitumen as there is no original information available on the fate of cutback bitumen in the environment. The kerosene as a component of cutback bitumen will be released into the environment. There will be 80% of the constituent kerosene hydrocarbons that is expected to

evaporate within five years, when applied in a chip seal [36, 40]. Cutback bitumen in soils is expected to adsorb to soil particles and be immobilized. It is not considered soluble in water nor readily biodegradable [50, 51].

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CHAPTER 3
MATERIALS AND METHODS

3.1 MATERIALS

3.1.1 Cutback bitumen grade (MC-1)

The MC-1 Cutback Bitumen that was used as a corrosion coating was produced from bitumen that was been liquefied by blending a kerosene petroleum solvent. The kerosene was obtained from a local road contractor in Abuja, Nigeria. It was blended with 60/70 penetration grade bitumen manufactured by Kaduna Refining and Petrochemical Company Kaduna, Kaduna State, Nigeria to give MC-1 cutback bitumen with standard specification as shown below. The blend was mixed manually at 80°C with 54% volume of bitumen and 46% volume kerosene. The precise Kerosene concentration was determined by weighing the blend after cooling to allow for evaporative losses during mixing. The sample was stored in an airtight tin container at room temperature (~ 30°C).

Table 3.1 Composition of Bitumen Cutback

Bitumen cutback (BC) Type	Grade	BC Penetration Grade		Percent of Total Volume	Kerosene
		Limits	Preferred		
MC	1	85 -100	60/70	54	46

Table 3.2 Specifications for Medium Curing Cut Back Bitumen

PROPERTY	BITUMEN MC-1		STANDAR D (ASTM/ AASHTO)
	Min	Max	
Viscosity @ 50°C	75	150	ASTM D 88 /AASHTO T72
Flash Point (Tag Open-Cup)	38		ASTM D3143 / AASHTO T79
Residue from distillation to 360°C, % (volume by difference)	60		
Test on residue from distillation Distillation:	120	300	ASTM D 5 / AASHTO T49 ASTM D 402 /AASHTO T 78
Distillate, volume % of total			
Distillate to 360°C to 190°C		20	
to 225°C	25	65	
to 316°C	70	90	
Penetration at 25°C, 0.1mm	100	-	
Ductility at 25°C, cm	100		ASTM D113 / AASHTO T51
Solubility in trichloroethylene	99.5%		ASTM D2402 / AAHTO T44

3.1.2 Low Carbon Steel

A sectioned API 5L X65 steel pipes with dimension 508 mm external diameter and 20 mm thickness were used for this work. They were obtained from SCC (NIGERIA) LTD, Ushafa Abuja, Federal Capital Territory, Nigeria.

3.1.2.1 CHEMICAL COMPOSITION OF LOW CARBON STEEL (API 5L X65)

The EDX chemical analysis of the low carbon steel (API 5L X65) samples revealed the important constituents of the X65 steel, as shown in Table 3.2:

Table 3.3: Chemical composition of the low carbon steel coupons

Elements	C	Mn	Ni	Cr	Mo	Si	Al	Cu	V	P	S
Composition %	0.08	1.6	0.04	0.02	0.01	0.3	0.04	0.02	0.05	0.009	0.0005

3.1.3 Chemicals for Test Media

The experiments were carried out using following reagents as test media:

Analytical grade hydrochloric acid (HCL) and sulphuric acid (H₂SO₄) was obtained from Finlab Laboratory Wuse II, Abuja, Nigeria.



Fig 3.1 Test media for Corrosion experiment

3.2 EQUIPMENT

The different equipment used for spraying of the coatings, pH measurements, temperature increase, weighing and other experimental processes for effective analysis include:

- Spraying machine gun (Hand sprayer, Wenling BSS Air Tools Co., Ltd, Mainland, China)
- Weighing balance (8-14.5V, 6W) (Adventurer model, Ohaus, New Jersey, Liberty State, USA)
- Painting brush
- Starter pH meter (300C, Ohaus, New Jersey, Liberty, USA)
- Petri-dishes
- Air-furnace (120V, 12.4A) (Model F62735, Thermo Scientific Barnstead/thermolyne, Dubuque, Iowa, USA,)
- Digital optical microscope (Model 44345, Celestron, Torrance, California, USA)



Fig 3.2 Spraying machine gun



Fig 3.3 Air Furnace
(Barnstead/thermolyne 120V, 12.4A)



Fig 3.4 pH meter (Starter 300C , 4A, 1.5V)

3.3 EXPERIMENTAL METHODOLOGY

3.3.1 Surface Preparation of the Coupons

3.3.1.1 Cutting

The test samples were prepared with the aid of electric hack saw. The low carbon steel was cut into small samples of dimension 10 mm x 10 mm x 11 mm. The samples were first cleaned with 50 grit size emery paper in order to remove the dirt and grease from the metal surface.



Fig 3.5 Cut samples

3.3.1.2 Coarse grinding

The cut samples were subjected to rough grinding on 60, 120 and 240 grits emery papers, using a grinding machine. The grounded surfaces were oriented normally to the axis of the mount. Hence the initial scratches and the resulting scratches that were produced were roughly at right angles to each other.



Fig 3.6 Grinding machine

3.3.1.3 Fine Grinding

The samples are subjected to fine grinding after the coarse grinding stage. This was done with the use of a series of emery papers (MIPOX Abrasives India PVT, Bengaluru, Kaarnataka, India) with grit sizes of 320, 400, 600 and 2400. The samples were oriented at 90° to the prior scratch marks formed by the preceding step. This positioning made it easier to determine when the scratches from the preceding grade of emery paper.



Fig 3.7 Grinding machine

3.3.1.4 Rough Polishing

This stage ensured that the fine scratches on the surfaces produced during fine grinding stage are minimized by polishing the samples with a polishing machine. A 9µm diamond paste (MIPOX Abrasives India PVT, Bengaluru, Kaarnataka, India) was placed on texmet cloth surface of the rotating-polishing wheel. The samples were then pressed against the texmet cloth of the rotating wheel with manual, to produce highly polished surfaces on the samples.

3.3.1.5 Final Polishing

This stage was carried out on the samples to eliminate the fine scratches remaining from the rough polishing stage. This ensured that the samples had scratch-free mirror-like surface finishes. The final

polishing was performed on a rotating wheel covered with a texmet cloth (Buehler, dusseldorf, Germany) and a polishing compound of alumina powder suspension with a sub-micron particle size.



Fig 3.8 Polishing machine

3.3.2 Preparation of the Uncoated and Coated Samples into Different pH solutions

3.3.2.1 Preparation and Immersion of the Uncoated Samples into Different pH Solutions

The initial weight measurements of the polished samples were obtained using a weighing balance. A set of uncoated samples was then totally immersed in beakers containing prepared hydrochloric solutions of pH 2, 3, 4 and 7. The samples were withdrawn from the different pH media after every 72 hours, they were then cleaned with acetone before drying them and measuring the weights with weighing balance. The experiments were conducted at 72 hours, intervals for a total of 648 hours. The different pH media were maintained at room temperature (25^oC-30^oC) through the duration of the experiment.

3.3.2.2 Preparation of Spray-coated Samples and Immersion into Solutions of Different pH

A second set of the samples was spray-coated with MC-1 cutback bitumen using a spraying gun model. The spraying operation was carried out at room-temperature to introduce bitumen coating with thickness of 0.04mm. The samples were then weighed with a weighing balance (Adventurer model, OHAUS, New Jersey, Liberty State, USA) before immersing them in beakers that were left at room-temperature (25^oC -30^oC) in a water bath for 504 hours. The weights of the specimens were measured at intervals of 72 hours during these exposures.

3.3.2.3 Preparation of Brush-coated samples into Different pH solutions

The third set of samples was brush-coated with MC-1 cutback bitumen. This brushing operation was done at room-temperature 25°C-30°C to introduce bitumen coatings with an approximate thickness of 0.05mm, The coated specimen were then immersed in test media with controlled pH (2, 3, 4 and 7). In this way, the specimens were exposed to room-temperature (~ 25°C). The subsequent weight gain was also measured at intervals of 72 hours over a duration of 504hours (21 days).



Fig 3.9 Uncoated coupons at 25°C



Fig 3.10 Coated coupons at 25°C

3.4 CORROSION RATE DETERMINATION FOR UNCOATED AND COATED COUPONS

The average corrosion rate (r), of the coupons (measured in millimeter per year, mpy), was determined using the following expression [1-5]:

$$r = \frac{534W}{\rho AT}$$

where W is the weight loss in milligrams, ρ is the density of coupons in milli-grams/cm³, A is the exposed area of the test coupon in m² and T is the exposure time in hours.



**Fig 3.11 Weighing balance
(Adventurer model, OHAUS, New Jersey, Liberty State, USA)**

3.5 REFERENCES

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CHAPTER 4
RESULTS AND DISCUSSION

4.1 WEIGHT LOSS AND WEIGHT GAIN MEASUREMENT

Table 4.1: Weight loss measurement of X65 steel immersed in various pH of HCl solution and distilled water

Uncoated samples	HCl pH	Percent Weight change measurement as a result of exposure time								
			0 Day	3 days	6days	9days	12 days	15days	18days	21days
A	2	0	0.073	0.139	0.192	0.462	0.310	0.337	0.436	
B	3	0	0.025	0.0957	0.101	0.349	0.197	0.231	0.276	
C	4	0	0.0693	0.145	0.263	0.423	0.277	0.326	0.402	
D	7	0	0.006	0.12	0.133	0.373	0.213	0.227	0.287	

Fig 4.1: Plot of weight loss change of uncoated (control) samples against exposure time in different pH HCl media.

The corrosion behavior of uncoated low carbon steel (X65) in hydrochloric acid is given in Table and Figure 4.1. This was studied by conventional weight loss method for 21 days (504 hours) at room temperature. Fig 4.1 shows more increase in weight loss in HCl media of pH 2, as compared to the other concentrations. There is general increase in weight loss of the samples in different pH with slight sharp decrease followed by increase in weight again. The increase in weight loss can be explained by the dissolution of the metal, where a passive oxide layer is being formed with time at the surface of the steel. This reduces weight loss till around 360th hour where the presence of chloride ions and moisture breakdown the porous passive oxide layer that is form resulting in more corrosion of the steel samples.

Table 4.2: Weight change of uncoated and sprayed X65 steel samples in pH 2 of HCl solution

samples	HCl pH	Weight change measurement as a result of expos ure time							
			0 Day	3 days	6days	9days	12 days	15days	18days
W	2	0	0.428	0.0517	0.0222	0.0444	0.318	0.207	0.370
A	2	0	-0.073	-0.139	-0.192	-0.462	-0.310	-0.337	-0.436

Fig 4.2 Plot of percentage weight change of uncoated and spray-coated steel against exposure time in pH 2 HCl solution

Table 4.2 and Figure 4.2 show the corrosion behavior of uncoated and bitumen coated X65 steel in pH 2 of HCl solution. There is weight loss for the uncoated steel as shown in Fig 4.1.

The sprayed bitumen coated steel showed a sharp increase in weight or swelling and sudden decrease in weight is due to the water uptake of the bitumen coating and its disbond from the metal. These cyclic effects as seen from the fig 4.2 can eventually compromise the barrier properties of the coating.

Table 4.3: Weight change of uncoated and brushed X65 steel samples in pH 3 of HCl solution

samples	HCL pH	Weigh t chang e measu rement as a result of expos ure time							
			0 Day	3 days	6days	9days	12 days	15days	18days
B	3	0	-0.025	-0.0957	-0.101	-0.349	-0.197	-0.231	-0.276
X	3	0	0.17	0.198	0.104	0.0942	0.283	0.235	0.292

Fig 4.3: Plot of percent weight change of uncoated and brush-coated steel against exposure time in pH 3 (HCl)

The increase in weight of the coated sample is due to the water absorption of the bitumen coating through pores and micro-cracks as shown in Figure 4.3. This resulted in gradual coating debonding and the formation of blisters at the coating-substrate interface as corrosion could occur in the disbondment area leading to subsequent decrease in weight. The small reduction in the weight of the coated steel could be due to formation of iron (II) oxide and the attack of the chloride ion on the sharp edges of the steel samples which could not be properly coated due to the geometry. The comparison of the uncoated (control sample) and the brush coated sample shows though there is high water uptake of the coating, a lower smaller amount of corrosion product is formed from the brushed coated sample, as can be observed from the weight measurement.

Table 4.4: Weight change of uncoated and sprayed X65 steel samples in pH 4 of HCl solution

Uncoated samples	HCL pH	Percent Weight change measurement as a result of exposure time							
			0 Day	3 days	6days	9days	12 days	15days	18days
C	4	0	-0.0693	-0.145	-0.263	-0.423	-0.277	-0.326	-0.402
S	4	0	0.576	0.545	0.650	0.545	0.668	0.558	0.567
L	4	0	0.495	0.417	0.469	0.295	0.547	0.564	0.573

Fig 4.4: Plot of percent weight change of uncoated, brush and spray-coated steel against exposure time in pH 4 HCl solution

Fig 4.4 shows similar trend weight change behavior for both sprayed and brushed coated steel samples in HCl media of pH 4.0. The cyclic behavior in the increase and decrease in weight of the samples at pH 4 is due to the water absorption of the bitumen coatings through the micro-pores and gradual disbond of the coating from the metal respectively. This contributes to blisters formation being observed at the coating surface. The decrease in weight of the coated steel could also be as a result of the sharp edges of the coupons that did not adhere to the coatings. This allows the gradual dissolution of the metal, due to direct attack of the chloride ions on the oxide layer.

Table 4.5: Weight change of uncoated, brushed and sprayed X65 steel samples in pH 7 of HCl solution

Samples	HCL pH	Percent Weight change measurement							
			0 Day	3 days	6days	9days	12 days	15days	18days

		Percent weight change as a result of exposure time							
		0	3 days	6 days	9 days	12 days	15 days	18 days	21 days
D(uncoated)	7.0	0	-0.006	-0.12	-0.133	-0.373	-0.213	-0.227	-0.287
J(brushed)	7.0	0	0.517	0.0349	-0.021	-0.118	-0.118	-0.021	-0.133
R(sprayed)	7.0	0	0.380	0.285	0.212	0.095	0.0731	-0.0219	0.241

Fig 4.5: Plot of percent weight change of uncoated, brush and spray-coated steel against exposure time in pH 7 HCl solution

The weight percent behavior of the uncoated (control) and bitumen coated steel in distilled water solution of pH 7 is different from HCl solutions of pH 2, 3 and 4. This is due to different diffusion behavior as a result of abrupt change in the concentration of the solution. Fig 4.5 shows decrease in weight, for both brush and spray-coated samples, after an initial increase in the weight of these coated samples. The comparison of the uncoated and coated samples shows that the coated samples corrodes less than the uncoated samples.

CHAPTER 5 CONCLUSION

5.1 Summary and Concluding Remarks

This study presents of an experimental study of the effects of bitumen coatings on the corrosion of API 5L X65 low carbon steel. Corrosion was studied in different concentrations of hydrochloric acid (pH 2, 3 and 4) and distilled water at a pH 7 at room temperature. To understand the corrosion behavior of the uncoated samples and the water absorption behavior of the cutback bitumen coatings on X65 steels, the weights of the samples were measured. Greater weight loss was observed in the uncoated samples

immersed in HCl solution with a pH of 2. This is mostly due to the attack of chloride ions on the surface of the steel. The weight changes in the coated steel (in the different pH of HCl) are attributed to the effects of water absorption (uptake) due to diffusion mechanisms, de-bonding of the coating and the corrosion of the substrate.

The visual examination and weight changes showed that spray-coated samples are more likely to corrode less than brush-coated samples. Blisters formation and coating de-bonding were observed in some of the coated samples after the exposure time of 504 hours (3 weeks). These are attributed to the effects of hydrostatic stresses that can open up micro-pores and micro-cracks following the swelling of bitumen coatings.

These preliminary results suggest that cut-back bitumen may have the potential for future applications as a coating on X65 steels and pipeline steels in general. The results also show that cutback bitumen may be applied using brushing or spray deposition techniques.

5.2 Suggestion for Future Work

There is strong recommendation that further study should be carried out on:

- The study of the swelling, interfacial cracking, and corrosion behavior in well controlled environments at both room temperature and higher temperature.
- The modeling of swelling, interfacial cracking and corrosion degradation of phenomena using measurements of layer properties obtained from indentation measurements.
- The use of electrochemical measurement techniques along with the weight measurements method to characterize the organic coatings and analyze the degradation of coated metal surface.

- The provision practical guidelines for maintenance of bitumen-coated pipelines.