

DESIGN OF A TYPICAL OFFSHORE TRANSPORTATION SYSTEM FOR INTERNAL CORROSION**A. Shittu¹,**

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ABSTRACT: The internal corrosion assessment of a typical transportation system has been presented. A system of Pipelines has been designed that will convey hydrocarbons from a land based process facility to an offshore loading platform where it will be exported via bulk carriers. The candidate material selected carbon steel L450 was found to be satisfactory as it showed effective resistance against the internal environment of the pipeline. Sour corrosion has been examined to be the most probable form of corrosion to occur within the pipeline given the data provided. The corrosion allowance selected was found to be sufficient within the design life to provide the integrity of the pipeline as the corrosion rate was computed as 0.1mm/yr (Upset/worst condition).

Keywords: Offshore transportation system, Pipeline, Corrosion allowance, hydrocarbon

1.0 INTRODUCTION:

In the oil and gas industry, corrosion is one of the main issues that have to be considered from basic design phase until decommissioning of a system under service. Estimates of annual cost of corrosion in oil and gas pipelines have indicated tremendous economic loss and much can be done

to reduce this (Fontana, 1986). Weakening of the pipeline by corrosion will reduce the resistance of the pipeline to external forces and will accentuate materials and fabrication weaknesses (Palmer and King, 2006). The battle against corrosion and its devastating effects is never ending in all engineering disciplines (Roberg, 2000).

The three main reasons for the importance of corrosion assessment are economics, safety, and conservation (the structure must be safe to prevent contamination of the environment and reduce wastage of resources). Examples of losses resulting from corrosion include shutdown, loss of product, loss of efficiency and contamination of product (Revie and Uhlig, 2008).

Corrosion can be described as the destructive attack of a metal by chemical or electrochemical reaction with its environment (Revie and Uhlig, 2008). The process by which metals convert to the lower-energy state is called corrosion. The following are the four requirements of an aqueous corrosion cell (Jp-Kenny, 2008):

- (1) There must be an ionic path or an electrolyte (such as moisture containing internal fluids and the surrounding seabed soil containing sea water)
- (2) There must be a metallic path electrically connecting the anode and cathode where electron transfer can take place (Normally, this will be the pipeline itself)
- (3) There must be an anode which suffers corrosion or corrodes preferentially and is a site where oxidation reaction occurs and with removal of electrons.
- (4) There must be a cathode.

Elimination of any of the four requirements for the corrosion cell stops the corrosion reaction. Several types of aqueous corrosion can take place internally either when the pipeline is in operation or not, and the common types include (Palmer and King, 2006; Heidersbach, 2011):

- (1) General/ Uniform attack
- (2) Pitting
- (3) Galvanic
- (4) Crevice
- (5) Inter-granular
- (6) Erosion-Corrosion
- (7) Stress Corrosion
- (8) Hydrogen Damage
- (9) Sweet Corrosion
- (10) Microbial Induced Corrosion.

The environmental factors that influence corrosion rate are:

- (1) CO_2 partial pressure
- (2) H_2S partial pressure
- (3) Fluid temperature
- (4) Water salinity
- (5) Water cut
- (6) Fluid dynamics
- (7) pH

Internal corrosion is normally controlled by one or more of the following:

- (1) Material choice
- (2) Use of Inhibitors
- (3) Treatment of the environment
- (4) Structural design including corrosion allowances
- (5) Scheduled maintenance and inspection

The purpose of this work is to undertake corrosion assessment for the proposed pipeline so as to evaluate and nominate candidate materials on the basis of code compliance and materials performance within the expected operating environment and to satisfy the requirement of high standards for material selection and corrosion control (to have a pipeline system that can provide a

safe, robust, reliable, durable and cost-effective means of transporting crude oil). This work deals with the internal corrosion assessment of the proposed export pipeline carrying the hydrocarbon. ANSI NACE MR0175/ ISO 15156-2 (2009) will be employed to carry out the corrosion assessment for the proposed pipeline. It was observed from design data that the crude oil has been fully stabilized from the onshore processing facility.

2.0 BACKGROUND OF WORK

For aqueous corrosion to occur internally within pipelines free water must be present. In the absence of oxygen, corrosion is determined by the concentrations of CO_2 or H_2S in the hydrocarbon. Other factors affecting corrosion rates include temperature and pressure which determine the nature of liquid or gas on the metal surface and the minor constituents in the liquid water phase.

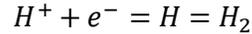
Crude oil is a generally benign (or non-corrosive) environment but minor constituents of the crude oil can cause corrosion if they separate into the water phase. Some micro-droplets of water may remain in suspension to suggest that separators do not completely remove water from the oil coupled with the fact that a long service pipeline can act as a separator and small quantities of water could separate at the bottom of the pipelines (Palmer and King, 2006). If the velocity of flow of the oil is sufficiently high, water is entrained within the oil resulting in oil wetting of the pipeline surface. Under such conditions corrosion occurrence is unlikely. Corrosion occurs internally in the pipeline only if free water is present

2.1 Hydrogen Sulphide (H_2S) Environments

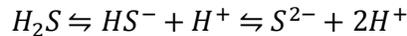
Sour corrosion can be described as a form of corrosion which takes place in environments containing H_2S due to the presence of Hydrogen sulphide H_2S . Sulphur is a measure of “sourness” and “sweetness” of crude (CMES, 2010). If the amount of sulphur content in the crude oil is greater than 0.5% then it is sour grade whereas if the sulphur content is less than 0.5% then the crude oil is said to be the sweet grade. The sourness of the crude oil can be linked to sour corrosion (Heidersbach, 2011). Sour corrosion occurs in fluids due to the presence of H_2S in the crude oil. According to Palmer and King (2006), a fluid can cause a form of sour corrosion if the partial pressure of hydrogen sulphide is greater than or equal to $0.34kPa$.

The metabolism in some micro-organisms involves sulphur and production of H_2S which is a form of Microbial Induced Corrosion (MIC). Several forms of cracking can occur as a result of H_2S such as Sulphide Stress Cracking (SCC), Hydrogen Induced Cracking (HIC), Stress Oriented Hydrogen Induced Cracking (SOHIC), etc. (Bardal, 2004). Steels that are susceptible to hydrogen related cracking such as carbon steels are more likely to do so in a sour environment where H_2S promotes the ingress of atomic hydrogen; and problems associated are more serious due to the formation of hydrogen gas. The presence of H_2S can cause pitting corrosion (if H_2S concentration is 100 ppm in the product) in such a way that clusters of small pits are created on the pipe surface. The following can be used to describe the mechanism of hydrogen absorption:

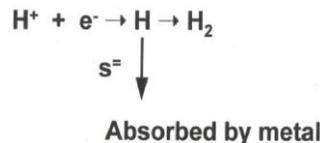
In normal acidic conditions, the cathodic reaction is:



But in the presence of H_2S :



H_2S forms a weak mineral acid when dissolved in water which can lower the pH, make the environment acidic and increase corrosion rate. In addition, the sulphide ion inhibits the cathodic reaction and prevents the formation of diatomic hydrogen. Consequently, the monatomic hydrogen formed becomes rapidly absorbed by metals which is preceded by adsorption:



It is not clear how much water is required to cause sour corrosion therefore it is safe to assume that only a trace of water may be sufficient to induce sour corrosion. If a fluid contains traces of H_2S , it is wise to select the pipeline materials that are resistant to such environment because (Jain, 2012): (a) inspection and repair is extremely costly especially if production is disrupted (b) there is uncertainty in predicting the amount of H_2S content. (c) Carbon steel pipes resistant to sour service are only nominally expensive compared to non-sour service materials.

If the $P_{H_2S} > 0.34kPa$ then SSC can occur whereas if $P_{H_2S} > 0.69kPa$ HIC can occur (Jain, 2012) in the presence of water. However, occurrence of HIC largely depends on the partial pressure of CO_2 in the product (Heidersbach, 2011). Also, the risk of Sulphide Stress Corrosion Cracking (SSCC) reduces at temperatures above $80^\circ C$, and that of HIC diminishes with temperatures above $65^\circ C$. Pitting corrosion and environmental cracking are the two most probable forms of degradation which lead to pipeline failure.

Several models (Nesic et al., 2005; Hernandez et al., 2006; Gartland et al., 2003) are available for estimating corrosion rate such as the one proposed by Nesic et al. (2008) where a mechanistic H_2S corrosion model which includes the kinetics of iron sulphide growth by solid state reaction was developed.

2.2 Erosion Corrosion

Erosion Corrosion occurs as a result of a combination of chemical environment/ electrolyte and high fluid surface velocities (Heidersbach, 2011) or relative motion between the electrolyte and the corroding surface (Fontana, 1986). Hence, there is an increase in the rate of attack on the metal surface. This results in wearing away of protective scale or coating on the metal surface as dissolved ions, or it forms solid corrosion products that are mechanically swept from the metal surface. The main cause of this type of corrosion is associated with turbulent flow and this exists mostly around pipeline bends, elbows, valves and joints, grooves, gullies, rounded edges, and waves

on the metal surface which usually indicates directionality, characterizes this form of damage (Roberge, 2000).

Corrosion allowance is usually specified to take care of erosion corrosion among other types of corrosion. In all aqueous corrosion processes, it is necessary for a solution to be present before the corrosion reaction can take place likewise erosion corrosion.

Scales tend to build up over a period of time after an initial high corrosion when the flow in the pipeline is low and when water phase is present. The formation of protective siderite films results in a reduction in corrosion rate but if the rate of flow becomes high, product scales and inhibitors if applied will erode away. The velocity at which the protective scale formation on the pipe surface cannot occur and erosion corrosion is initiated is known as 'erosional velocity'. This velocity can be determined from the following formula (Heidersbach, 2011). Although this formula is strictly for topsides equipment piping, it can be expressed as:

$$V_{\text{eros}} = \frac{1.23C_e}{\sqrt{\rho_P}} \quad (1.1)$$

where V_{eros} is the erosional velocity (m/s), ρ_P is the fluid density and C_e is a constant with its value depending on the pipe material. The value of C_e for carbon steel is taken to be 100 for solids-free continuous service, 125 for solids-free intermittent service, 150-200 for solids-free, noncorrosive continuous service and 250 for solids-free, noncorrosive intermittent service.

The temperature of internal fluid and presence of sand can affect the severity of erosion corrosion. In this pipeline it is not necessary to reduce the flow velocity as constituents which could lead to erosion corrosion has been removed and the corrosion allowance provided has covered for any form of corrosion unforeseen.

Galvanic corrosion involving two metals can influence erosion corrosion rates when two dissimilar metals are in contact in a flowing system, this can be referred to as galvanic effect. The galvanic effect may be nil under static conditions but may be greatly increased when there is movement (Bardal, 2004).

The following are methods which can be used for mitigating the damage due to erosion corrosion (Bardal, 2004) (1) Material with better resistance to erosion corrosion (2) Design: Altering the flow velocity, use of less bends, fittings, increasing pipe diameter, corrosion allowance, the use of readily replaceable components; (3) Alteration of the environment, etc.

There are various forms of corrosion involving the interaction between a corrosive environment and stress, some of which are: (1) Stress corrosion cracking (SCC) which includes: sulphide stress corrosion cracking and chloride stress corrosion cracking. (2) Corrosion fatigue (cyclic stress) (3) Stress oriented hydrogen induced cracking (SOHIC) (Roberge, 2000).

2.3 Hydrogen Embrittlement

Hydrogen embrittlement can be described as a phenomenon whereby hydrogen is absorbed in the metal by diffusion, exerts local stresses, and leads to embrittlement of materials such as high

strength steels (Heidersbach, 2011; Zaki, 2006). There are several situations which can cause HE some of which include poor manufacturing, poor fabrication processes, excessive overprotection currents from CP systems, sour environments, etc.

Improper welding procedures can also introduce monatomic hydrogen into metals. The exact mechanisms of HE in steels have not been completely understood.

Carbon steels are considered more susceptible to hydrogen embrittlement than austenitic alloys. HE can result in a reduction in the yield strength of carbon steels, cause severe embrittlement of the metal and then result in brittle fractures in the presence of stress. HE failures are associated with relatively low temperatures below 100°C. On the other hand, exposing carbon steels to high temperatures can have counteracting effects. The metal surface is being exposed to increased amount of hydrogen generated due to accelerated corrosion or other chemical reactions which enhances atomic diffusion as well as subsequent outgassing. Areas where HE is suspected can be treated using techniques which introduce compressive stresses on the surface (Zaki, 2006).

2.4 Hydrogen Damage

This is the most important form of sour corrosion and thus a major threat to carbon steel pipelines (NACE, 1985). The following are the types of hydrogen damage as the mechanism by which hydrogen diffuses into the steel has been described.

2.4.1 Sulphide Stress Corrosion Cracking (SSC)

High strength steels of Rockwell hardness above 22 in sour environments are generally more susceptible to this form of corrosion. Since it occurs only if stress is present and causes severe embrittlement, it is referred to as a special case of stress corrosion cracking and hydrogen embrittlement. As a result of the formation of metallic sulphides, the monatomic nascent hydrogen formed due to the reduction reaction between the steel and H₂S, rapidly dissolves in the metal matrix causing internal cracking.

In order to mitigate the severity of SSC the following should be adopted: (1) The use of alloys less susceptible to SSC. (2) The use of steels with Rockwell hardness less than 22 (3) Minimize tensile stresses in the system, etc.

2.4.2 Hydrogen Induced Cracking (HIC)

HIC also called stepwise cracking, staircase cracking, and Cotton cracking is caused by the diffusion of atomic hydrogen into the metal such that it becomes trapped in a non-metallic inclusion or at grain boundaries to produce molecular hydrogen. As a result of this, a high pressure is localised at the inclusions or grain boundaries until bulging occurs and then production of blisters or cracks. These cracks are parallel to the surface along the original laminates generated at the various depths. These are finally connected together; stepwise cracking occurring when short blisters at varying depths within the steel link together to form series of steps (Zaki, 2006).

HIC is a major concern in H₂S containing environments and is a form of hydrogen damage which does not require tensile stress. Figure 1.2 (Heiderbach, 2011) shows the environmental conditions where HIC is considered important for pipeline steels.

An example of nonmetallic inclusions is manganese sulphide. In the past, manufacturing techniques were often conservative such that sulphides are contained in carbon steels. Manganese present in carbon steels and sulphur react to form manganese sulphide inclusions. The use of Thermomechanically Controlled Processing (TMCP) often compounds the problem because as the metal is rolled the inclusion become flat and stress concentration at the tip ensues. This entails high tendency of cracking when atomic hydrogen diffuses into the metal. Today, the problem has been solved as HIC resistant steels are manufactured with low sulphur content.

In low-sulphur steels, factors such as the presence of ferrite - pearlite banding, also promote HIC. The following are the conditions necessary for HIC to occur: (a) The presence of water phase (b) the presence of atomic hydrogen (c) an agent that retards the formation of molecular hydrogen at the surface such as H₂S (d) presence of grain boundaries or inclusions, etc.

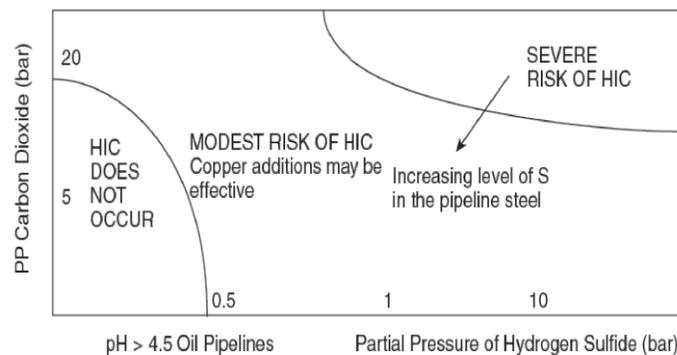


Figure 1: Environmental Conditions where HIC is important. Source: Heidersbach (2011)

The risk of HIC is reduced by selecting a suitable composition of the steel as well as by using manufacturing techniques that minimize inclusions. Others include changing the corrosive environment, alloying the material and the use of coatings.

2.5 Stress Oriented Hydrogen Induced Cracking (SOHIC)

This is associated with presence of applied stresses in steel combined with HIC which results in interconnecting cracks formed to form stepwise cracks and the result being relatively long cracks in a such away as to resemble a combination of SSC and HIC failure patterns. Pipelines are found to exhibit this type of failures. The hoop stresses in pressurized pipelines containing sour fluids have been found to be linked to SOHIC.

2.6 Microbially Influenced Corrosion (MIC)

MIC can be defined as an electrochemical type of corrosion in which certain micro-organisms have a role, either enhancing or inhibiting. Like most other forms of corrosion, MIC is an electrochemical process which requires water and thus if water is not present MIC is not likely (Zaki, 2006). In the presence of water, microbes can survive and their activities affect the severity of corrosion. MIC can occur in environments where corrosion is usually not anticipated such as areas isolated from oxygen or other apparent corrodants and could occur rapidly (Heidersbach, 2011).

There are various issues generally associated with the activities of microbes in the oil field some of which include:

(1) Reservoir souring (2) Increase in the H₂S concentration (3) Rapid production decline (4) Metal sulphide scales (5) Inefficient oil or water separation, etc.

Bacteria attached to metallic surfaces begin to form thin biofilms containing cells which could be living or dead plus water and debris originating from the environment. Growth of these films could lead to changes in the chemical concentrations of the water at the interface between the biofilm and metal substrate. Localised areas could be produced and can lead to growth of Sulphate Reducing Bacteria (SRB) since they thrive in such anaerobic environments. The formation of biofilms can lead to concentration gradients creation and thus production of electrochemical cells.

Typical examples of such environments where MIC exist include improperly drained and dried pipelines which have been hydrotested with untreated seawater containing microbes. Sessile bacteria attach themselves to metal surfaces while planktonic bacteria are mobile.

Sessile bacteria cause most of the corrosion problems in oilfield equipments. Planktonic bacteria can produce corrosive chemicals which can lead to corrosion and H₂S related cracking. According to NACE, the following are classified as the most important types of bacteria in the oilfield: (1) SRB (2) Iron-oxidizing bacteria (3) Acid-producing bacteria (APB) (4) Sulphur-oxidizing bacteria (SOB) (5) Slime forming bacteria. However, the most widely used classification is the distinction between aerobic and anaerobic bacteria (i.e. either requiring oxygen for metabolism or not).

Due to the surface roughness of Welds, they are preferential locations where bacteria colonies cultivate in such a way that their growth protects them from the action of biocides. Areas of lower flow velocities are sites where biofilms can grow under deposits; and it was claimed that biocides are not effective in killing sessile bacteria.

However, it is easy for chemical biocides to eliminate planktonic bacteria as they are unprotected by scale, debris, or biofilms. MIC is not an issue for pipelines operating at temperatures around 80 °C. The addition of chlorine as a biocide results in the acceleration of the rate of cathodic reaction. The reaction in carbon steels is under cathodic control, and the cathodic curve can be displaced such that the rest potential exceed the pitting potential. This can result in pitting corrosion and stress corrosion cracking in the presence of residual or thermal tensile stress.

2.7 Carbon-dioxide (CO₂)

The most serious corrosion problem in oil and gas production is caused by CO₂ (Bardal, 2004). But it only occurs in systems containing carbon dioxide combined with the absence of or only a trace of hydrogen sulphide (Palmer and King, 2006). Sweet systems contain none or only very small amount of H₂S less than 100ppm. If free water is not present, the presence of CO₂ cannot be considered a threat since CO₂ must dissolve in water to form carbonic acid.

2.8 Inhibitors

According to Fontana, (1986), an inhibitor is a substance that, when added in small concentrations to an environment, decreases the corrosion rate. In pipelines, corrosion inhibitors can be applied when a new pipeline is commissioned or at any other time within the operation of pipeline to transport the corrosive medium.

The effect of applying the anodic inhibitors is that the anodic curve is displaced such that the corrosion current reduces and thus the rate of the corrosion reaction. The same concept applies to cathodic inhibitors but in this case the cathodic curve is being displaced. In the mixed inhibitor both curves are displaced so that the corrosion current will be reduced. In this work [H₂S] of 9ppm suggests that the use of inhibitors can effectively take care of any threat. However, the crude oil has been fully stabilized and inhibitors will not be required except in situations where water leaks into the pipeline.

2.9 Sediments and Water

The major constituents of sediments include fine particles of sand clay, volcanic ash, drilling mud, rust, iron sulphide, metals and scale. This can only pose a threat if present in significant amount in the pipeline (University of Petroleum, 2010).

2.10 Pour Point

The pour point of the crude oil is a rough indicator of the relative paraffinicity and aromaticity of the crude. The lower the pour point the lower the parafin content and the greater the content of aromatics. The pour point indicates the relative amount of wax present in crude oil and is the temperature below which pumping and transportation problems may be encountered. Along with viscosity, the pour point is used in pumping and design calculations. Wax content may be normal paraffins above C₁₆ which are solid at somewhat ambient temperatures and these affect the flow behaviour of crude. The characterization factor KUOP is a measure of parafinity vis-a-vis aromaticity of crude and a high value is desired in terms of flow assurance (University of Petroleum, 2010).

2.11 Salt Content

It is measure of contamination in crude that can cause corrosion in the pipeline if in high concentration. Chloride salts can cause SCC (University of Petroleum, 2010).

2.12 Deposits

Black powder deposits such as iron sulphides and oxides, hydrocarbon solids, and other debris, which are found in pipelines, can pose significant threat because such powders may accumulate at low velocity locations in the pipeline and can cause blockage. Also, under deposit or crevice corrosion can occur due to the presence of such deposits (Heidersbach, 2011).

2.13 Elemental sulphur

According to Fang et al. (2008), contact of elemental solid sulphur (formed as a result of oxidation of hydrogen sulphide or oxygen contamination) in the presence of water can lead to the onset of catastrophic corrosion process. The process is function of the inherent temperature and pressure of the hydrocarbon. Also, studies show that elemental sulphur can cause localized corrosion of mild steel when they are in direct contact (Fang et al., 2008).

3.0 MATERIALS AND METHODS

3.1 Prove of Sour Corrosion

From the basic design data, it can be said that the crude oil is sour since the sulphur content is 1.87wt% which is higher than the required 0.5wt%. Sweet crude oil pipelines are usually susceptible to sweet corrosion while sour crude oils are not. Sour crude oil pipelines are usually susceptible to sour corrosion.

ANSI/ NACE MR 0175/ISO 15156-2 (2009), table 1 confirms that this code specification applied to this work (crude oil pipeline). The partial pressure of H_2S was found as follows:

(1) As provided in the design data 9 ppm of H_2S is dissolved in the crude oil on basis of weight (Density of crude oil $kg/m^3 = Specific\ gravity \times 1000 = 0.8562 \times 1000 = 856.2kg/m^3$),

$$1ppm_{weight} = \frac{1mg}{1kg}$$

1kg of the crude oil occupies a volume of $\frac{1}{856.2}m^3$ then,

$$1ppm_{weight} = 856.2mg/m^3$$

$$9ppm_{weight} = 9 \times 856.2 = 7705.8mg/m^3 = 7.71mg/L$$

(2) Using the following procedure the $[H_2S]$ in gas can be estimated (Robinson, 2011):

Finding Henry's law constant (Sander, 1999),

$$K_H = K_H^\theta \exp \left[\frac{d \ln K_H}{d \left(\frac{1}{T} \right)} \left(\frac{1}{T} - \frac{1}{T^\theta} \right) \right]$$

Where T is the operating temperature, $K_H^\theta = 1 \times 10^{-1} M/atm$, $\frac{d \ln K_H}{d \left(\frac{1}{T} \right)} = 2000K$ (According to Lide and Frederikse, 1995) and $T^\theta = 298.15^\circ K$. Therefore

$$K_H = 1.0 \times 10^{-1} \times e^{2000 \left(\frac{1}{273+80} - \frac{1}{298.15} \right)} = 0.035$$

(3) We need to convert to ppmv in gas so that we can use it in the ANSI/NACE MR0175/ISO 15156-2 (2009). Converting the H_2S in ppm dissolved in the crude oil to ppm dissolved in the gas using Henry's law is as follows

$$[H_2S] = \frac{S}{K} = \frac{9}{0.035} = 257.14 \text{ ppm in gas}$$

(4) Absolute pressure = atmospheric pressure + guage pressure i.e. $90.2 \text{ barg} + 1 = 91.2 \text{ bara}$.

(5) Using Figure C.1 of ANSI/ NACE MR 0175 /ISO 15156-2 (2009), the H_2S partial pressure was found to be 23 kPa

Since the partial pressure of H_2S is greater than 0.34 kPa and greater than 0.69 kPa then it is true that the crude oil can lead to SSC and HIC (or sour corrosion).

Using Figure 1 of the same code, we can have an idea about the severity with respect to the SCC of carbon steel but we need to know the pH first. Figure D1 annex D can be used for calculating the pH. Assuming the partial pressure of CO_2 is 0.5 (since it is sour regular crude oil), the pH corresponding to the partial pressure $P_{CO_2+H_2S} = 23.5 \text{ kPa}$ was found to be 4.3 . From Figure 1 of the same code, the region of severity corresponding to the pH value obtained was found to fall in region 3.

3.2 Corrosion Rate Calculations

The pH of the sour environment for the crude oil pipeline was calculated as 5.29 as shown below:

$$9 \text{ ppm in liquid} = \frac{\text{ppm in gm/liter}}{\text{Molecular Weight}} = \frac{7.71 \times 10^{-3}}{34.08} = 2.26 \times 10^{-4} \text{ molar solution}$$

$$pH = -\log_{10} [\sqrt{K[H_2S]}] = -\log_{10} [\sqrt{10^{-7} \times 2.26 \times 10^{-4}}] = 5.32$$

Using Figure 2 herein (Robinson, 2011) the corrosion rate corresponding to the pH was estimated to be $0.0094 \text{ ipy} = 0.2439 \text{ mm/year}$ (i.e. considering a worst condition if water and oxygen is allowed into the pipeline). However, the method has several limitations some of which include the following: (a) This estimate applies only to a case where oxygen and water are present in the system at room temperature (Oxygen reduction is the cathodic reaction) (Revie and Uhlig, 2008). (b) The corrosion rate should be lower than the predicted by this curve due to the presence of iron sulphide film formed on the metal surface except at pH values below 3 (Nesic et al., 2005; Koteswarani, 2010). 'Oxygen is approximately 50 times more corrosive than CO_2 and more than a hundred times more corrosive than H_2S ' (Heidasbach, 2011).

Since oxygen is more corrosive than H_2S (Heidersbach, 2011), the corrosion rate in the absence of oxygen can be approximated thus:

Using the graph in figure 3,

$$0.24 \text{ mm/yr} = 9.84 \text{ mpy} \approx 10 \text{ mpy}$$

10 mpy corresponds to [dissolved O_2] of 4.2 ppm = [H_2S] of 420 ppm

This corresponds to $4 \text{ mpy} = 0.1 \text{ mm/yr}$

According to NACE (1985), corrosion data surveys shows that the corrosion rate of steel at around 93°C and around 10% [H_2S] in water was between 0.02 and 0.05 ipy. Also, at around 20°C and 10% [H_2S] corrosion rate was found to be less than 0.02ipy. NACE (1985) also confirms that it is true that the environment can cause SCC of carbon steel. Hence, it can be said that the corrosion rate estimated is not unrealistic.

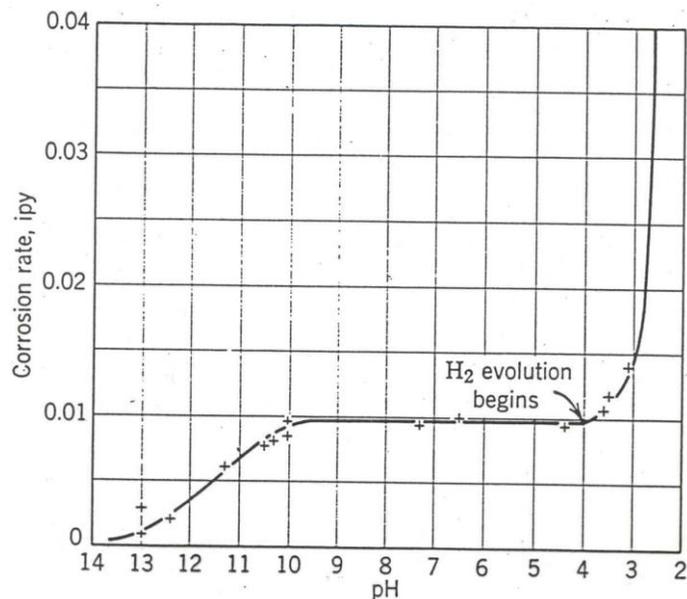


Figure 2: The effect of pH on general corrosion rate. Source: Several authors (Robinson, 2011; Koteeswarani, 2010; Revie and Uhlig, 2008)

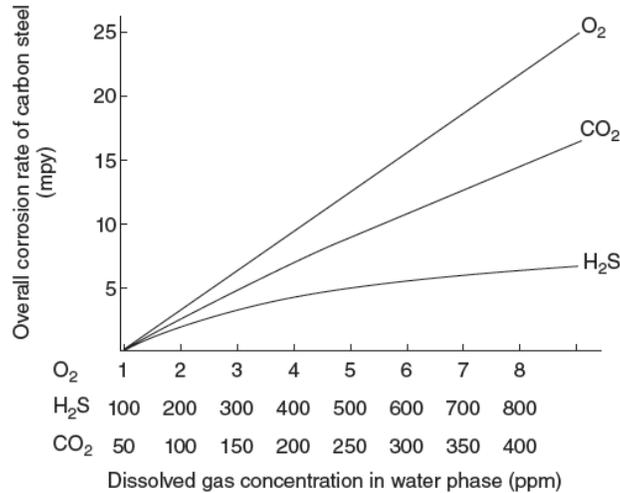


Figure 3: the effect of dissolved gases on the corrosion of carbon steel. Source: Heidersbach (2011)

3.3 Calculation of Erosional Velocity

The highest fluid velocity that can be tolerated before erosion corrosion will occur considering solids-free, noncorrosive continuous service,

$$V_{eros} = \frac{1.23C_e}{\sqrt{\rho_p}} = \frac{1.23 \times 100}{\sqrt{856.2}} = 4.23 \text{ m/s}$$

4.0 RESULTS AND DISCUSSION

The internal corrosion of a subsea pipeline is determined by the internal operating environment. This includes the operating pressure, temperature, and the occurrence of corrosive substituent in the production fluids. From the basic design data provided it can be observed that the crude oil has been fully stabilized such that it does not contain unwanted substances such as moisture (ionic path eliminated), coupled with the fact that crude oil is benign. Hence, the use of inhibitors will not be necessary for controlling internal corrosion since water that can cause corrosion is absent, except for situations where corrosion is suspected.

The fully stabilized crude oil should have oil wetting on the wall of pipeline, hence corrosion is unlikely (since only a trace amount of water and sediments is present and free water is absent). Internal corrosion over the service life will not be expected, apart from upset and offline conditions where water (perhaps with dissolved oxygen) leaks or is allowed to enter into the pipeline or in the unlikely situation of bacterial contamination. The general salt content is very high since its value 18lb/bbl is greater than the required 10lb/bbl, it represents a serious corrosion threat (University of petroleum 2010).

A likely source of bacterial contamination is during hydrotesting in such a way that untreated sea water, allowed into the pipeline system can bring bacteria (Heidersbach, 2011). It is recommended that before use, the seawater is treated with biocides and if bacteria contamination is suspected, the line should be cleaned and flushed using the process of pigging. However, the uses of biocides are no longer employed as new methods are available such as the introduction of smooth surfaces that can make attachment of biofilms very difficult thereby minimizing MIC (Heidersbach, 2011).

It has been proven that the crude oil that will be transported via the proposed pipeline can cause sour corrosion and according to ANSI/NACEMR0175 /ISO 15156-2, the region of severity was found to fall within SSC region 3. The material selected is satisfactory.

In the presence of water (and dissolved H₂S), the corrosion rate was estimated to be 0.1mm/yr (Upset/ worst condition). This suggests that it will require a process upset lasting 30 years for the corrosion allowance provided to be completely lost as a result of corrosion due to dissolved H₂S. Thus, the use of carbon-steel line pipe with a minimum 3mm corrosion allowance is considered sufficient to provide integrity through the service life of the line, and protect against process upsets that may occur. However, according to NACE (1985), materials with low penetration rate in a given corrosive environment may be unsuitable or failure may occur by some mode irrelevant to penetration (such as SCC).

The Multi Corp software MULTICORP V4.2, developed by Corrosion Centre Joint Industry Project (CC JIP) Institute for Corrosion and Multiphase Technology (ICMT), Ohio University can be used to estimate the corrosion rate for sour crude oil pipelines (Nesic et al., 2005). However, the use of proprietary software is not within the scope of this work. This is recommended for further consideration.

The use of internal corrosion lining will not be necessary due to the various disadvantages some of which include (Heidersbach, 2011): (a) they may not be suitable if the product contains sand. (b) Internal lining may not be practical for long pipelines. (c) Internal pipeline linings are not usually used due to difficulty in their application at field joints (d) They can de-bond due to decompression and they are subject to mechanical damage from inspection pigs and other sources.

Cleaning and pigging may be required to manage the pipeline to mitigate MIC threat, if contamination is suspected. It is recommended to do topside corrosion monitoring for the platforms especially for bacteria activity on regular basis. Pigs can be pushed through the pipeline accompanied by slugs of treatment chemicals designed to coat freshly exposed metal surfaces with corrosion inhibitors or to kill microbial communities disturbed by its passage.

In order to avoid the possibility of microbially induced corrosion, procedures should be put in place during pipeline construction and commissioning to prevent the ingress of untreated seawater which could then cause bacterial corrosion if left in place for any length of time.

The level of CO₂ and thus the partial pressure of CO₂ is expected to be very low coupled with the fact that the fluid is fully stabilized crude oil and considering oil wetting at wall of linepipe. Therefore

there is very low possibility of CO₂ corrosion to occur. The natural presence of oxygen in this pipeline is considered highly unlikely however there is a possibility of accidental introduction of oxygen into the pipeline during pre-commissioning and commissioning from untreated seawater or during maintenance. The highest fluid velocity that can be tolerated before erosion corrosion will occur considering solids-free, noncorrosive continuous service was found to be equal to 4.23m/s.

The flow conditions should be such that any elemental sulphur will be fully entrained in the crude and therefore not to be expected to drop out and result in increased internal corrosion (Jain, 2012). During offline condition, the pipeline should be filled up with diesel or any other substance which can prevent oxygen and moisture from contacting the pipeline internal surface. This will also prevent the growth of bacteria.

5.0 CONCLUSION

A system of Pipelines has been designed that will convey hydrocarbons from a land based process facility to an offshore loading platform where it will be exported via bulk carriers. The candidate material selected was found to be satisfactory as it showed effective resistance against the internal environment of the pipeline. Sour corrosion has been examined to be the most probable form of corrosion to occur within the pipeline given the data provided. The corrosion allowance selected was found to be sufficient to provide the integrity of the pipeline as the corrosion rate was computed as 0.1mm/yr (Upset/ worst condition).

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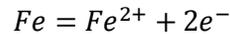
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APPENDIX A

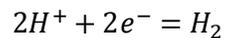
A.1. CORROSION REACTIONS

Reaction at the anode:

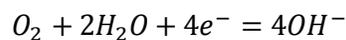


Reactions at the cathode are difficult to predict but can be categorized into one of the following reduction reactions:

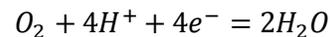
1. Hydrogen evolution



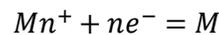
2. Oxygen reduction in neutral solutions



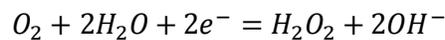
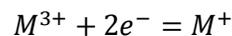
3. Oxygen reduction in acids



4. Metal deposition on cathode

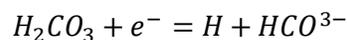


5. Metal ion reduction

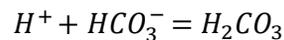


6. Sweet corrosion

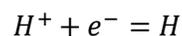
Carbonic acid



Regeneration



Net reduction



APPENDIX B

B.1. DATA:

Aim: To design a system of Pipelines that will convey hydrocarbons from a land based process facility to an offshore loading platform where it will be exported via bulk carriers.

Design life of pipelines: 30 years

Pipeline Material Data

Description	Units	Parameters
Linepipe Nominal Diameter	Inch (mm)	48 (1219)
Pipe Material	-	Carbon Steel
Linepipe Material Grade	-	L450
Manufacturing Method	-	SAW (Submerged Arc Welding)
Corrosion Allowance	mm	3

Operating/ Product Data

Parameters		Unit	Values
Service		-	Regular Crude Oil
Pressure	Design	Barg	96
	Maximum Operating	Barg	90.2
Pipeline Hydrotest Pressure		Barg	To be determined as per Code
Temperature	Design	°C	80
	Maximum Operating	°C	60
Specific Gravity at 15.6 °C		-	Regular 0.8562

Regular Crude Oil Properties

Characteristics		
1.	Specific Gravity @ 60°F	0.8562
2.	API Gravity	33.8
3.	Water Content, vol. %	<u>Nil</u>
4.	Water & Sediment, vol. %	Trace
5.	Asphalten Content, wt %	0.45
6.	Sulphur Content, wt %	1.87
7.	Salt Content, lb/ 1000bbl	18.0
8.	Wax Content, wt %	1.05
9.	H ₂ S Dissolved in Crude Oil, ppm	9.0
10.	Carbon Residue, wt %	3.16
11.	Pour Point, °C	< -20
12.	Characterization Factor (KUOP)	12.0
13.	Reid Vapor Pressure @ 100 °F, psi	7.2
14.	Kinematic Viscosity, cSt.	
(a)	@ 21.1°C (70 °F)	11.25
(b)	@ 37.8°C (100 °F)	7.361
(c)	@ 48.9°C (120 °F)	5.711
(d)	@ 60.0 °C (140 °F)	4.612

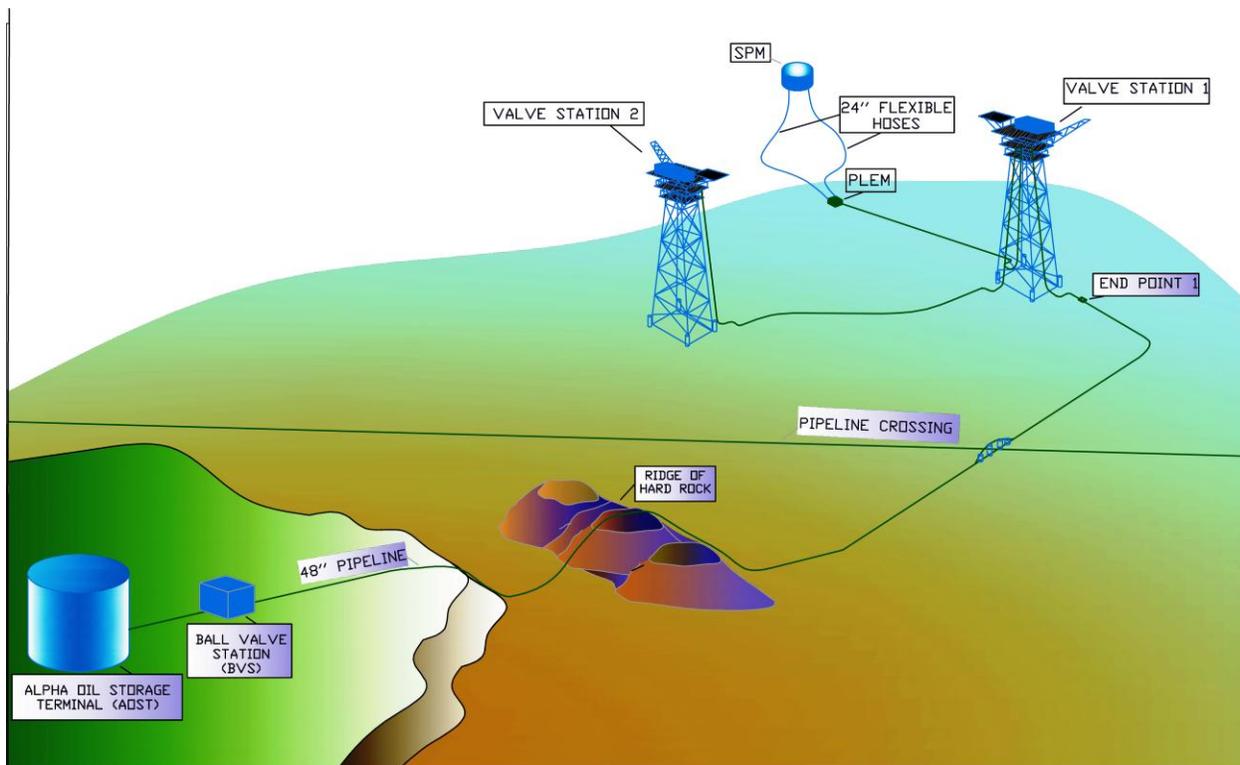


Figure B.1: Pipeline Field Layout. Source: Project Data

APPENDIX C

C.1. OTHER CORROSION TYPES

C.1.1 Uniform/ General Corrosion

Uniform attack can be described as metal loss which is fairly evenly distributed over the metal surface and consequently leading to a relatively uniform reduction in thickness. The product of the electrochemistry involved in general corrosion is the formation of hydrated ferric oxide (or rust). Homogeneous materials without any significant passivation tendency or immunity in a corrosive environment are liable to this form of corrosion (e.g. carbon steel). Uniform corrosion is assumed to be the most common form of corrosion and particularly responsible for most of the material loss (Bardal, 2004). As metal loss occurs only at the anode, a uniform corrosion rate over the surface results from the sites for anode and cathode reactions exchanging places at intervals thus at any given time multiple anodes and cathodes are operating on the metal surface.

C.1.2 Pitting Corrosion

Pitting corrosion is a form of localised corrosion of a metal surface where small areas corrode preferentially leading to the formation of deep holes in such a way that the bulk of the surface remains free from attack. The penetration rates of pitting corrosion are usually high since metal loss is concentrated at small anode sites and the cathodic reaction occurs over a large area of the metal surface. Pitting is the most insidious form of corrosion and it causes failure by perforation with only small percent of weight loss of the pipeline such that the detection of pits is usually difficult. The damage caused by pitting could entail that the whole structure be replaced as a remedy (Zaki, 2006; Revie and Uhlig, 2008; Fontana 1986).

The presence of deposited particles on the pipe surface may also lead to pitting. Also, the presence of elemental sulphur contained in the crude oil has been found to increase acidity (due to sulphur hydrolysis) at high temperatures and increase the rate of pitting when iron sulphide films are formed on the surface of carbon steel (Fang et al., 2008). Inclusions represented by manganese sulphide particles at the surface of carbon manganese steels (introducing inhomogeneity) can result in the initiation of pitting corrosion (David, 2000) Crevice corrosion and under-deposit corrosion usually results in pitting corrosion.

Mechanical removal of occlusions such as rust bubble or tubercule can be used to arrest pitting corrosion such as the use of pigs. Pitting corrosion in carbon steels is minimized by the use of corrosion inhibitors. Also, this type of corrosion can be called oxygen attack as it occurs as a result of the presence of dissolved oxygen in production fluids. This seldom occurs in pipelines transporting crude oil as crude oil contains some constituents such as wax that can inhibit oxygen attack.

Loss of passivity on carbon steel surfaces may bring the potential to the transpassive range such that evolution of oxygen or the formation of hexavalent chromium ions leads to rapid dissolution (or metal loss). This results in pitting and perhaps stresses corrosion cracking in the presence of stress. Conditions within pits could become acidic as a result of hydrolysis of metal ions. Once the pit has been formed it is difficult for a wall of the pit to re-passivate thus the process is often described as being auto-catalytic. The presence of salt solution and differential aeration cell due to limited oxygen within the pit can contribute to further corrosion. According to Heidersbach, the Pitting Resistance Equivalent Number (PREN) can be expressed as:

$$PREN = W_{CR} + 3.3(W_{MO} + 0.5W_W) + 16W_N$$

Where: W_{CR} is the weight percent of the chromium in the alloy; W_{MO} is the weight percent of the molybdenum in the alloy; W_W is the weight percentage of the tungsten in the alloy; W_N is the weight percent of the nitrogen in the alloy.

A large value of PREN indicates that the material has greater resistance to pitting corrosion. Pitting is usually associated with stagnant conditions such as a liquid trapped in a low part of an inactive pipe system. Increasing velocity of fluid flow often decreases the tendency of pitting attack. If

vibration is inherent in the structure such that relative motions exist between two substances in contact either one or both being metals could usually lead to a series of pits at the metal interface (Revie and Uhlig, 2008). This type of corrosion can be referred to as fretting corrosion and it is common at bolted joints (Zaki, 2006).

C.1.3 Galvanic corrosion

Galvanic corrosion occurs as a result of contact between two metals whereby one is more noble than the other and corrosion rate of the more electronegative is higher than that of (and can provide protection to) the more noble metal. There must be an electrolytic connection between the metals such that a closed circuit is established before the corrosion reaction can take place (Bardal, 2004).

It is apparent that the best way to control galvanic corrosion is to avoid the use of dissimilar alloy systems in the same electrolyte. When connections involving two incompatible metals are unavoidable, it is essential that the smallest metal must be cathodic to the surrounding metals. The use of a third metal active to both metals in the couple and sacrificial anodes such as Aluminium alloys (AlZnIn) can be a solution for any form galvanic couples or assemblies formed. Modifying the environment or the use of Inhibitors also is a solution. In designing the components, replaceable parts should be used so that only the corroded parts could be replaced instead of the whole assembly (Zaki, 2006).

It is possible for galvanic corrosion to occur between or within the same metal provided variation in potential is inherent. Filler metals for welding should always be cathodic to the base metal being joined. Welding produces changes in metallurgical structure and improper welding procedures can lead to a galvanic cell such that the Heat Affected Zone (HAZ) becomes the anode and thus corrodes preferentially. This problem is common around girth welds and this is the reason pipeline inspection (internal pig inspection) is essential in such a way that the inspection is concentrated on weld areas which are potential corrosion sites (Heidersbach, 2011).

The use of electrical insulation in flanged connections involving two dissimilar metals can be employed in order to avoid galvanic corrosion. Ringworm corrosion is another type of galvanic corrosion which occurs when the metal in the HAZ near a welded tool joint corrodes. In order to deform a pipe it may be heated to a temperature of 750°C which leads to variation in micro-structure. Also the same occurs during welding as HAZ are created due to high temperatures involved in the process.

Luders bands also referred to as stretcher marks, Hartmann lines or Piobert lines are localized bands of plastic deformation that can occur on carbon steels and other materials in regions of localized plastic deformation. They form in carbon steel when the initial resistance to deformation has been exceeded and plastic deformation (or localized yielding) occurs. This localized deformation is usually at an angle approximately 45° to the primary stress axis and may form ripples known as Luders bands, when the deformation reaches the metal surface. This deformation indicates that parts of the metal have been stressed more than other parts which are at lower

energy states and less susceptible to corrosion. If the difference in stress is not removed Luders Band corrosion is bound to occur.

Full length normalizing should be used to control luders band or ringworm corrosion. Also, it is important that large-diameter pipelines such as used this work (48") is handled and bent very carefully to avoid localized region of high stress and the formation of Luders bands.

C.1.4 Crevice Corrosion

The mechanism of crevice corrosion is essentially the same with that of pitting since the chemical conditions which is formed in pits also occurs within crevices. Crevice corrosion is formed as a result of depletion of oxygen as well as high metal ion concentration in the crevice which polarises the cathodic reaction such that when passivity is lost the rest potential moves in the active direction. This type of attack is usually associated with small volumes of stagnant solution (Fontana, 1986).

Underdeposit corrosion can be said to be crevice corrosion by virtue of differential aeration cell mechanism. The differential aeration mechanism may lead to loss of passivity at sites where they exist which results in the formation of pits (or pitting corrosion).

The difference between the crevice and pitting corrosion is that the crevice which is the corrosion site is visible to the unaided eyes. Failures due to this form of corrosion are recorded mostly on bolted connections due to differential aeration cell created. Under deposit corrosion can be said to be crevice corrosion by virtue of the same differential aeration cell mechanism. The differential aeration mechanism may lead to loss of passivity at sites where they exist which results in the formation of pits (pitting corrosion).

The deposit can be caused by the presence of marine growth which is described as microbially influenced corrosion. Other areas where crevices are formed include partially lapped joints, holes, detached coatings, gaskets and flange gaps, and occur at similar rates to pitting (Palmer and King, 2006). All metals are susceptible to crevice corrosion provided the crevice width is sufficiently narrow (e.g. $1\mu m$ or less).

Possible ways in arresting this form of corrosion include the careful selection of material, avoidance of the use of bolt connections and use of suitable coating materials. Flange faces can be machined with grooves which reduce capillary attraction and act as 'crevice breakers'.

C.1.4 Intergranular corrosion

This can be described as a form of localized attack on the grain boundaries of a metal or alloy in corrosive media, which results in the loss of strength and ductility and the localized attack could lead to dislodgment of the grain (Zaki, 2012). Many metal objects are more prone to corrosion on surfaces perpendicular to the rolling direction, where grain boundaries are closer (Heidersbach, 2011). Generally this type of corrosion is rare and is not a threat in carbon steels and should not be a concern. However, intergranular corrosion could be an issue in carbon steel pipelines if an

inappropriate weld procedure has been used. Sulphide and nitrate attack can result in this form of damage, though only sulphide damage is relevant in pipelines (Palmer and King, 2008).

C.1.5 Corrosion Fatigue

Corrosion fatigue is a process in which a metal fractures by fatigue prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels than would be otherwise required in the absence of a corrosive environment (Zaki, 2006).

A component may be subjected to rapid cyclic stresses very quickly such that the effect of corrosion will be insignificant. Again, the environment may be highly corrosive such that the pipeline section corrodes to failure before the cyclic stress effect becomes significant. Wave loading on offshore structures have varying values of cyclic stresses as opposed to the simplistic assumption which suggests these values are the same on each repetition, thus inherent uncertainties like this increases the difficulty in modeling corrosion fatigue (Heidersbach, 2011).

Corrosion fatigue usually initiates from weak stress concentration sites such as corrosion pits, machined notches, Inclusions or second-phase particles, twin boundaries or surface scratches. Consequently, a combination of cyclic stress and localized fatigue leads to the development of occluded cell concentration variation compared with the environment and then the interaction between chemistry and mechanical loading becomes extremely complex. Sulphide ions are particularly aggressive species as they encourage hydrogen embrittlement of the steel which leads to a reduction in the fatigue resistance of carbon steel (Palmer and King, 2006). Fatigue failures occur when suspended pipelines encounter vortex shedding due to subsea or river currents. Usually, corrosion fatigue is rare in submarine pipelines but has been observed to occur on spanning pipe sections (Palmer and King, 2006). Sour service pipelines have been found to be more susceptible to corrosion fatigue (Jain, 2012). Material selection, use of inhibitors etc. are possible methods of preventing corrosion fatigue.