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Pitting and Crevice Corrosion of Stainless Steel under Offshore Conditions

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PREFACE

This report was written at the Norwegian University of Science and Technology (NTNU) and at Det Norske Veritas (DNV) Stavanger office, in the spring 2012. This work completes the module TMT 4900 “Materials Chemistry and Energy Technology, Master Thesis”.

It is anticipated that the reader of this report has some technological background. All the features of crevice corrosion, pitting corrosion and statistics have not been presented, but only a brief introduction to each topic is given.

I would like to thank my supervisors, Prof. Kemal Nisancioglu (NTNU), Prof. Marvin Rausand (NTNU) and Dr. Maneesh Singh (DNV) for their guidance and support during this study.

I would also like to thank the Inspection Management group at DNV, with Frode Wiggen and Kjetil Eikeland as Head of Department, for their hospitality and many interesting discussions during this study. I would especially like to thank Thom Fosselie and Jan Vaasland Jessen for always having time to answer my questions and for suggestions during writing of this thesis.

Declaration

I declare that this work has been performed independently and in accordance with the rules and regulations at the Norwegian University of Science and Technology (NTNU).

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ABSTRACT

AISI 316/316L has traditionally been used in offshore topside environments when operating under low temperatures. It has been observed that the AISI 316/316L piping suffer from severe attacks of pitting and crevice corrosion on external surfaces. It is therefore important to emphasise the comments within the statements that give the limitations on the use of the material. While temperature is the main parameter in the standards, there seem to be others, such as location, presence of tags and coating, which affect the initiation and propagation of pitting and crevice corrosion. This thesis discusses the various operating parameters that affect the susceptibility to pitting and crevice corrosion of AISI 316/316L piping and proposes procedures for identifying piping that are most prone to attack, and calculations of the probability of failure of such piping.

In the first part of the thesis, a literature survey of the parameters that affect the pitting and crevice corrosion of AISI 316/316L in an offshore environment is presented.

In the second part, a procedure for the identification of piping that is prone to pitting and crevice corrosion is presented. This procedure has been developed taking into consideration the parameters that are assumed to be important and suitable for use in RBI analysis. In the first step, the parameters that affect both pitting and crevice corrosion, that is, the chloride content due to the location of the pipe, coating and temperature, were considered to be the most important ones. In the second step, the possibility of crevice corrosion was assessed.

In the third part, a procedure for assessing the possibility of pitting corrosion in the offshore topside environment based on the pitting potential E_{pit} was developed. The temperature of the external pipe surface was used to find the solubility of NaCl in water. The chloride concentration was used to determine the E_{pit} in order to find the possibility of pitting in the topside offshore environment.

The last step was to develop a procedure for calculating the probability of failure of a pipe as a function of time. In this step, the functional life of the coating and the rate of pitting corrosion have been considered.

SAMMENDRAG

Stålkvalitetene AISI 316/316L har tradisjonelt vært brukt i offshore topside miljøer ved operasjonsforhold med lave temperaturer. Erfaringer viser at rør i materialet AISI 316/316L er utsatt for alvorlige angrep av grop- og spaltkorrosjon på utvendige flater. Det er derfor viktig å undersøke de kommentarene som er gitt i standardene om begrensninger i bruk av materialet. Temperaturen er den viktigste parameteren i standardene, men det ser ut til at andre parametere, som plassering, merkelapper på overflaten og belegg, også påvirker initiering og vekst av grop- og spaltkorrosjon. Denne avhandlingen drøfter de ulike rammebetingelsene som påvirker sannsynligheten for grop- og spaltkorrosjon på AISI 316/316L rør og foreslår prosedyrer for å identifisere rørene som er mest utsatt for angrep, og beregninger av sannsynligheten for feil i slike rør.

I den første delen av oppgaven presenteres et litteraturstudie rettet mot parametere som påvirker grop- og spaltkorrosjon på AISI 316/316L i et offshore miljø.

I den andre delen av avhandlingen presenteres en prosedyre for identifisering av de rørene som kan være utsatt for grop- og spaltkorrosjon. Prosedyren tar hensyn til de parametrene som antas å være viktigst og som er egnet for bruk i en RBI-analyse. I første trinn ble parametrene som påvirker både grop- og spaltkorrosjon tatt med. Her ble kloridinnholdet, belegg og temperatur ansett som de viktigste parametrene. I andre trinn ble mulighetene for spaltkorrosjon vurdert.

I den tredje delen er det utviklet en prosedyre for å vurdere muligheten for gropkorrosjon i et offshore topside miljø, basert på groptæringspotensialet. Temperaturen på ståloverflaten ble brukt til å finne løseligheten av NaCl i vann. Kloridkonsentrasjonen ble brukt til å finne groptæringspotensialet slik at muligheten for gropkorrosjon i et topside offshore miljø kunne bestemmes.

I siste del er det utviklet en prosedyre for å estimere sannsynligheten for svikt i et rør som funksjon av tiden. Her er den funksjonelle levetiden til belegget og gropkorrosjonshastigheten vurdert.

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ABBREVIATIONS

Abbreviation	Explanation
AISI	American Iron and Steel Institute
ASTM	American Society for Testing and Materials
CCT	Crevice Corrosion Temperature
CPT	Critical Pitting Temperature
DNV	Det Norske Veritas
DFT	Dry Film Thickness
EN	Electrochemical Noise
HISC	Hydrogen Induced Stress Cracking
Localised Corrosion	Crevice and Pitting Corrosion
NORSOK	Norsk Søkkel Konkurransesepisjon
PoCF	Probability of Coating Failure
PoF	Probability of Failure
PoPF	Probability of Pipe Failure
PoPI	Probability of Pitting Initiation
PRE _N	Pitting Resistance Equivalent
RP	Recommended Practice
RBI	Risk Based Inspection
UV	Ultraviolet

NOMENCLATURE

Symbol	Unit	Explanation
A	V	Parameter Dependent on Temperature and Concentration of Sulphate
B		Parameter Dependent on Temperature and Concentration of Sulphate
c_{Cl^-}	mol/L	Chloride Concentration
D		Parameter Dependent on Temperature and Concentration of Sulphate
d	mm	Pipe Wall Thickness
d_p	mm	Maximum Allowed Corrosion Depth
d_s	mm	Predicted Corrosion Depth
E_{corr}	V	The Corrosion Potential
E_{pit}	V	The Pitting Potential
E_r	V	The Repassivation Potential
k		Parameter Dependent on Temperature and Concentration of Sulphate
m		Parameter Dependent on Temperature and Concentration of Sulphate
M_{NaCl}	g/mol	Molecular Weight of NaCl
n		Parameter Dependent on Temperature and Concentration of Sulphate
t	years	Time
T_1	years	Time to Failure of Coating
T_2	years	Time from Coating Failure to Pipe Failure
T_{F_i}	years	Time from Installation to Pipe Failure for Pit i
T_{max}	°C	Maximum Temperature
T_{min}	°C	Minimum Temperature
t_i	s	The Induction Time
μ	mm/year	Mean
σ	mm/year	Standard Deviation

CHAPTER 1

Introduction

1.1 Background

There are stringent requirements regarding safety and design life when choosing a material for use in an offshore environment. Topside piping is used for transport of flammable oil and gas and is under continuous exposure to harsh marine environment. Consequently, it faces corrosive attacks and as a result it can develop leakages, which may lead to ruptures. In order to reduce these problems, pipings are subjected to regular inspection and maintenance programs. Since the inspection of pipings is an expensive task, inspection engineers use Risk Based Inspection (RBI) analysis to optimise the use of resources.

One of the major steps in carrying out the RBI analysis is to identify pipings that are prone to corrosion attacks. This step is carried out taking into consideration a number of factors like material of construction, composition of fluid, operating conditions and location.

Austenitic stainless steel pipings are commonly used in offshore installations. The choice of construction material is guided by the Norsok standard M-001[1] that states: *“Type 316 is acceptable up to operating temperature 70 °C provided located indoor or in sheltered areas and not insulated”*. Its inspection schedule is guided by the DNV Recommended Practice, DNV-RP-G101[2], that states: *“Uncoated stainless steels can be expected to have a probability of failure of 10^{-4} per mm wall thickness. Note that the excessive presence of deposits, and water traps under clamps, labels etc. should be given special attention and may justify manual evaluation of the PoF”*.

Even though austenitic stainless steels are commonly used in offshore topsides conditions, there have been reports of pitting and crevice corrosion under conditions where these were not expected.

A Statoil report[3] from an inspection on an offshore field in the North Sea documents that the close visual inspection results show several external corrosion damages on topside offshore AISI 316 pipes. Localised corrosion was detected in the form of crevice corrosion under clamps, tape and coating remnants on the pipes. The most severe form of corrosion that included almost 90 % of the attacks was crevice corrosion, while the remaining 10 % of attacks was due to pitting corrosion. Pitting corrosion was detected on all clock positions, but especially on 5–7 o'clock on the pipe. The most severe attacks due to pitting corrosion were observed in partly open areas and at high temperatures. Similar inspection results[4, 5] are found on other installations in a similar environment. The most severe attacks from Statoil's inspection were found on horizontal pipes located under roofs and without walls. In fully open

areas, or areas with a controlled environment, no corrosion was observed. It was observed that more severe pitting occurred on large diameter pipes rather than small ones.

It is of interest to investigate why these stainless steel pipes, which were not supposed to corrode according to the standards, experienced crevice and pitting corrosion. There seems to be factors other than temperature that need to be evaluated if the susceptibility to crevice and pitting corrosion is to be determined. This study attempts to identify some important factors and discusses their relevance. When the different factors are evaluated, they can be used to estimate the possibility of pitting corrosion. Several studies[6-8] carried out by a research group attempted to devise a method to predict the possibility of pitting corrosion on stainless steel at evaporative conditions. In this thesis, a procedure is developed to determine if AISI 316/316L in an offshore environment is susceptible to crevice and pitting corrosion.

1.2 Objectives

The purpose of this study is to assess the corrosion resistance against external crevice and pitting corrosion of AISI 316 stainless steel piping in a topside offshore environment. The objectives are listed below.

1. Perform a literature survey in order to identify the parameters that affect the susceptibility to crevice and pitting corrosion of AISI 316 stainless steel.
2. Develop flowcharts with the purpose of easily identifying the possibility of localised corrosion based on the different parameters.
3. Develop a quantitative model to determine the possibility of pitting corrosion based on the important parameters.
4. Develop a model to predict the probability of failure as a function of time.
5. Assess the statements given in NORSOK M-001 and DNV-RP-G101 based on the result of this study.

1.3 Limitations

This study is limited to the stainless steel AISI 316/316L in an offshore topside environment, since it is on these pipes that unexpected corrosion problems have been observed during inspection. Some simplifications and assumptions have been made during this study, in order to be able to construct a simple procedure that is suitable for use in risk based inspection (RBI). Factors that affect the perforation of a pipe are presented in Chapter 2, but only the ones that are considered most significant are accounted for in the model. It is not possible to be certain that all factors that affect the susceptibility to pitting and crevice corrosion have been taken into account in Chapter 2. To be able to meet the thesis objectives within the given time frame and with the available data, the following limitations and simplifications have been applied.

- Risk assessment contains a large number of assessment methods. In this study it is only focused on risk based inspection (RBI), since this is the basis of the standard DNV-RP-G101: *Risk Based Inspection of offshore topsides static mechanical equipment*, where the problem addressed in this study is mentioned.
- Only pipes in topside offshore conditions are considered, where topside means located on an installation above the waterline.
- Only pipes are considered. Other equipment that may be connected to the pipes, for example, valves, pumps and heat exchangers have not been considered in this study.
- Only the bulk of the pipe is considered, so welds, flanges and other places where localised corrosion is likely to occur are out of scope for this study.
- Only crevice and pitting corrosion, which are localised corrosion forms, are focused on. Other corrosion mechanisms that may be present and contribute to degradation of the pipe material are not taken into account.
- Only damage to external wall of the piping is considered. This implies that if the pipe experiences internal corrosion then it is not accounted for in the models. Factors like flow and media in the pipes are therefore not considered and all literature mentioned is for stagnant conditions.
- Only the thin liquid film on the metal surface and the surface itself is considered. Different gases effect on localised corrosion is out of the scope of this work. Only HCl(g), which dissolves in the thin film, increasing the amount of chloride in the solution is considered.

1.4 Approach

A literature survey is performed to evaluate research carried out to study the susceptibility to crevice and pitting corrosion. The expected important factors are presented in flowcharts that are developed to give a clear picture of what affects the susceptibility to crevice and pitting corrosion. For piping that are expected to encounter pitting corrosion, a quantitative procedure for estimating the possibility of failure is developed. Finally, for piping that may suffer corrosive attacks, the probability of failure as a function of time is calculated by analysing two processes — the protection offered by the coating and the attack from pitting corrosion on the destruction of the coating. This gives information that can be used to comment on the importance of the notes in the statements, telling when the statements are valid.

1.5 Structure of Thesis

Chapter 1 gives an introduction to this study and its background, objectives, limitations, approach and structure. Chapter 2 gives the result of the literature survey, which identifies the parameters that affect the susceptibility to crevice and pitting corrosion. In Chapter 3, the most important parameters from the literature survey are presented as flowcharts in order to give a simple procedure that can be used in RBI. In Chapter 4, the possibility of pitting

corrosion is assessed, while in Chapter 5 the probability of failure due to pitting corrosion and coating degradation is estimated as a function of time.

CHAPTER 2

Crevice and Pitting Corrosion in Stainless Steel

2.1 Introduction

This chapter presents the result of a literature survey performed to assess the parameters that affect the susceptibility to crevice and pitting corrosion on an external surface of a pipe in a topside offshore environment. This background information is necessary to develop a procedure that is suitable for use in RBI. The procedure should be an easy method to decide if the existing AISI 316/316L steel piping would suffer from pitting and/or crevice corrosion or not. In the text, localised corrosion or just corrosion refers to these two corrosion forms only, except where it is explicitly specified otherwise. The text mentions pitting and crevice corrosion, but it is important to note that one does not imply the other. They may occur separately even though they often are present simultaneously.

Stainless steels do not rust like normal steels and were first believed to withstand the environment, protected against all types of corrosion. The surface is protected by an oxide film, which forms instantly on the surface, if the surface is exposed to oxygen. This chromium rich oxide film passivates the surface. The problem is that this film has good electrical conductivity, which enables reduction on the surface of the metal, and this makes the surface prone to pitting and crevice corrosion[9]. An offshore environment is where the pipe experiences a humid and salt-containing environment, with the salt consisting mainly of chloride ions. The humidity and chloride content is dependent on the location of the pipe and conditions on the installation. These conditions are the weather, testing of deluge systems and washing of the plant with seawater.

Some assumptions and limitations have been made in order to be able to develop the procedure, and some of them have already been presented in the introduction. All parameters that may affect the susceptibility are not considered. Only the ones considered to be most important have been considered. It is the susceptibility to crevice and pitting corrosion for different stainless steels in general that is assessed in this chapter, not only AISI 316/316L, but this material is the main focus in this study. The offshore environment is not constant, so the values from one specific experiment do not provide the answers to the problems, so exact values are not focused on, just trends. Since the results are supposed to be used in RBI, somewhat conservative estimates are useful.

The lack of measuring methods and the difficulties in controlling the atmosphere when assessing corrosion in an offshore environment—both artificially in the laboratory and testing in the actual environment—results in little research on localised corrosion in an offshore environment. Laboratory tests are preferably conducted to measure only one parameter at a time and its effect on localised corrosion. Most research in the laboratory is carried out on species immersed in solutions, where it is easier to keep the specimens under controlled environment. All polarisation experiments mentioned in this chapter are of immersed samples. The results are therefore not directly comparable to the topside offshore environment, which depends on three states of aggregation. There are few good measuring methods for atmospheric corrosion, one example is the accelerated salt spray tests. In recent years, new methods[10-13] have been developed to measure atmospheric corrosion where a thin layer of water is present on the surface, which are more similar to real atmospheric corrosion occurring offshore.

A brief introduction and the mechanisms of these two corrosion types are given in Section 2.2. In Section 2.3 the choice of material, AISI 316/316L, and the environment where the pipe is placed is discussed. Section 2.4 presents the rest of the different parameters that have to be investigated to decide the susceptibility to pitting and crevice corrosion, while Section 2.5 summarizes the literature survey and compares it to the work done in this thesis. The result of this chapter is used in this study to develop a procedure that can be used in RBI. In Chapter 3 the most important parameters from this chapter are used to assess the possibility of localised corrosion. In Chapters 4 and 5, the possibility of pitting corrosion and the probability of failure as a function of time are assessed, respectively.

2.2 Crevice and Pitting Corrosion

Crevice and pitting corrosion are forms of localised corrosion, which means that the corrosion occurs in a limited area on the pipe. The corrosion rate is often high and is generally higher than that for uniform corrosion, due to a large cathode/anode ratio. A severe attack is therefore usually observed, and the pit or crevice may cut through the pipe wall thickness to form a hole. Section 2.2.1 presents the mechanism of crevice corrosion, while section 2.2.2 presents the mechanism of pitting corrosion.

2.2.1 Mechanism of Crevice Corrosion

The crevice corrosion mechanism is dependent on several parameters and it may change accordingly with a change in the parameters[14]. The attack happens in a restricted area, often a narrow fissure with a width of normally only a few micrometers. These fissures can occur where there are external agents such as paint remnants, tape or insulation, that forms a crevice against the pipe surface. The chemistry within the fissure develops differently from the rest of the bulk solution. In a review[15], several mechanisms were proposed for crevice corrosion, since any single mechanism fails to explain all aspects of crevice corrosion. Here, only

deoxygenation-acidification, also called the passive dissolution mechanism, of crevice corrosion proposed by Oldfield and Sutton[16] is briefly explained to give an introduction to crevice corrosion. In fissures the most common reduction reaction, which is a requirement in order to introduce crevice corrosion, is the oxygen reduction reaction. Other reduction reactions may also occur, for example, reduction by chloride ion. The only reduction reaction at the cathode, is the proton (H^+) or water reduction reaction; in the case where no oxidising agent is left in the pit, or depletion of oxygen is called deoxygenation. This is caused by too slow oxygen diffusion into the crevice and therefore a concentration gradient builds up between the crevice and the outer passive surface of the material. Hydroxide forms in the crevice in alkaline seawater, causing a rise in the pH. This is the first part of the initiation phase[14].

The second step is hydrolysis-acidification, which is directly induced by the deoxygenation. The depletion of oxygen causes the cathode reaction to move to the outer passive surface, where oxygen is more easily accessible, while the oxidation of the components of the alloy continues in the crevice. The components in AISI 316/316L that dissolve are Cr, Fe, Mo and Ni, where the formation of chromium hydroxide seems to exert the most influence on the pH. The dissolution causes a predominance of cations; so anions, that is, chlorides, starts migrating into the crevice to restore electroneutrality. These components of the alloy hydrolyse simultaneously producing protons which lower the pH in the crevice, thereby causing acidification. The last step in the initiation phase is activation, which is when the critical solution chemistry is aggressive enough to cause oxide film breakdown. The time until all the three steps have occurred is normally called the initiation time and is discussed in section 2.4.10. There is no attack of the crevice in this phase; the attack occurs in the propagation phase. The initiation phase consists of the evolution of an aggressive crevice solution where a steady state develops and this phase is assumed to occur much faster than the propagation phase that follows[14, 17].

The propagation phase that comes after initiation is shown in Figure 2.1. It can be seen from the graph that the corrosion current rapidly increases. As the crevice continues to corrode, its growth is directed towards the mouth of the crevice. It is the IR drop that limits its growth. The resistance decreases as the corrosion progresses towards the crevice mouth, causing an increase in the current. It can be seen from the graph that IR limits the growth. The resistance decreases as it grows towards the mouth, while the current increases. The anodic current limit is attained when the growth of the crevice reaches the mouth, and the IR drop no longer limits the corrosion reaction. The dissolution of metal or the cathodic reaction at the surface are the limiting factors of corrosion. After a while the corrosion rate starts decreasing due to an increased resistance in the solution between the oxidation of metal in the crevice and the cathode reaction on the bare surface. The products of corrosion that build up at the crevice mouth are the reason. Another reason that limits the corrosion rate is the cathodic reaction reducing proton to hydrogen, which increases the pH of the solution[18, 19].

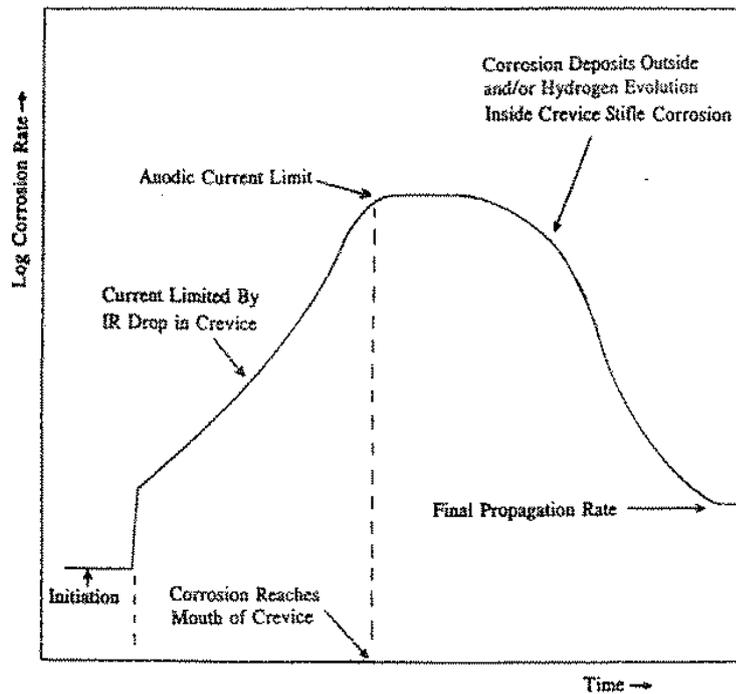


Figure 2.1: Diagram presenting the corrosion rate of crevice corrosion against time from [18].

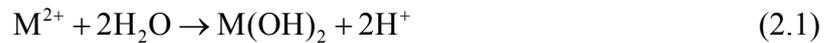
The Oldfield and Sutton model [16] is criticised due to tests [20] of changes in solution composition during the initiation stage of crevice corrosion. The three elements tested were Cr, Fe and Ni. It was shown that Cr does occur in very small amounts before breakdown of the passive film, compared to the actual amount of Cr in the alloy. After breakdown the Cr content increased considerably and the possible reasons for this were tested. Adsorption and pH drop were evaluated doing only one experiment for each and thereafter ruled out as possible reasons. Acidification (pH drop) did not occur in the crevice before breakdown, unlike in the Oldfield and Sutton model [16] and is therefore a result and not a reason for the occurrence of breakdown. It was concluded from the results that the only possible reasons could be that dissolved oxygen developed a surface oxide of chromium, or that chromium did not dissolve at all.

2.2.2 Mechanism of Pitting Corrosion

The mechanism for pitting and crevice corrosion has some similarities and pitting is often seen as the precursor of crevice corrosion [21]. Some researchers see crevices as big pits [22], while others [23] regard both corrosion forms as crevice corrosion, where pitting corrosion is considered a special form. Galvele [24] used Tafel's law to confirm the strong relationship between the mechanisms for pitting and crevice corrosion presented by Wilde and Williams [25] for solutions containing NaCl and in seawater. Crevice corrosion is regarded as most severe [25, 26], which confirms what was observed from Statoil's inspection [3]. Both corrosion forms can lead to perforation of the pipe, which is reviewed in Chapter 5 [27].

In experiments, the ASTM G48 is a common procedure to test pitting corrosion with specimens immersed in 6 % FeCl₃, that is, in an oxidizing environment with chlorides. It is difficult to decide which part of pitting corrosion is the most important. Pitting corrosion normally starts with chlorides rapidly penetrating the protective oxide film covering the metal surface, and these points act as initiation sites for pitting corrosion. Selective dissolution is another way to initiate pitting corrosion and it occurs when one of the components dissolves faster than other components[28]. The breakdown of the film causes oxidation at local sites on the metal surface, often with oxygen as the main reducing agent.

As this localised dissolution continues, a pit forms in the metal surface after some time, as can be seen in Figure 2.2. The corrosion products are shown as Fe(OH)₃, but will also contain other species when a stainless steel is dissolved, such as Cr, Ni and Mo. The pit experiences a depletion of oxygen due to the cathodic reaction. Electrons are transported from the pit to the outer passive surface where these participate in the reduction reaction. The concentration gradients formed due to oxygen and salt discrepancy on the surface compared to the pit, produces a potential gradient, which works as a driving force for the corrosion process[9]. The dissolution of the different alloy components is represented by iron which can be seen as Fe²⁺-ions going into the pit, while oxygen is reduced to form water. The dissolution of metal increases the number of cations, and therefore anions, which mean chlorides migrate into the pit to uphold the electroneutrality of the pit. Equation (2.1) shows the hydrolysis of the cations which occurs within the pit, where M represents the different metals, which are Cr, Mo, Ni and Fe for AISI 316/316L[27].



The increasing H⁺ content reduces the pH in the pit, thereby creating a more aggressive environment. This environment favours sustained growth and the pit is said to be autocatalytic. The critical solution is maintained, keeping the potential in the bottom sufficiently high to avoid repassivation of the pit. The potential at the surface is always higher compared to the potential in the bottom of the pit. The rate determining step varies with ohmic effects, activation control and mass-transport control or these combined in some way[27].

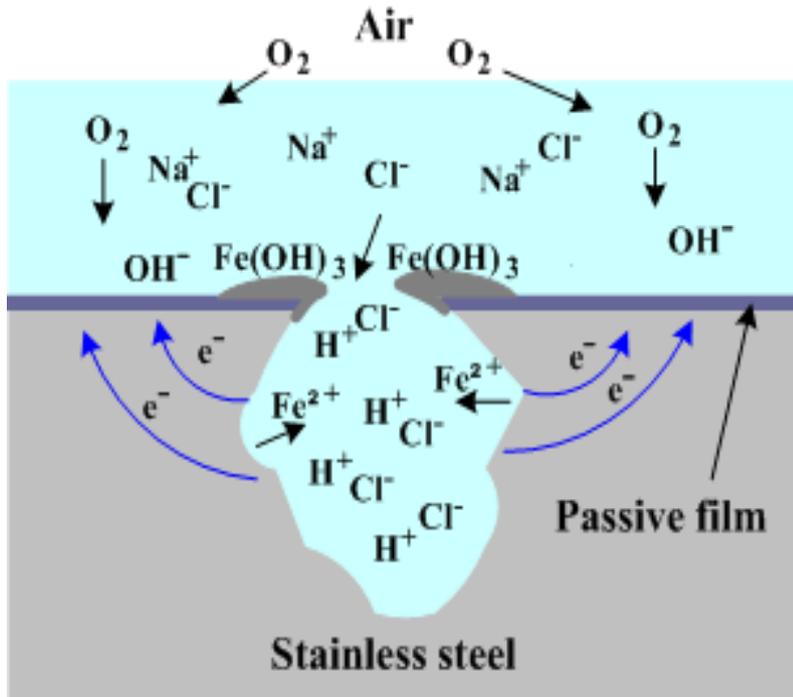


Figure 2.2: Sketch of a pit from[29].

The metastable pits are the incipient growth of the initiated pits, and must survive in order to become stable growing pits. These are normally small pits, of only a few microns in size and last only a few seconds before the surface repassivates. The metastable pits may survive and become stable growing pits depending upon the composition of the material, the critical solution, mass-transport and the potential at the bottom of the pit. Stable pitting corrosion occurs when the corrosion potential, E_{corr} , exceeds the pitting potential, E_{pit} [27]. The corrosion potential is also called the open circuit potential. It depends on the alloy; it is measured on the metal surface and determined by the rates of oxidation and reduction. Polarisation tests[30] shows that the open circuit potential in 4 % NaCl increases slightly with longer immersion times, which may be due to passive film reparation[8].

The measure of a material's ability to undergo stable pitting corrosion in a certain environment is defined as the pitting potential, E_{pit} [21]. A different definition of E_{pit} given by Galvele[24], as a limit where the growth of pits happen above and a passive surface is maintained below or it is defined as the potential where stable pit growth occurs[30]. As can be seen, several definitions of the pitting potential are given. The first and last definitions are probably the best since when pitting starts at E_{pit} there is a possibility of stable pitting corrosion under the pitting potential. Metastable pit formation can occur below the pitting potential, so these cannot be seen as initiation points for pitting[27]. Measuring the value of E_{pit} can be used to determine under what conditions pitting corrosion occurs.

The pitting potential depends on both the environment and the alloy[8]. Extensive amount of studies have been carried out to understand the effect of different parameters on E_{pit} and only a modest selection is mentioned here. Much of the research mentioned in this chapter is for assessing when pitting is initiated, but E_{pit} can only be used for assessing this when there are no crevices present[25]. This is not possible in the real environment, where both crevice and pitting corrosion are normally present. Previous research[31] have shown that it is difficult to measure the exact value of E_{pit} during experiments, and it can be seen as a random variable compared to critical pitting temperature (CPT). CPT is the corresponding temperature where pitting occurs and is discussed in section 2.4.1. At low potentials the pit dissolution experiences mixed control, which is a combination of both activation and ohmic control. The pit is then protected by a cover that preserves the solution chemistry in the pit. At higher potentials, the cover is broken and a salt film protecting the pit is present, and this dissolution is controlled by diffusion[30].

Another potential that is important is the repassivation potential, E_r , also called the protection potential. Pits repassivate when E_r is reached, which means that there is no further growth of the pits. E_r is therefore always smaller than E_{pit} [27]. The higher the pitting potential and repassivation potential for the material, the higher is the pitting corrosion resistivity[27] and fewer pits are initiated due to higher pitting potentials[32]. The E_r seems to be influenced by the amount of pit propagation, where E_r decreases with increased pit depth[24, 25].

For AISI 316L stainless steel, the pits are assumed to grow at a constant rate, as no significant potential drop is experienced in the pit[33]. The depth is estimated as a function of time for AISI 316L in both diluted and concentrated (4 M NaCl) solutions. In concentrated chloride (exceeding seawater) solutions, it is assumed that the growth of pits is constant for stainless steels. For AISI 316L this is assumed valid for all solution compositions.

Different shapes of pits are possible, which are due to chemistry in the pit needed to maintain stable growth and initial growth direction of the pit. Some examples are shown in Figure 2.3.

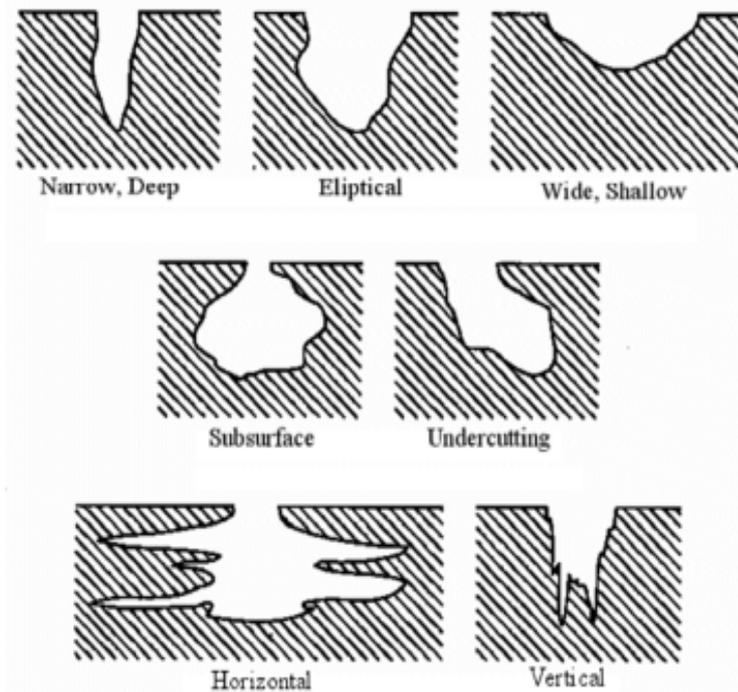


Figure 2.3: Sketch of pitting cavity from Statoil's report[3]. The outer surface of the metal is passivated.

A pitting mechanism that depends on a cation concentration limit was evaluated. The growth of the pit was assumed to be hemispherical initially. Figure 2.2 shows a sketch of a pit that has experienced undercutting. This is assumed to occur due to passivation of the surface near the pit mouth when the concentration of cations is significantly lower than the saturation concentration at the pit mouth. The hemispherical pit starts undercutting the material that is passivated and the growth may eventually reach the surface again, and in the process a part of the material is detached from the rest of the surface. Diffusion is possible when a hole develops in the surface and then the cycle starts again with undercutting. The formation of a lacy cover can be detrimental as the extent of pit growth is hidden. The cover of corrosion products protects the mouth of the pit so that localised chemistry of the pit solution maintains an aggressive environment inside. It is difficult to measure the depths of the pits offshore, as it is measured vertically from the opening, which does not necessarily have the largest pit depth. It can be somewhere else depending on the growth direction. The pit growth was tested and it was seen that the pit grew more in length than depth, and the length grew linearly with time. A nearly parabolic growth of the depth was observed. A few microns thick lacy cover was also observed[34].

2.3 Stainless Steel and the Environment

This section first presents explanations for the choice of material and why it is chosen for use in an offshore environment. Second, it presents the conditions of the environment that may have an effect on the susceptibility to pitting and crevice corrosion.

2.3.1 Choice of Material for Offshore Structures

When choosing a material for use in an offshore environment, it is important to select a robust material. This implies a material that minimises risk of material failure at an acceptable cost. The term cost also includes maintenance cost in the total design life of the structure[35].

Several materials are used in an offshore environment, like carbon steel, Cu-, Ti- and Ni-alloys and stainless steels, where AISI 316/316L is an austenitic stainless steel. Steel is the biggest metal market in the world and it is the most widely used in industry for structures. The most flexible is mild steel, which is also cheap and easy to produce. The problem with mild steel is that it cannot tolerate aggressive environments, and for this purpose the use of AISI 304 and 316 became customary for structures. These two and other stainless steels are much used owing to reasonable cost and accessibility. For piping, which experiences dynamic or flow conditions, the 316-alloys are the most reliable for corrosion resistance and are therefore often used in an offshore environment. The problem is that if there are chloride ions present under stagnant or static conditions, the 316-alloys can be prone to localised corrosion. The specification for the composition of AISI 316 and 316L is given in Table 2.1. It is seen that AISI 316L has lower carbon content than AISI 316 in order to increase the weldability of the material[21, 36].

Table 2.1: The composition of AISI 316 and AISI 316L from[37].

Grade	C (%)	Cr (%)	Mn (%)	Mo (%)	N (%)	Ni (%)	P (%)	Si(%)	S (%)
316	≤ 0.08	16.0–18.0	≤ 2.0	2.0–3.0	≤ 0.10	10.0–14.0	≤ 0.045	≤0.75	≤0.03
316L	≤ 0.03	16.0–18.0	≤ 2.0	2.0–3.0	≤ 0.10	10.0–14.0	≤ 0.045	≤0.75	≤0.03

The susceptibility to pitting and crevice corrosion of these stainless steels provided the reason for trying to find another steel type. Ni-based alloys were tried, but they are very expensive, which severely limits their use. The alloys have a high Cr content and contain Mo for corrosion protection (see section 2.4.4 for more about each element). From 1960s onwards, stainless steels with 6 % Mo were used to prevent localised corrosion, called “high alloy stainless steels”[21, 36].

It is important to be aware of the susceptibility to corrosion as early as possible during the design of the structure. By choosing a robust material and eliminating sharp edges and crevices in the design, fabrication and installation of the pipes, the susceptibility to corrosion can be reduced considerably. The susceptibility to corrosion can also be reduced by applying a proper coating system, about which more information is given in section 2.4.9[38].

2.3.2 Offshore Environment

The next step is to evaluate the offshore environment where the pipe is placed. An offshore structure can be divided into four zones depending on the different environmental conditions present in each zone as shown in Figure 2.4. The pipes under consideration are located topside

in zone 1, which is in a marine atmosphere equal to the offshore environment mentioned in the introduction of this chapter. Zone 2 is the splash zone, while Zone 3 are pipes that are fully immersed in seawater. Zone 4 is mud, meaning pipes are located in the subsoil. A curve in the figure shows the relative corrosion rate in the zones, where it is seen that the splash zone experiences the most severe corrosion attack among all the zones[38].

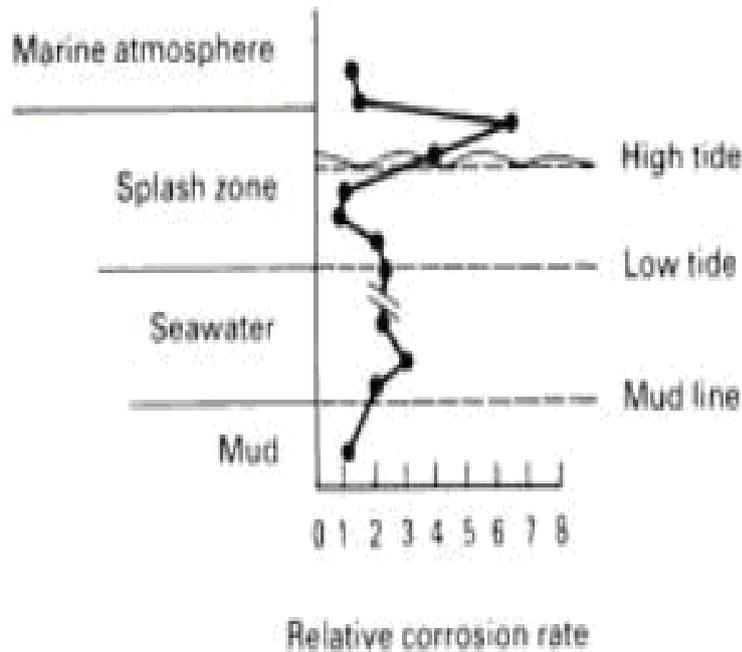


Figure 2.4: Plot of different corrosion zones for steel and their corresponding corrosion rate from NACE RP-01-76[39].

In this study the focus is on Zone 1, marine atmosphere, and it is therefore the only zone given in Table 2.2, while the three remaining zones are not considered. In the table there are given both a description of the environment and the specific corrosion behaviour of the exposed steel.

Table 2.2: Classification of zone 1 in a marine environment from Schumaker[40].

Marine zone	Description of environment	Characteristic corrosion behaviour of steel
Atmosphere (above splash)	Minute particles of sea salt carried by wind. Corrosivity varies with height above water, wind velocity and direction, rainfall, dew cycle, season, temperature, solar radiation, dust and pollution. Even bird droppings are a factor.	Sheltered surfaces may deteriorate more rapidly than those boldly exposed. Top surfaces may be washed free of salt by rain. Coral dust combined with salt seems to be particularly corrosive to steel equipment. Corrosion usually decreases rapidly as one goes inland.

The weather in the North Sea depends on the season and the location of the installation. The temperature, snow, rainfall, air humidity and sea mist, waves, splash, amount of storms, wind direction and velocity all have an effect of the susceptibility to pitting and crevice corrosion. These parameters contribute to the actual environment on the pipe surface, and most important are their effect on humidity and the salt concentration on the surface. For example, sun and warm temperature cause evaporation giving a more concentrated chloride solution on the surface, while rain can wash away accumulated salt on the surface. Sea mist can transport chlorides that deposit on the surface of the pipe when it condenses. The pipe surface is humid at almost all times due to conditions on the installation mentioned in the introduction, caused by, for example, high atmospheric humidity and testing of deluge systems. All these effects will be dependent on the actual installation that is assessed and on how exposed the pipe is to weather conditions. It is difficult to comment on the actual effect of each of these parameters; the condition on the installation, including specific weather data from one exact installation is needed as well as the exact location of the pipe. As discussed later in this thesis, it is found that the specific location of the pipe on the installation may be equally important as the changes in weather between seasons.

The salinity in seawater is assumed to be 3.5 %, which is the content of dissolved salts. The salinity in seawater depends on the location of the ocean. Evaporation increases the salinity, while rain decreases it[41]. An example of the seawater composition is shown in Table 2.3.

Table 2.3: Gulf seawater composition used in pitting corrosion experiments. The pH is 8.2[36].

Ions		Concentration mg/L
Calcium	Ca ²⁺	508
Magnesium	Mg ²⁺	1,618
Sodium	Na ⁺	13,440
Potassium	K ⁺	483
Strontium	Sr ²⁺	17
Bicarbonate	HCO ₃ ⁻	176
Chloride	Cl ⁻	24,090
Sulphate	SO ₄ ²⁻	3,384
Bromide	Br ⁻	83
Fluoride	F ⁻	1
Total dissolved solids TDS		43,800

It can be seen from the table that the salinity is a measure of the total dissolved salts, which in the table is 43,800 mg/L. In the sea, it is reported by some that the salt contains approximately 55 % chloride[38], while others[42] found it to be 80 %. The actual amount is not discussed further here, as it has no relevance to this study. What is important is that the salt mainly contains chloride ions. The effect of sulphate and calcium on pitting and crevice corrosion is

discussed below; the other ions are in very small amounts or do not have any effect on corrosion and their effect can be assumed to be negligible.

The ions contribute to electrical conductivity in seawater, which is higher than in fresh water and it is possible for the attack to affect larger areas[38]. A brine is defined as water that has higher concentration of dissolved salts than seawater[43]. A brine can contain salt concentrations more than five times higher than the salt content of average sea water[44]. This means that the salt content on the pipe can vary a lot, from a diluted solution to a brine with concentrated chloride depending on conditions on the installation and location of the pipe. It is also changed by migration and diffusion due to electrochemical reactions in the pit and on the surface of the pipe. Analysing the exact solution chemistry on the surface of the pipe and within the pit and crevice is therefore extremely difficult. When sea water comes in contact with the pipe surface due to splash, condensation and so on, the water flows downwards leading to precipitation of salt on the underside of the pipe. A change in the solution composition takes place due to alteration in the ionic ratio of the different components in sea water. There are four different ways that the chemical composition can alter. These are: by ligand protonation; the formation of metal complexes, which also comprise the solubility products; the hydrolysis of metals; and lastly, the dissociation of water. The solubility product of a salt cannot be used in multicomponent systems as a measure of solubility, since the different components affect each other[6, 7].

Sulphate is often tested as a possible compound that can reduce the chlorides' damaging effect on the susceptibility to pitting corrosion. The stainless steel AISI 304 was investigated[6] by potentiodynamic measurements in concentrated solutions caused by precipitation of salts due to evaporation. It was reported that while increased chloride concentration increases the susceptibility to pitting corrosion, sulphate does the opposite. In the experiments, crevice corrosion was mitigated by a special test system. It was found that there was no increase in E_{pit} when adding sulphate, as long as it does not equal or exceed the value of chloride. The increase in E_{pit} experienced by one special ionic ratio does not correlate with the same ratio at a higher concentration of the species. Another experiment[7] found a similar result; it was observed that the sulphate contributed only when the chloride concentration was held below 1 M NaCl. A similar experiment[8], testing concentrated chloride, showed that it was impossible to get high enough sulphate values to prevent pitting corrosion.

If calcium is present, tests of different solutions of sodium, chloride and calcium shows that evaporation can alter the ionic ratio of chloride and sulphate considerably. It is believed that larger amount of calcium precipitates with sulphate due to lower solubility than sodium sulphate and the concentration of chloride in the solution increases[6, 8].

2.3.3 The Effect of pH

The pH in the solution on the pipe surface and in the crevice or pit is difficult to measure as the composition varies at both places. Especially since the pH inside a crevice or a pit can be widely different from that of the bulk solution on the surface of the pipe due to hydrolysis that takes place inside, and this acidifies the solution. The composition of seawater shown in Table 2.3 has a pH of 8.2.

It was found[45] that pH values from 1–10 experienced a linear increase with E_{pit} of about 200 mV in a 4 % NaCl solution. Electrochemical tests[46] found a falling corrosion rate with rising pH between 4 and 9, which means that the corrosion rate increases with increasing acidity of the solution. Potentiodynamic experiments[7] were carried out with distilled solutions containing chlorides but precautions were taken to prevent crevice corrosion. It was found that a pH of 3 gave a little lower pitting potentials than solutions of pH 5 or 6–7 with low chloride content. No effect of pH was seen at higher chloride content. This indicates that pH has little effect on pitting potentials in a chloride solution and therefore does not much change the susceptibility to pitting corrosion in the pH range 3–7.

2.4 Other Parameters Taken to Determine the Susceptibility to Pitting and Crevice Corrosion

This section presents the parameters that seem to have an effect on the susceptibility of pitting and crevice corrosion. Only a brief description of each parameter is presented.

2.4.1 Effect of Temperature

According to DNV-RP-G101[2] and NORSOK[1], temperature is the main reason for localised attack of stainless steels in a topside offshore environment. Therefore, in this section the basis for this assumption is examined. It is assumed that the temperature varies between 0 °C and 100 °C in an offshore environment in the North Sea, depending on what the pipe transports and the weather conditions. Several authors [3, 21] report that with an increase in temperature the E_{pit} decreases and the damage caused by corrosion increases. The increasing temperature causes higher current transients and promotes the conversion of metastable pits into stable growing pits. Electrochemical studies[47] were carried out in micro- and large-scale, both in chloride free and in chloride solutions. In chloride free solutions, the increase in temperature caused an increase in the dissolution of MnS inclusions, while in a chloride environment the growth of pits increases. The increase in temperature may form new inclusions, but this is considered less important.

Experimental work on temperature is often focused on finding the critical pitting temperature (CPT) or the crevice corrosion temperature (CCT). The CPT is defined as the lowest possible

temperature where pitting occurs[26] or a better definition may be “*the lowest temperature at which the growth of stable pits is possible*”[31]. The second is a better definition because it is important to note that metastable pitting can occur below the CPT, but stable pitting only occurs when the solution temperature exceeds the CPT for that exact solution. It does not say when the CPT is exceeded, stable pitting can continue even though the temperature is lowered below the CPT later on. The second parameter is the CCT, which is the lowest possible temperature for stable crevice corrosion. It is important to be aware that those values for CPT and CCT found through tests are only valid for that exact environment[26]. This means that values found in experiments from other environments does not give information on the offshore environment that is studied here but just indicates the trends. Electrochemical tests[46] found that E_{pit} is a linear function of temperature in a chloride solution. The temperature increase causes a decrease in E_{pit} .

A potentiostatic method[48] was used to determine the potential independent CPT, which is independent of the environment as well. This was determined for low temperatures and attributed to the resistance of a stainless steel to stable pitting. At higher temperatures, the CPT depends on the E_{pit} . As the temperature increases the E_{pit} decreases and this potential dependent region is attributed to the parameter of initiation of pits.

In a study metastable pitting was seen at 15–20 °C lower than the experimental CCT value. It was seen that around the CCT value there was an increasing amount of metastable pits. This indicates that metastable pitting initiates crevice corrosion. Time may be a factor, where crevice corrosion occurs at all temperatures, as long as a sufficient amount of time is allowed, if the metastable pitting rate does not fall to zero with time[15].

For testing the CPT and CCT, standard tests can be found in ASTM G48 (FeCl₃) and G150 (NaCl). The standard test (G48) was used to measure the CPT of three stainless steels, among them AISI 316. The resistance to corrosion is determined as the CPT. An alteration of the CPT may be caused by a small alteration in the microstructure of the surface or its homogeneity. The pH of the test was adjusted to 1 with HCl. The pH, the external potential used, and where the temperature scan starts, may impose an effect on the value of CPT[49]. This method and the others to determine the value of CPT are designed to avoid crevice corrosion, so that only pitting is measured.

In Figure 2.5 the CPT and CCT for different stainless steels are given as found with the ASTM G48, where the specimens measured are immersed in 6 % FeCl₃. The CCT for AISI 316L is –10 °C and the CPT is 10 °C, which is not encouraging for placing it in an offshore environment. However, it is important to note that this is for immersed conditions and is not directly comparable to the offshore environment topside.

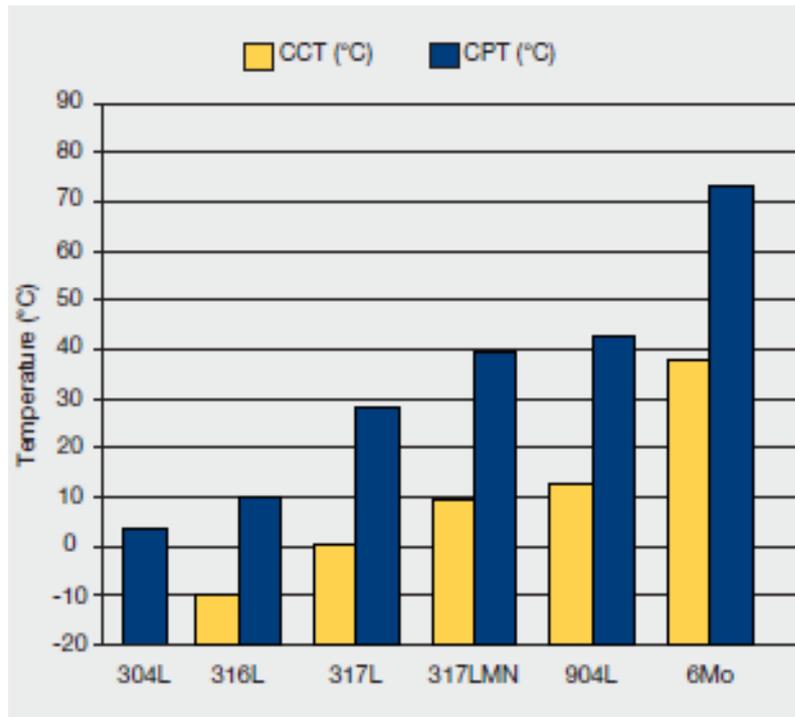


Figure 2.5: Different unwelded stainless steels were tested in solution annealed condition by ASTM G48 in 6 % FeCl₃ to determine the critical pitting temperature and crevice corrosion temperature for [50].

Other experiments with varying temperature are presented later as different parameters are addressed.

2.4.2 Effect of Chloride Concentration

A pipe located in topside in an offshore environment is in a humid environment with chlorides. The chloride content present on the pipe at a certain time varies with conditions on the installation. This determines the thickness and the chloride content of the thin oxide film on the surface. The chloride ion is tiny and therefore easily permeates the film due to its high diffusivity[27]. It is believed that the adsorption of chlorides destroys the oxide film, and this causes a rise in potential that acts as a driving force for the adsorption[27].

Figure 2.6 shows the anodic polarisation curve in a plot of potential as a function of the logarithm of the current density. The curve is plotted for two different chloride concentrations. E_{pit} is shown as E_p and it can be seen that it increases with decreasing chloride content. In the figure there are numbers 1–3, where number 1 is applicable if the corrosion potential E_{corr} is smaller than the E_{pit} , then no pitting occurs. In 2, the E_{corr} and the E_{pit} is approximately equal, and small changes in the environment plays a decision-making role in whether pitting corrosion occurs or not, due to that the E_{corr} slightly rises. If at number 3, then pitting corrosion occurs as E_{corr} is equal to E_{pit} [8].

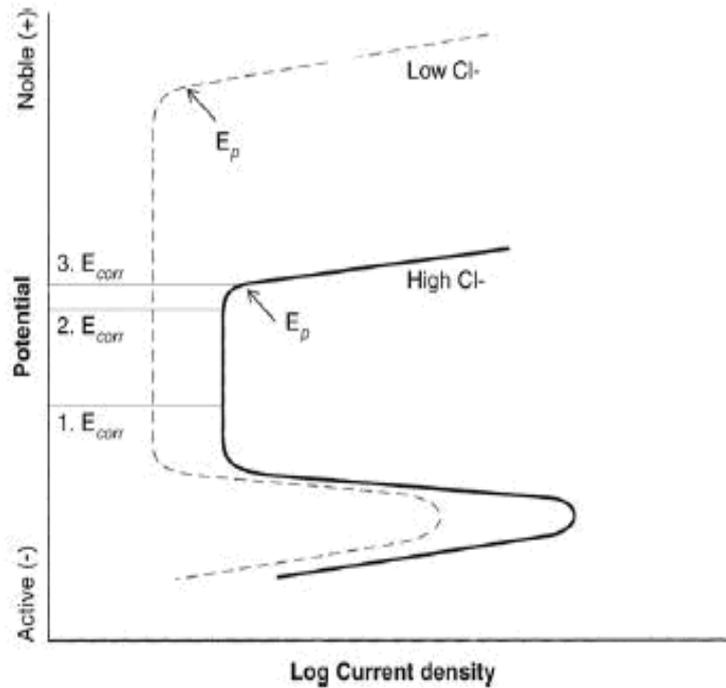


Figure 2.6: Anodic polarisation curve showing potential as a function of the logarithm of the current density from[8].

There is a large volume of published studies describing the relationship between E_{pit} and the chloride content. Different polarisation measurements[30, 36, 45, 46, 51] demonstrated that the pitting potential was a linear function of the logarithm of the chloride concentration. High alloyed stainless steels are less affected by increasing chloride content, and E_{pit} changes only slightly[51]. An increasing chloride concentration therefore gives an increasing susceptibility to pitting corrosion.

Figure 2.7 presents the CPT as a function of chloride content for seawater. It can be assumed that the chloride content on the pipe surface varies with the amount of chloride deposited on different parts of the pipe and the conditions on the installation. The graph for AISI 316 shows that the CPT decreases with increasing chloride content, meaning that the susceptibility to pitting corrosion increases.

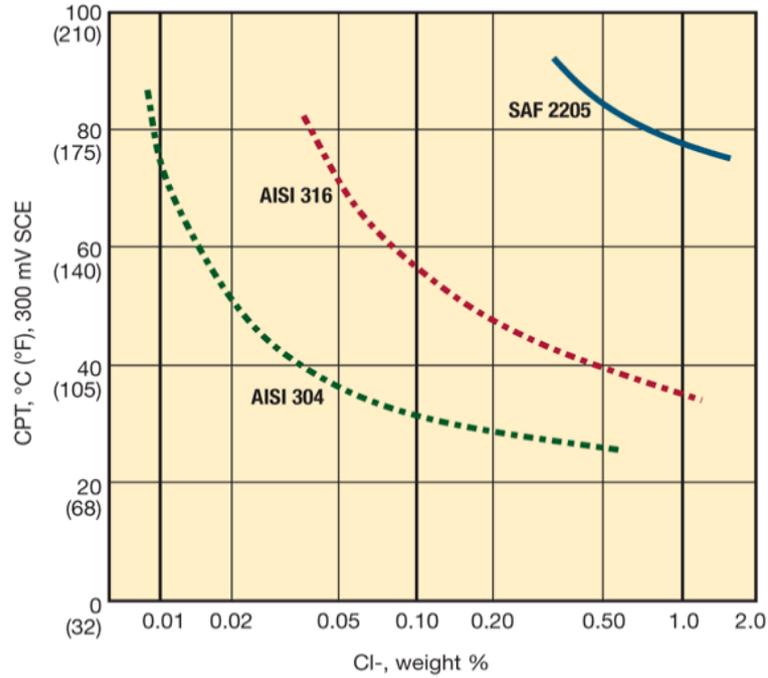


Figure 2.7: The critical pitting potential (CPT) as a function of chloride content at + 300 mV, which is the same as for seawater, from Jepsen[4].

In Figure 2.8 the CPT is plotted against chloride concentration for two different stainless steels at a potential of +300 mV, which corresponds to seawater[52].

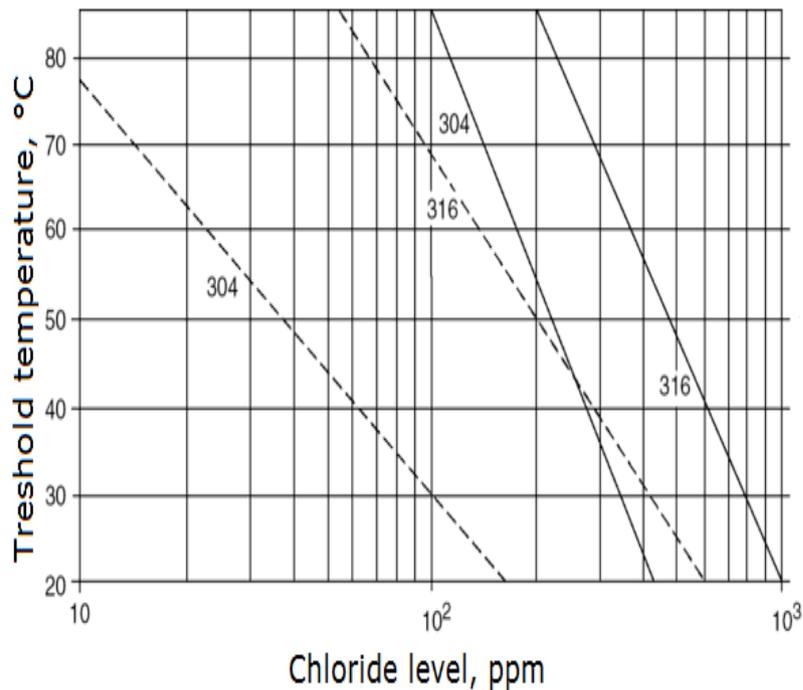


Figure 2.8: The CPT(solid line) and CCT(dashed line) for AISI 304 and 316 as a function of the chloride content in a solution saturated with oxygen from[52].

Solutions of 4–30 % NaCl at temperatures between 30–100 °C were used in potentiodynamic tests[45] to measure the pitting potential. An increasing Cl^- content in the solution will result in a decrease in CPT.

Potentiodynamic experiments[7] were used to test the susceptibility to pitting corrosion at evaporative conditions, avoiding crevice corrosion. The test solution contained distilled water with NaCl and Na_2SO_4 . It was found that when the chloride concentration became high, different temperatures did not have much effect on the pitting potentials, as when changing the temperature between 40 °C and 50 °C.

2.4.3 Corrosion Rate

When studying corrosion, it is found[53] that the corrosion rate decreases after a period of pit and crevice growth. It is not clear why this occurs, but several reasons for the decrease in the corrosion rate have been suggested. One is that in the bottom of deep pits, the ohmic drop in potential causes E_{corr} to fall below E_r . The large cathode/anode ratio that acts as a driving force for the pit growth reactions may decrease, lowering the corrosion rate. If a pit grows actively, there can arise a limitation of mass transport of aggressive ions to the bottom of the pit or crevice, due to dissolution of many species at the bottom. If a pit or crevice loses its critical chemistry, the aggressive species are no longer present in such a high concentration, which reduces the attack at the surface. If inhibitive anions like sulphate migrates into the pit, it can reduce the effect of chloride attacking the surface. The acidic pit environment can be enriched by dissolution of components in the alloy that are stable in this environment, resulting in passivation.

The corrosion rate for the different corrosion zones where found[54] using the weight loss coupon method. Here the zones were identified as domains where the coupon was fully immersed, partially immersed or above sea level. The chemical composition of the water used was approximately the same as the one given in Table 2.3. The fully submerged experienced a higher corrosion rate than the one that was located above sea level. There were a few aberrations, one of them being AISI 316L, which had a higher corrosion rate above sea level. This is due to the fact that the density and depth of pits were higher. The partially immersed zone had higher corrosion rate for all the alloys in the experiment than for other locations. At water level the attack was most severe, especially for AISI 316L and 304, perhaps due to the formation of a differential aeration cell.

A electrochemical linear polarization resistance technique[21] was used to measure the effect of chloride concentration on corrosion rates at 50 °C, which was found to be very low. AISI 316L seem to experience more severe corrosion attack in seawater than at 5000 ppm chloride. A significant active shift is experienced by the pitting potential, as the chloride concentration increases, caused by a passive oxide film that forms on the surface. Immersion in seawater and salt spray tests were performed at 25 °C and 50 °C in order to find the corrosion rate. The

results were very low. An electrochemical polarization technique was also used and it showed low corrosion rates. The time lag is due to the interval during which the protective oxide film stabilises. This is mentioned as the reason for the gap in results of the measured corrosion rates.

Salt spray tests[51] were performed on conventional and high alloy stainless steels for 5000 hours to test crevice corrosion. The corrosion rates obtained were extremely small. Salt spray tests gave lower values of corrosion rates compared to that obtained from electrochemical polarization techniques. It was assumed to be caused by the time it took for the oxide film to become stable. Crevice exposure tests were done for different stainless steels immersed in Gulf seawater for temperatures of 25 °C and 50 °C, and for periods of 180 and 150 days, respectively. The room temperature tests did not show any crevice corrosion, while in the 180-day tests at an elevated temperature the alloys corroded.

The Arrhenius plot is shown in Figure 2.9, while the seawater composition is presented in Table 2.2. The plot is for temperatures of 25–90 °C for AISI 316 immersed in seawater, which shows a linear relationship as a function of the logarithm of the corrosion rate and the reciprocal of the absolute temperature. This was found by electrochemical studies[21] and the activation energy is determined from the slope of the plot. The E_{pit} becomes constant, when the temperature exceeds 65 °C, which was proposed as a decrease in the solubility of oxygen caused by a temperature increase.

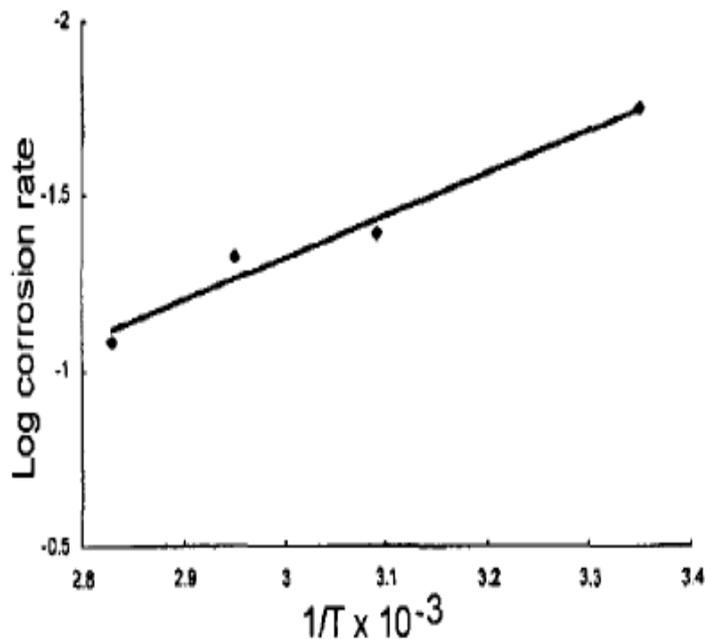


Figure 2.9: The corrosion rate of AISI 316L dependence on temperature[21].

Tests[36] on different types of stainless steels at 50 °C and a difference in corrosion rates were found to depend on the measurement method. It was found that electrochemical polarization techniques gave one order of magnitude higher corrosion rates than long duration salt spray tests with 5 % NaCl. The time lag before the salt spray tests gave time for the stabilisation of the oxide film and this is the assumed reason for a lower corrosion rate for this method. The corrosion rate seemed to be dependent on Cr and Ni content, the PRE_N value and the induction time. It was mentioned that no corrosion would occur if the steels were used in crevice/deposit-free systems in fully immersed conditions in seawater; which is not in agreement with other results given in this literature survey. The corrosion rate for Type 316L in natural gulf seawater was low. It was noted that the corrosion rate did not depend on the chloride content, a pipe in the chloride solution (max 5000 ppm) did not always have a lower corrosion rate than the specimen in seawater.

A linear rise in corrosion rate was found[46] with rising Cl^- concentration (100–5000 ppm) and a higher amount and depth of pits were seen. Between pH 4 and 9 the corrosion rate fell as the pH increased. The best conditions for initiation and propagation of pitting corrosion in AISI 316/316L, appears to be a stagnant condition with low pH and high Cl^- concentration. A rise in temperature results in a corresponding rise in the corrosion rate.

2.4.4 Material Properties

The composition of AISI 316 stainless steel is given in Table 2.1. From the table it can be seen that the alloy contains C, N, Cr, Mn, Mo, Ni and Si in an iron base and in some cases there are also small amounts of phosphor and sulphur present. Electrochemical polarization tests were performed on 316L in synthetic seawater to back up a literature review on initiation sites for pitting. In agreement with previous literature, pitting was found mainly at sulphide inclusions, probably MnS inclusions[55]. The amount of sulphur in the steel should therefore be minimized to reduce the susceptibility to pit initiation.

The austenitic structure is promoted by the use of carbon and nitrogen in the alloy, since they are the strongest austenite formers. Carbon reduces resistance to intercrystalline corrosion cracking, but both increases the mechanical strength of the alloy. Nitrogen is added to the alloy in order to increase the resistance to localised corrosion.

Nickel promotes an austenitic structure, increases toughness and ductility. It increases the corrosion resistance by lowering the corrosion rate, because it simplifies the formation of the passive film[26, 56, 57]. Tests carried out on stainless steels in 50 °C seawater showed that an increasing amount of Cr and Ni gave a lower corrosion rate. The effect of chromium can be seen in Figure 2.10, where chromium has a large transpassive area. The corrosion resistance of the alloy is primarily due to the passivating effect of chromium, which shows increasing resistance with increasing content. The resistance to oxidation at elevated temperatures is also improved. It can be seen in the figure that molybdenum has a smaller transpassive area, which

contributes to protection of the material for a while, after which dissolution of the metal continues. The corrosion resistance to both general and galvanic corrosion is improved by molybdenum. This is for the same reason as that for nickel, but it also stabilises the film and it gives a slight increase in mechanical strength. It can be seen from the graphs that the E_{corr} of the austenitic alloy is approximately the same as that of nickel and molybdenum, but more noble than that of iron and chromium[36].

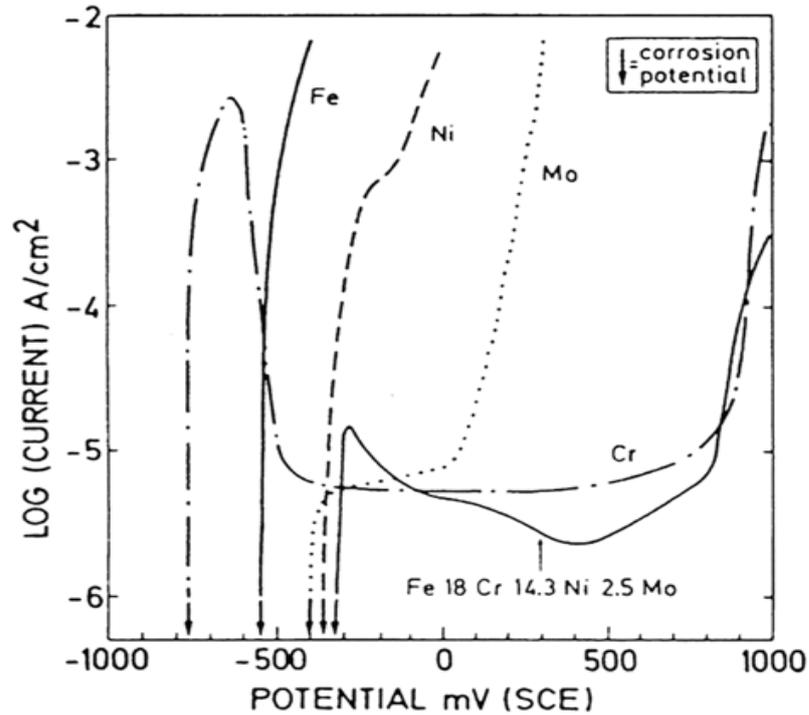


Figure 2.10: Log(current) is plotted as a function of potential for the metals Cr, Fe, Mo, Ni and the alloy Fe18Cr14.3Ni2.5Mo (atom%), which gives anodic polarisation curves from [57]. The solution was 0.1 M HCl + 0.4 M NaCl at 25 °C and the sweep rate was 3 mV/s.

AISI 302 and 316 were compared[30] to study the effect of chloride on E_{pit} . It was seen that the 316 had higher E_{pit} at all chloride values, due to the addition of 2.5 % Mo. Dissolution of the stainless steel is mitigated by the Mo.

Tests[36] of different types of stainless steels at 50 °C were carried out and it was found that E_{pit} could be represented as a linear function of Cr and Cr + Ni. The corrosion rate seemed to be dependent on Cr and Ni content.

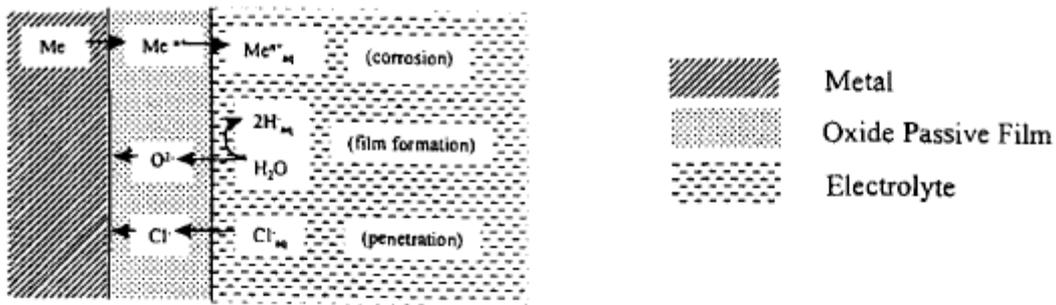
2.4.5 Oxide Film

When AISI 316/316L stainless steel is exposed to the aggressive environment offshore it starts corroding. The corrosion products develop an oxide film on the surface, protecting it against further corrosion. If there were no chlorides present, the film would be able to provide

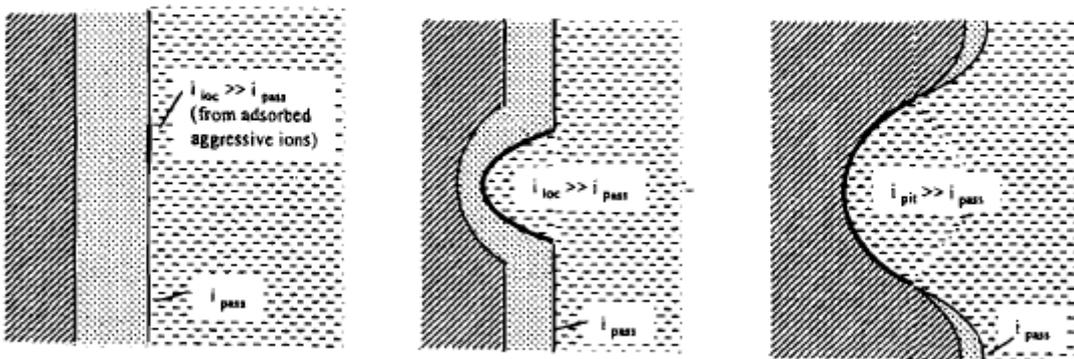
adequate protection to the surface. Chlorides attack the surface, causing pitting and crevice corrosion.

Figure 2.11 shows passive film penetration, adsorption and film breaking, which are thought to be the most common mechanisms of passive film breakdown and the initiation of pitting. Figure 2.11a) shows the penetration mechanism, where aggressive ions like chlorides migrate—assisted by a high electric field in the film—to the metal surface and stimulates dissolution. The initiation time before pitting corrosion starts is in agreement with this model. Figure 2.11b) shows the adsorption mechanism, where adsorption of anions like chloride and oxygen's effect on the surface film is considered. Figure 2.11c) shows the third of the mechanisms of initiation of pitting, the film breaking mechanism. In this mechanism it is assumed that the film constantly grows and breaks down, depending on the environment. When chloride is present, the growth of the film that should protect it from further breakdown does not normally occur[27].

a) Penetration Mechanism



b) Adsorption Mechanism



c) Film Breaking Mechanism

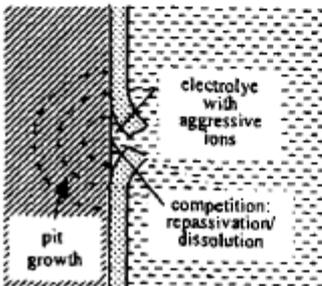


Figure 2.11: Sketches of different types of pit initiation from [27]. The sketches show the mechanism of a) penetration, b) adsorption and thinning and c) is the film breaking.

2.4.6 Effect of PRE_N Value

The abbreviation PRE_N stands for pitting resistance equivalent. A higher potential is needed to initiate pitting in alloys with large PRE_N values than alloys with low values. In Equation (2.2) the pitting resistance equivalent is shown:

$$PRE_N = \%Cr + 3.3\%Mo + 16\%N \quad (2.2)$$

To assess whether an alloy can resist pitting corrosion, the PRE_N is mentioned in several studies[21, 26, 51] as an important parameter. To resist pitting when immersed in seawater PRE_N > 38. When crevice corrosion is initiated, for high alloyed stainless steel with PRE_N >

40 immersed in seawater, it is possible for it to propagate at a much lower temperature than when initiated. The PRE_N value for AISI 316L is 26 and it is therefore not used for seawater applications.

The mechanism for crevice and pitting corrosion are similar to each other. In Figure 2.12, tests performed in a 6 % $FeCl_3$ solution for specific types of steel show that the value of CPT and CCT are correlated. The CCT starts at a temperature that is lower of the two for every type of steel, and crevice corrosion is the most brutal, as mentioned in the Statoil report[3] findings[26].

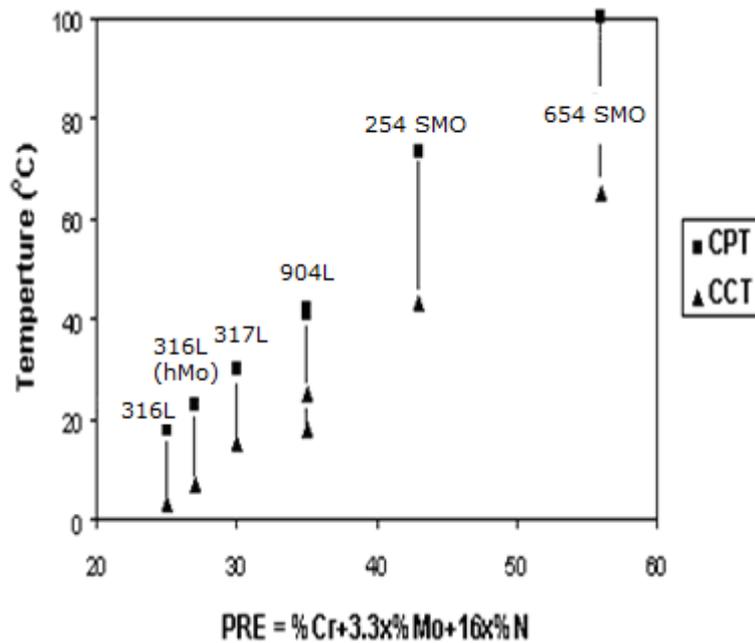


Figure 2.12: Temperature as a function of pitting resistance equivalent (PRE). The graph show the correlation between the critical pitting temperature (CPT) and crevice corrosion temperature (CCT) for different steel types in 6 % $FeCl_3$ taken from [26].

In Figure 2.13 the critical pitting temperature is plotted as a function of the PRE_N value for steels in 1 M NaCl. It can be seen that the CPT increases almost linearly with increasing PRE_N value. Tests on stainless steels in seawater at 50 °C, which gave a corrosion rate that was dependent on the PRE_N value, which decreases as the PRE_N value increases. E_{pit} is a linear function of the PRE_N value[36].

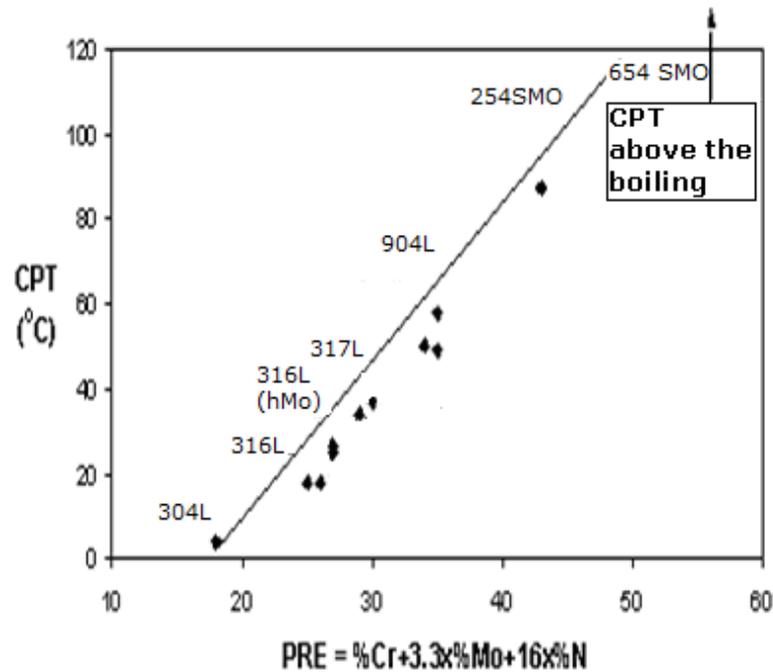


Figure 2.13: Critical pitting temperature (CPT) as a function of the pitting resistance equivalent(PRE) in 1 M NaCl, taken from [26].

2.4.7 Effect of Surface Roughness

A material surface has a certain roughness depending on the surface preparation. This preparation is done to ensure proper adhesion of the coating and protect the pipe from the environment by making a smoother surface to reduce the possibility of localised solutions occurring. A rough surface is a good place to sustain a localised concentrated solution[31]. Often a surface contains inclusions, which are surface defects. If little treatment is done and the surface is rough, then there are more surface inclusions on the surface. These are considered as weak spots on the surface and previous studies[55] report that initiation sites for pitting is found mainly at sulphide inclusions, probably MnS inclusions. It is not easy for pits to initiate on smooth surfaces as there are fewer initiation sites[58].

Tests[31, 59] have been carried out to study the relationship between critical pitting temperature (CPT) and surface roughness. With an increase in surface roughness, the CPT decreases and the standard deviation of the test results increase. The reasons for higher chance of stable pitting in rough surfaces, are attributed to longer lengths of diffusion and larger micro-crevices surrounding the inclusions. Both electrochemical noise (EN)[59] and potentiostatic[60] tests in different NaCl solutions show that rough surfaces have a lower CPT value than smooth surfaces. The standard deviation has been found to increase with increasing surface roughness.

Contrary, testing[19] found that it is preferable with a rough surface to mitigate crevice corrosion attack and that the attack increased with increased smoothness of the surface.

2.4.8 Effect of Pipe Diameter

Statoil's report[3] informs that large diameter pipes show more severe attack of pitting corrosion than pipes with smaller diameters. Laboratory tests are most often carried out on coupons and rarely on actual pipes. No other research report indicates this, so this is very uncertain if it has an effect or if it was observed only for this particular inspection.

2.4.9 Effect of Coating

There are several ways of protecting an installed pipe against an aggressive environment and coating systems is one method that has been developed to protect external surfaces against corrosion. The coating used is evaluated after DNV-RP-G101[2] recommendation for the evaluation of coatings, since RBI is considered in this thesis. In this standard, the use of coating is considered to provide 100 % protection to the pipe for the first five years of use, but thereafter it deteriorates gradually to zero protection after approximately 15 years. This is represented in Figure 2.14 with the area covered by the coating as a function of the age of the coating. This figure is representative of all types of coated surfaces, and is not just for stainless steel only. The surface preparation of the material, choice of coating, quality of the coating and the maintenance carried out are obviously critical factors. The application procedure is also important. A special coating system is chosen for this material to give the best adhesion between the material and the coating and protection against the environment. Normally, if the application of the coating follows the Norsok M-501 standard[61], then the degradation rate can be calculated.

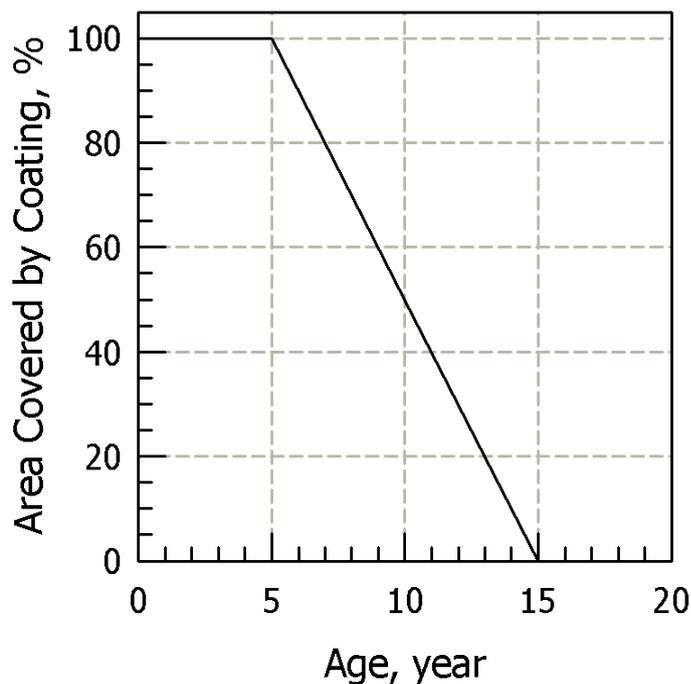


Figure 2.14: Degradation of the coating shown as function of time from DNV-RP-G101[2].

According to NORSOK, system 6A can be used on stainless steel when coating is required. In Table 2.4, the required surface preparation and coating specifications are given. DFT is the dry film thickness, which is the thickness of the coating after hardening. It is important to note that zinc should not be present in coatings used on stainless steels due to the risk of HISC.

Table 2.4: Coating used for AISI 316/316L from [61]. DFT is the dry film thickness of the coating.

Application	Surface preparation	Coating system	DFT [μm]
Un-insulated stainless steel when painting is required.	Sweep blasting with non-metallic and chloride free grit to obtain anchor profile of approximately 25 μm to 85 μm .	1 coat epoxy primer:	50
		1 coat two component epoxy:	100
		<u>1 coat topcoat:</u>	<u>75</u>
		Minimum DFT(μm) of complete coating system:	225

Literature on anticorrosive coatings are reviewed and important findings that should be considered when using these coatings[62] are mentioned. When applying a coating on AISI 316L pipes, the organic coating used is always partly permeable to water and oxygen, but as long as the coating protects against aggressive ions reaching the surface, pitting corrosion is prevented. This is achieved by the barrier effect, which increases the resistance of ionic transport. This effect causes a high electrical resistance in the moisture between the coating and the material surface. The current moving from anode to cathode is very low as the conductivity is lowered by the effect. As mentioned previously the environment offshore is extremely aggressive. The epoxy primer is applied to provide adequate adhesion between it and the material surface, and provide protection against pitting corrosion. The two-component epoxy coating is applied to ensure that the coating is thick enough to block the aggressive ions from reaching the material surface. The topcoat is the third layer and offers protection against the aggressive offshore environment. The durability of the coating is reduced by the environment, the temperature of the media in the pipe and UV radiation. Experience shows that most paints have defects present after application. Repair should preferably be done a few months after application, to avoid further damage to the coating and pipe surface. Crevice corrosion becomes a problem when degradation of the coating surface starts and painting remnants form crevices against the surface of the material.

2.4.10 Induction time

Induction time is often called initiation time, and is the elapsed time before crevice and pitting corrosion starts. Different stainless steels at 50 °C were immersed in chloride solutions under open circuit potential measurements[36, 46] and it was found that the pitting potential could be presented as a linear function of initiation time, t_i , where A and B are constants that depend on temperature.

$$E_{pit} = A + B \cdot \log(t_i) \quad (2.3)$$

Electrochemical measurements[46] of the open circuit potential showed that the logarithm of the induction time decreases linearly with increasing chloride content and increasing temperature, where the test temperatures were 30, 50 and 80 °C. In Equation (2.4) the initiation time, t_i , can be shown as linearly dependent on the logarithm of chloride concentration, where C and D are constants that depend on temperature.

$$t_i = C + D \cdot \log[Cl^-] \quad (2.4)$$

Open circuit potential measurements[36] found that the initiation time for AISI 316L in Gulf Sea water at 50 °C is 14 hours. This is higher than the value found for 304L, 317L and 904L. As the corrosion rate decreases the initiation time increases. This does not seem to correlate well with the values that were found for AISI 304L and 904L. The PRE_N value has a linear relationship with the induction time, the higher the PRE_N value of the steel the longer the induction time for pitting for high alloy stainless steels. The initiation time was considerably higher for high alloy steels than conventional steels. For conventional stainless steels (for example AISI 316L) a decrease in the initiation time occurs with increasing PRE_N . This is probably due to low Mo content and may not contribute considerably to pitting resistance.

2.5 Discussion of the Parameters

This chapter discusses the effect of various parameters on the susceptibility of austenitic stainless steels to pitting and crevice corrosion. Only brief description of each consideration are presented. Not all considerations are included in this literature survey since they are out of the scope of this work.

CHAPTER 3

Proposed Procedure for Assessing the Possibility of Localised Corrosion of Stainless Steel Piping in Topsides

3.1 Introduction

A number of different parameters must be assessed in order to decide on the susceptibility to pitting and crevice corrosion for a given material. This chapter presents a simple procedure for evaluating the susceptibility of AISI 316/316L piping in topsides offshore environment. The procedure attempts to provide a rough guideline that can be utilized at the screening stage of RBI analysis, even with a limited amount of data. Chapter 2 presents an overview of some of the research done on austenitic stainless steels in an offshore environment. Not all of the parameters mentioned can be measured or found, hence, only those parameters that are regarded as most important, which can also be estimated have been considered.

Section 3.2 gives an overview of the procedure presented as flowcharts. The main flowchart applies for pitting and crevice corrosion. The flowchart in Figure 3.2 only applies for crevice corrosion. Section 3.3 outlines the arguments for the parameters used in the procedure and the logical sequence of steps in the flowcharts are explained. The steps in the flowcharts are discussed in detail in Section 3.4. Section 3.5 presents the outputs of this chapter.

If the result of this chapter is low possibility of corrosion, then it is assumed that localised corrosion does not normally occur at the pipe's location and no further assessment of the pipe is necessary. On the contrary, if there is a possibility of localised corrosion, further evaluation should be done. In Chapter 4 the possibility of pitting corrosion is determined based on finding the value of E_{pit} and comparing it to the environment. Chapter 5 outlines the methods to estimate the probability of failure with respect to time because of coating degradation and pitting corrosion.

3.2 Overview of Procedure

In this section, a procedure developed in form of flowcharts is presented that can be used in RBI to decide the possibility of localised corrosion in an 316/316L pipe in an offshore environment.

The main flowchart is shown in section 3.2.1. The first three steps are required for assessing the exposure to the corrosive chloride environment based on the location of the pipe. The three subsequent steps in the main flowchart are for judging the quality of coating, range of operating temperature and any reported corrosion. The second flowchart presented in section 3.2.2 applies for estimating the possibility of crevice corrosion. The number in each step in the flowcharts refers to sections where detailed explanations of the steps are discussed.

3.2.1 Main Flowchart

The main flowchart given in Figure 3.1 consists of six steps. Exposure to chloride is evaluated in the first three steps. This is based on the location of the offshore pipe. The quality of coating is evaluated to find its degree of protection against pitting and crevice corrosion. Range of operating temperature is the fifth step that has to be decided. It is compared to crevice corrosion temperature (CCT) and critical pitting temperature (CPT). If there is low possibility of localised corrosion for the first five steps, checking for any reported corrosion is the sixth step. In this step, a check is carried out to find if there is any earlier reported corrosion and if so, similar pipes should be inspected. The possibility of corrosion can then be assessed based on the result of the steps in the flowchart, which are explained in sections 3.4.1–3.4.6.

3.2.2 Possibility of Crevice Corrosion

Figure 3.2 presents a flowchart for determining the possibility of crevice corrosion. This flowchart is used as a supplement to the main flowchart, to determine if there is an increased possibility of crevice corrosion. This can be due to installation, general maintenance and/or impurities, which may affect the integrity of the pipe. The steps are explained in sections 3.4.7–3.4.12.

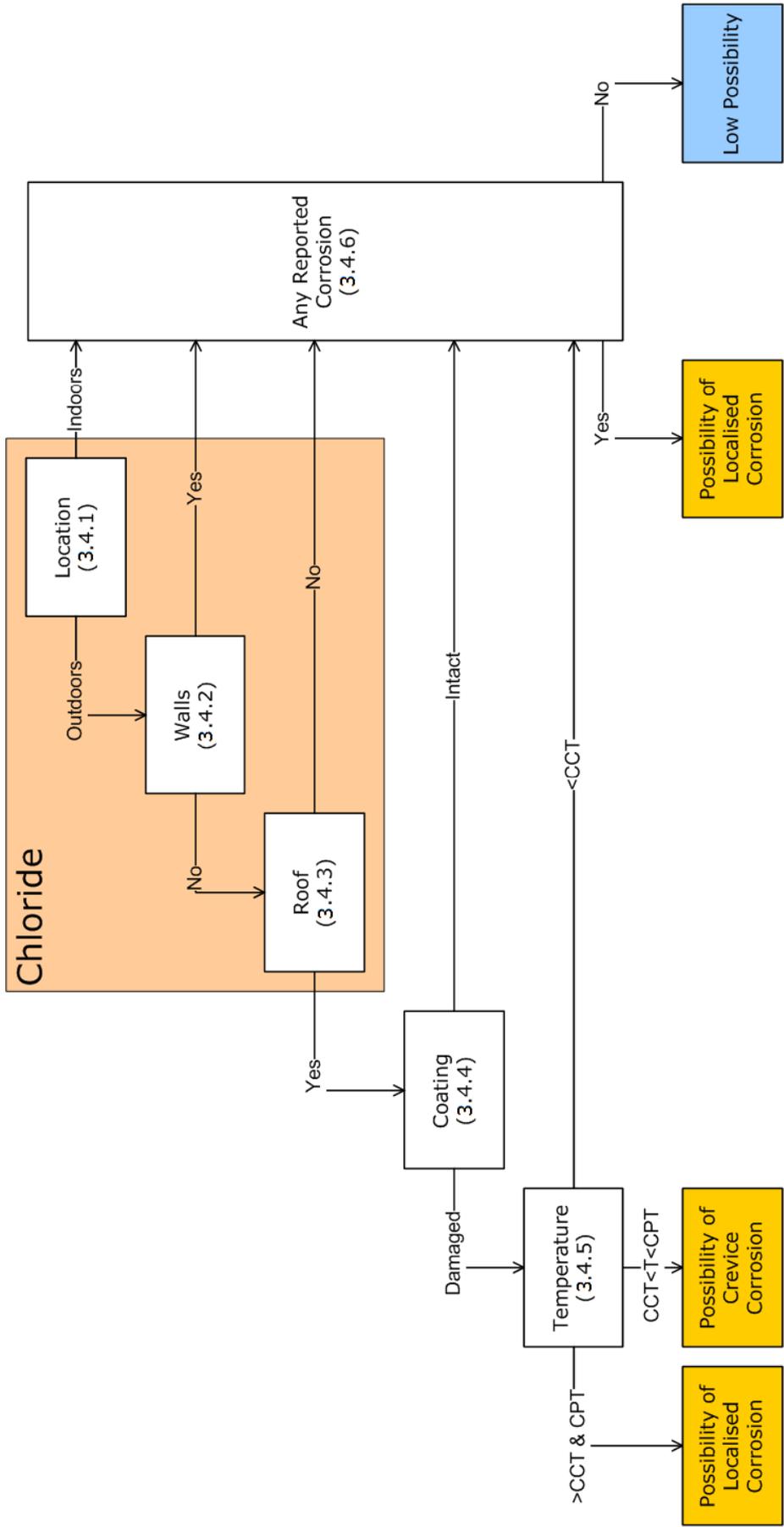


Figure 3. 1: Procedure to assess the possibility of localised corrosion.

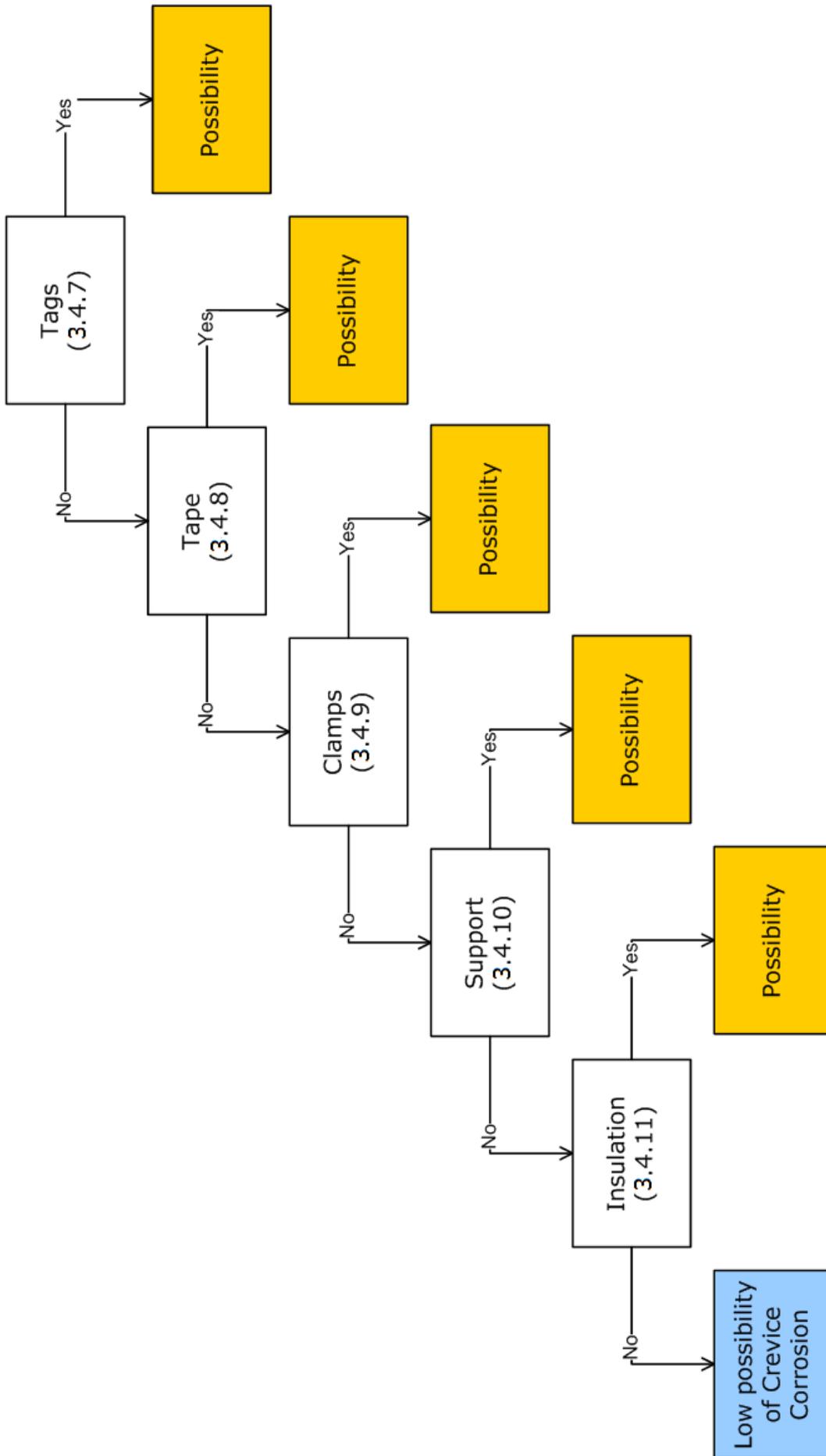


Figure 3. 2: Determining the possibility of crevice corrosion.

3.3 Choosing Parameters to Use in the Procedure

In order to develop a procedure that can easily be used in RBI, the applicability of the parameters is assessed. First, arguments for the choice of parameters used in the procedure are presented and then the sequence of the steps in the flowcharts is explained.

3.3.1 Arguments for Choice of Parameters

Little can be done about the material properties since the specifications of the material are a design choice. The PRE_N value has not been used in this procedure, since AISI 316/316L was already the material of choice and it has one specific PRE_N value, which is used to compare different stainless steels. When ordering 316/316L, it can be difficult to get information about the composition of the steel produced and for later RBI it can be even worse. This is especially true for older 316/316L pipes, where even less information may be available. Experience shows that some lots of pipes are less susceptible to pitting and crevice corrosion. This is believed to be due to higher molybdenum content, but it is not certain. It is important to note that the pipe should contain as little sulphide as possible. This is to reduce the number of inclusions and thereby reduce initiation sites, and this reduces the possibility of pitting corrosion. Again, it is a design choice and sulphide content is normally not information that is available during the RBI analysis.

The oxide film on a pipe protects it against uniform corrosion, but chloride may penetrate the film thereby increasing the possibility of localised corrosion. The oxide film thickness varies depending on the dissolution rate and the concurrent rate of formation of the film. This varies a great deal along the pipe surface, since it is exposed to conditions on the installation. This is not a parameter that can be used in the procedure since it is difficult to measure.

Surface roughness is a parameter that has a detrimental effect on the susceptibility of pitting corrosion. The more rough the surface, the larger the possibility of pitting corrosion due to an increased amount of initiation sites and easier development of a critical solution chemistry. For crevice corrosion it is opposite in nature, as the possibility of crevice corrosion increases with decreasing surface roughness. The surface roughness is a parameter that in general is difficult to know when doing an RBI analysis, since this information is not always easily available.

No information regarding the effect of pipe diameter on the localised corrosion could be obtained, other than that from the Statoil's report[3]. It is difficult to decide the limit as to exactly when a small pipe should be considered as a large one. The only relation that may be valid is that the possibility of localised corrosion seems to increase with increasing pipe diameter, but this is uncertain due to lack of research.

The solution chemistry is important though not constant. It is difficult to know the solution composition, and pH on the surface and in the pit or crevice, as conditions on the installation varies.

Sulphate and calcium are assumed to be in such small amounts compared to chloride that they do not have any effect on reducing the possibility of localised corrosion.

One important parameter is E_{pit} and this value is compared to the environment, since it is the deciding factor for the occurrence of pitting. It is dependent on several things, especially temperature and chloride concentration, and is therefore accounted for in the model through these. This is a qualitative procedure and since E_{pit} is a quantitative measure, it is considered in the next chapter. Chloride is assumed to be one of the important parameters, without chlorides there is low possibility of localised corrosion. The offshore environment always contains some chloride. What mainly determines the possibility of localised corrosion, is the amount of chloride deposited on the pipe due to conditions on the installation, and how well the pipe is protected from chloride in its location. Temperature is another important parameter. In this study only temperatures between 0 and 100 °C are considered. Increasing chloride content and temperature, increases the possibility of localised corrosion and both are used in this procedure.

Coating is also a parameter used in the procedure. It is important to apply coating in order to protect the pipe from the aggressive environment. It is possible to estimate the protection offered by the coating based on information about the coating and the quality of application.

Crevice corrosion is the more severe form among the two types of corrosion. A crevice has to be present for it to occur, compared to pitting corrosion that can initiate on a bare surface. In design, installation and maintenance work it is important to be aware of the danger of crevices forming. Almost anything that is in contact with the pipe for a period of time may form a crevice between the object and the pipe surface. The most common objects that form crevices on pipes offshore are considered in separate steps in this procedure.

3.3.2 Logical Sequence of the Steps in the Flowcharts

The main flowchart in Figure 3.1 has six steps, and the reasons for the sequence of the steps are explained here. The first three steps determine the exposure to chloride and are assumed as the most important steps for evaluating the possibility of localised corrosion. If there are no chlorides present the oxide film protects the surface against localised corrosion attack, but exposure to chloride destroys the protective oxide film. The location is put first since the other two steps are not applicable if the pipe is located indoors, because then there are both roof and

walls. If the third step (i.e., presence of roof) was put as the first step instead, the outcome having no roof but only walls would disappear, which may be an actual alternative.

Assessing the quality of the coating is the fourth step. If the applied coating is intact, it protects the pipe from the chloride environment and in the temperature range between 0 and 100 °C considered in this study. If there are no chlorides present then there is no need for a coating due to low possibility of corrosion. Therefore the coating step is placed below the chloride step. Temperature also does not contribute if there are no chlorides present, since the oxide film protects the surface and is placed below chloride as well.

The effect of temperature manifests itself in three ways: (a) possibility of pitting and crevice corrosion; (b) possibility of crevice corrosion; and (c) low possibility of corrosion. Low possibility leads to the next step, that is any reported corrosion. If this was placed at the top of the flowchart it would create many unnecessary branches, one tree from each of the two outputs wherever there was a possibility of corrosion and the third going to any reported corrosion step.

All pipes that are assumed to have a low possibility of corrosion should be checked if there is any reported corrosion on the pipe. This is the reason for any reported corrosion being placed to the right. This step accounts for unknown conditions that may lead to corrosion where it is not expected.

Figure 3.2 presents the second flowchart, which is only for crevice corrosion and has a different structure and output. The different steps are not correlated and all six are independent of the result of any other and the order is random. The result only indicates if there is a higher possibility for crevice corrosion, due to crevices present, if the first flowchart indicates a possibility of localised corrosion.

3.4 Explanations of the Flowcharts Presented

This section presents explanations for each step in the flowcharts given in Section 3.2. Each section number in Section 3.4 refers to the numbers given in the flowcharts. At the bottom of each section an output is found that is used as the point of entry to the next step in the procedure. Each step in the first flowchart has two outcomes: one of them is possibility, and in which case move on to the next step, and the other is low possibility, where the next step is any reported corrosion. For the crevice corrosion flowchart the output “yes” means that there is a possibility of localised corrosion. If “no” then it proceeds to the next step. If many of the steps can be answered as “yes” in Figure 3.2, then many places on the pipe have a susceptibility to crevice corrosion.

From the first flowchart, Figure 3.1, the possibility of localised corrosion can be found. Exposure to chloride is seen as the most important solution component affecting the

susceptibility to pitting and crevice corrosion in an offshore environment. The different features that affect chloride concentration are explained in detail in sections 3.4.1–3.4.3. Increasing chloride exposure increases the possibility of localised corrosion. The parameters for the coating in Figure 3.1 are explained in section 3.4.4. Section 3.4.5 presents how the temperature is determined. Step six is any reported corrosion and is given in section 3.4.6. The second flowchart in Figure 3.2 is only applicable for assessing crevice corrosion and the parameters are explained in sections 3.4.7–3.4.12.

If the pipe is washed with saltwater there is a possibility of localised corrosion. Chlorides are then present regardless of the surrounding environment and independent of any protection that the pipes may have against it. The evaluation can move directly to coating in section 3.4.4.

3.4.1 Location

Figure 3.1 is used in order to decide if chlorides are present. The location step branches into two different outcomes, which separates the location of the pipe as either indoors or outdoors. If the pipe is located indoors, it is shielded from the humid and high chloride containing environment that is present offshore. There is low possibility of corrosion in an indoor environment with roof and walls. The next step is then any reported corrosion given in section 3.4.6.

On the other hand, locating a pipe in a topside offshore environment outdoors exposes the pipe to an aggressive environment with chlorides and humid air. This means that the material maybe susceptible to pitting and crevice corrosion, caused by the environmental factors present. There is a possibility of corrosion and it must therefore be better evaluated. In the next section, the effect of walls in an outdoor environment is examined.

Output from step 3.4.1:

- Location of the pipe outdoors exposes it to chloride.

3.4.2 Walls

The second step in Figure 3.1 is used if the pipe is located outdoors, where there is a possibility of localised corrosion. This step considers if there are walls that protect the pipe from seawater splash. This is an uncertain step and each wall has to be individually evaluated for its possible degree of protection. If there are walls that protect the pipe from the splash of seawater, then there is low possibility of corrosion. The next step is any reported corrosion.

If there are no walls present, there is a possibility of localised corrosion. In this case the pipe is not protected from the splash of seawater and it has to be evaluated further. In the next step, the roof is evaluated.

Output from step 3.4.2:

- Some walls protect the pipe from seawater splash containing chloride.

3.4.3 Roof

The third step in Figure 3.1 is used if there is still a possibility of corrosion, as when the pipe is located outdoors and without walls. In this step, the presence of a roof, is divided into two branches: whether the pipe has a roof that shields it from rainwater and water coming from higher levels on the installation or not. When a pipe is located outdoors, rainfall washes away the salt that could have accumulated on the surface and thus reduces the susceptibility to pitting and crevice corrosion. Therefore, a low possibility of corrosion is assumed for this step. The next step is any reported corrosion.

A pipe can be located with a roof, but without walls. Then it is shielded from rainfall, but not sea spray. This causes accumulation of salt between the object mentioned in the steps of Figure 3.2 and the pipe surface causing crevice corrosion. Pitting corrosion is primarily found between 5–7 o'clock on the pipe due to water transport of salt, which accumulates on the external surface. Therefore, a pipe should not be located under a roof if no walls are present, then it would be better to remove the roof. When there is no roof present, there is a possibility of localised corrosion and the pipe should be evaluated further.

Output from step 3.4.3:

- Roof inhibits rainfall from washing the pipe and so chloride accumulates on the pipe.

3.4.4 Coating

In Figure 3.1, coating is the fourth step in the procedure. The step is divided into two branches with labels damaged and intact. A coating is considered intact if it is less than five years old and applied in agreement with DNV-RP-G101[2]. There is a low possibility of corrosion for the first five years and any reported corrosion is evaluated next.

The quality of coating is considered as damaged if there is no coating, the coating applied is not according to the standard, or if the coating is over five years old. It should be noted that having no coating increases the susceptibility to pitting and crevice corrosion, because the pipe then has an exposed external surface. After five years, localised corrosion can take place if no maintenance on the coating is carried out. Equation (3.1) from [2] can be used to determine the amount of protection provided by the coating between 5–15 years. After 15 years, the pipe is in the same condition as without a coating. A design life of up to 25 years is common, so maintenance is normally necessary. If the coating exceeds five years there is a possibility of corrosion, so the pipe should be evaluated further.

$$\text{Degradation rate} = \frac{(100 - \text{Effectiveness})}{100} \quad (3.1)$$

Output from step 3.4.4:

- The amount of protection given by the application of coating.

3.4.5 Temperature

The statements in the standards are based on an assessment of the effect of temperature on localised corrosion. The Norsok[1] standard claims that AISI 316/316L can be used up to 70 °C, while DNV-RP-G101[2] claims that the probability of failure is below 10⁻⁴ per mm wall thickness. Although the temperature is normally given as a process parameter controlled by the media that flows through the pipe, the external temperature and the sun also affects the temperature of the pipe. In this model it is assumed that the temperature of the pipe is the same as that of the media in the pipe, which is normal procedure in RBI. It was observed previously that the susceptibility to pitting and crevice corrosion increases with an increase in temperature, due to increased growth of pits, by promoting stable pit growth. It is difficult to exactly determine the CPT and CCT. Both are dependent on material properties and the environment and therefore vary a lot.

Determining the range of operating temperature and comparing it to CCT and CPT is the fifth step. As can be seen from Figure 3.1 the temperature step is divided into three branches. The label <CCT is where there is a low possibility of localised corrosion. Below this temperature, stable crevice corrosion does not occur, only metastable pitting may occur, which is assumed to pose no threat to the pipes. These pipes normally do not corrode, since the possibility is low, but any reported corrosion is evaluated in the next section, since not all parameters are used in the model.

If the temperature exceeds the CCT, but remains below the CPT, crevice corrosion may take place. No stable pit growth occurs—since it is below the CPT—but there is a possibility of crevice corrosion and since this is the most severe form of corrosion the pipe should be evaluated further.

Above CCT and CPT stable pitting and crevice corrosion becomes a problem that may cause failure of the pipe. It is therefore a possibility of localised corrosion and the pipe should be evaluated further.

Output from step 3.4.5:

- Increasing temperature above CCT and CPT promotes stable crevice and pitting corrosion.

3.4.6 Any Reported Corrosion

In Figure 3.1, the sixth step is any reported corrosion. The model does not account for all parameters that should be evaluated for finding out if there is a possibility of localised corrosion. This step is therefore a safety measure for low possibility pipes that are assumed to be safe from corrosion. This step further branches out to check for the presence of other pipes from the same manufacturer and with the same composition located at a similar place, or if there are no other pipes of its kind. If there is not any report of corrosion, then there is low possibility of corrosion for these pipes and the other similar pipes have low possibility of corrosion.

If any corrosion is reported and there are several pipes in the same environment, with the same properties and manufacturer, they may also be prone to a corrosion attack and should be checked. The specifications of the 316/316L pipe have some range of composition that can vary their behaviour, so there still is a possibility of localised corrosion on other similar pipes in the same environment and should therefore be evaluated further.

Output from step 3.4.6:

- Any reported corrosion on a pipe, means that there can be corrosion on similar pipes.

3.4.7 Tags

In Figure 3.2, the existence of tags is the first step in the procedure for determining the possibility of crevice corrosion. Tags are used to provide information about the material used in the pipe, what it transports and its destination. There are two types of tags. The first type has only two points of contact with the surface. This tag is normally moved after some time to prevent crevices from forming between it and the surface. By moving it regularly, severe crevice corrosion attacks on the surface due to the tag are inhibited. If this type of tag is used on the surface there is low possibility of crevice corrosion.

The other type of tag is like a sticker, it may cause severe crevice corrosion attack because of the development of crevices between it and the pipe surface and there is an increased possibility of crevice corrosion. A picture of an attack caused by this type of tag is shown in Figure 3.3.

Output from step 3.4.7:

- Tags in the form of stickers forms crevices against the pipe surface.



Figure 3.3: Picture of crevice corrosion found under a tag from an offshore installation in the North Sea.

3.4.8 Tape

The presence of tape is the second step in the procedure to determine the possibility of crevice corrosion. Tape remnants are often left behind during installation or maintenance work. If the pipe is located in an area that is difficult to reach, pieces of tape may often be left on the pipe as the main part is ripped off when construction work is completed. It is not commonly known that a small tape remnant can cause severe damage, and removing the tape remnants is often neglected. Tape remnants left on the pipe increases the possibility of crevice corrosion due to crevices forming against the pipe surface.

Output from step 3.4.8:

- Tape remnants left behind on the pipe, forms crevices against the pipe surface.

3.4.9 Clamps

Presence of clamps is the third step in Figure 3.2. It refers to clamps that have been placed on a pipe which have suffered corrosion, to protect it against further attack. If the work done when applying the clamps is not satisfactory, crevices may develop between the clamps and the pipe surface. This is contrary to the purpose of the clamps, which is to protect the pipe against further corrosion. Clamps may increase the possibility of crevice corrosion if they are not applied properly.

Output from step 3.4.9:

- Clamps can form a crevice against the pipe surface due to sloppy work during installation.

3.4.10 Support

Presence of support is the fourth step in Figure 3.2 and is often referred to as clamps in industry. There are two types of support: one is where the pipe lies in the support and the other is when the support surrounds the entire cross-sectional area of the pipe and is held together by bolts. The support is a place for accumulation of salt, especially on the bottom of the pipe from 5–7 o'clock. Therefore, the location of the support and its design should aim to minimize the accumulation of salt and water between the pipe and the support. Supports can form crevices, which increases the possibility of crevice corrosion.

Output from step 3.4.10:

- Supports can form crevices against the pipe surface.

3.4.11 Insulation

The fifth step in Figure 3.2 is the presence of insulation, which is used when the pipe has a passage through a wall. Walls not only protect the pipe from the environment, but also separate the different parts of the installation in case of accidents, like fire or explosion, and prevent it from spreading to other areas, such as living quarters. When a pipe goes through a firewall it has to be insulated, so that the pipe does not contribute as a thermal bridge between designated areas. As illustrated in Figure 3.4, often severe crevice corrosion attacks can occur at these passages through the wall. The insulation is supposed to be water tight, but often it is not. The insulation therefore increases the possibility of crevice corrosion.

Output from step 3.4.11:

- Passages of the pipe through protection walls are often filled with wet insulation, that contributes to forming crevices.



Figure 3.4: Picture of corrosion attack underneath insulation of pipe from an offshore platform in the North Sea.

3.4.12 Impurities

The last step in Figure 3.2 for assessing the possibility of crevice corrosion is the presence of impurities. Impurities in this context are all external objects that are not supposed to be present in contact with the pipe. Examples of impurities include painting remnants, cement, bird droppings, weld spatter and the like. Cavities can form at the contact boundary of the impurities. If the surface of the pipe is not clean because of impurities, there is an increased possibility of crevice corrosion.

Output from step 3.4.12:

- Impurities can form crevices against the pipe.

3.5 Model output

The two flowcharts together evaluate if there is a possibility of pitting and crevice corrosion. If the pipe is washed with saltwater the output from steps 3.4.1–3.4.3 will not matter, because the chlorides would certainly be present and the possibility would be there. This is independent of the environment and any protection from it, and there is a possibility of localised corrosion. The pipe is evaluated further in the coating step. Temperature follows and if there is low possibility of corrosion from the five first steps, then any reported corrosion is evaluated next in section 3.4.6. The possibility of crevice corrosion is evaluated in sections 3.4.7–3.4.12.

Outputs from steps 3.4.1–3.4.3:

- Location, walls and roof together determines if there is a possibility of localised corrosion based on if there is chloride present or not.

Outputs from steps 3.4.4–3.4.5:

- Coating and temperature determines if there is a possibility of localised corrosion, based on different parameters.

Output from step 3.4.6:

- Any reported corrosion determines if there is a possibility of localised corrosion for low possibility pipes, based on observations of corrosion.

Outputs from steps 3.4.7–3.4.12:

- Tags, tape, clamps, support, insulation and impurities determines if there is an increased possibility of crevice corrosion based on if there are crevices present or not.

If the result of the outputs is that there is a possibility of localised corrosion, then the possibility of localised corrosion should be evaluated further as discussed in Chapter 4.

CHAPTER 4

Proposed Procedure for Assessing the Possibility of Pitting Corrosion of Stainless Steel Piping in Topsides

4.1 Introduction

This chapter presents a simple procedure for estimating quantitatively the possibility of pitting corrosion on AISI 316/316L subjected to corrosive attack by a sodium chloride solution. As an example, AISI 316L has been considered, but the same procedure can be used for pipings made of other types of austenitic stainless steels. In this chapter crevice corrosion has not been considered due to the paucity of time. The procedure can be used in case a pipe is found to be susceptible to pitting corrosion based on the flowchart presented in Chapter 3.

Section 4.2 presents the procedure as a flowchart, which shows an overview on how to quantitatively assess the possibility of pitting corrosion. Section 4.3 gives explanations for the different steps in the procedure and their assumptions and limitations. The output from using the procedure is presented as a graph showing the possibility of pitting corrosion versus the concentrations of chloride solutions. Section 4.4 shows an example of calculations that can be done by using the procedure.

4.2 Overview of the Procedure

Figure 4.1 presents a flowchart that gives an overview of the procedure that can be applied to quantitatively determine the possibility of pitting corrosion. The number in each step in the flowchart refers to sections where explanations for the steps are presented.

4.2.1 Flowchart

Figure 4.1 is a flowchart that presents the four steps of the procedure. First, the process parameter, temperature, is acquired and is used to find the solubility of sodium chloride (NaCl) in the solution. Second, the solubility data is used to find the pitting potential E_{pit} . Finally, the E_{pit} is compared to the surrounding environment, indicating if there is a possibility of pitting corrosion.

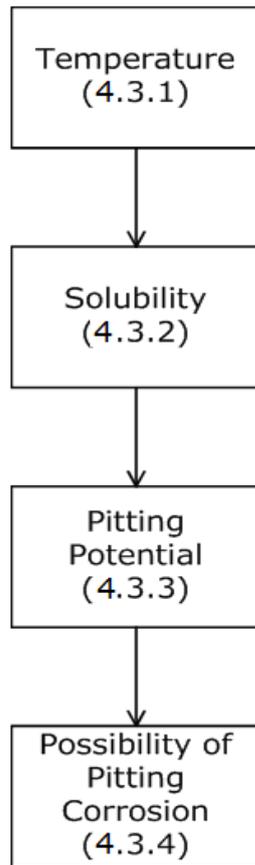


Figure 4.1: Flowchart showing overview of the procedure.

4.3 Explanation of the Flowchart Presented

This section presents the explanations for the steps drawn in the flowchart in Figure 4.1. The number in each step in the flowchart refers to the different sections. The output of each step is a value, which can be used in the next step, resulting in possibility of pitting corrosion in the end. The procedure consists of the following four steps.

1. Determination of surface temperature of the piping.
2. Determination of the solubility of NaCl at the surface temperature.
3. Determination of the pitting potential, E_{pit} , at the particular chloride concentration.
4. Determination of possibility of pitting corrosion using the value of the pitting potential, E_{pit} .

4.3.1 Determination of the Surface Temperature of the Piping

Determination of the surface temperature is the first step in the procedure shown in Figure 4.1. The temperature on the external surface of the pipe is a resultant value of the outdoor temperature and of the media in the pipe. The offshore atmospheric temperature in the North Sea normally ranges between 0 °C and 20 °C, for example, in the last 12 months the oil

platform Gullfaks C, experienced a temperature range of $T_{\min} = -0.3 \text{ }^{\circ}\text{C}$ and $T_{\max} = 19.0 \text{ }^{\circ}\text{C}$ [63].

The temperature of the media in the pipe is acquired from process data and is assumed to be between $0\text{--}100 \text{ }^{\circ}\text{C}$ for applications of 316L stainless steel pipe, depending on its use.

In this procedure, the external temperature on the pipe surface is assumed to be equal to the temperature of the media in the pipe, since it is probably the most influencing temperature and normally used in RBI.

4.3.2 Determination of the Solubility of NaCl at the Surface Temperature

The second step in the procedure is to determine the solubility of NaCl in water at the estimated surface temperature. This can be calculated using Equation (4.1). The equation is based on the work done by Langer and Offermann[64]. This equation is plotted in Figure 4.2 to show the “true” solubility curve. This was named “true”, because it was drawn with the assumption that it is independent of the quality of NaCl used, within reasonable limits. The curve is lower than normal solubility curves given for an exact NaCl quality and the reader is referred to Langer and Offermann[64] for a review of more solubility curves.

$$\xi_S^* = \frac{35.335 - 0.22947 \cdot \vartheta}{1 - 0.0069059 \cdot \vartheta} \quad (4.1)$$

The mass ratio of pure salt in a saturated solution, ξ_S^* , is designated g NaCl / 100 g H₂O. The temperature, ϑ , is designated $^{\circ}\text{C}$. In the original reference[64] Equation (4.1) has been plotted for temperatures between $20 \text{ }^{\circ}\text{C}$ and $80 \text{ }^{\circ}\text{C}$, but it is assumed that the plot continues for values that are both higher and lower on the same curve, so in Figure 4.2, the solubility as a function of temperature is extended from $20 \text{ }^{\circ}\text{C}$ down to $0 \text{ }^{\circ}\text{C}$ and from $80 \text{ }^{\circ}\text{C}$ up to $100 \text{ }^{\circ}\text{C}$. This seems to be a reasonable assumption, when compared to a previous plot of solubility drawn in the range 0 to $100 \text{ }^{\circ}\text{C}$ [65].

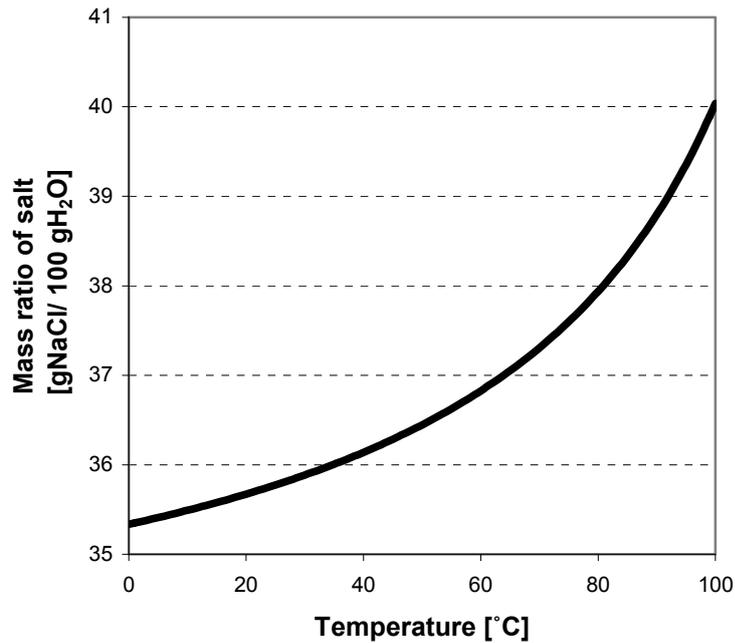


Figure 4.2: “True” solubility curve, showing mass ratio of NaCl against temperature based on Equation (4.1) from [64].

It must be noted that the use of Equation (4.1) introduces certain errors in the calculation. These errors are due to the following reasons.

- It does not represent the real environment under offshore conditions. There are other species present offshore that affects the solubility and the precipitation of the different species, thus changing the solution composition. The concentration of chlorides on the 316L pipe offshore is dependent on the conditions on the installation and the protection against the environment by its location. The solution on the pipe can be from a diluted solution to a supersaturated brine of chloride. The equation gives the value at saturated condition. Thus it is a very conservative estimate of the actual condition.
- An error in the determination of the surface temperature can result in errors in the value of solubility of NaCl [64].

The calculated solubility of NaCl in water is in the next section used to determine the pitting potential.

4.3.3 Determination of the Pitting Potential, E_{pit} , at the Particular Chloride Concentration

The solubility of NaCl found from Figure 4.2 has to be converted to concentration of chloride before it can be used further. This is done by multiplying the solubility value by 10 to convert

it to g/L and then dividing it by the molar mass of NaCl, which is 58.5 g/mol. This gives the molar concentration of chloride, calculated using Equation (4.2).

$$c_{Cl^-} [mol / L] = \frac{Solubility [g / L]}{M_{NaCl} [g / mol]} \quad (4.2)$$

Using the value of chloride concentration, the pitting potential can be read from a plot of the pitting potential as a function of chloride concentration for AISI 316L. An example of this kind of plot is Figure 4.3, which has been developed by Pohjanne et al.[8]. The authors measured the E_{pit} as a function of chloride concentration under evaporative conditions. The equivalent to AISI 316L in the figure is the curve to the right, which is labelled 1.4432. The plot is for no sulphate and a temperature of 22 °C. Seawater actually contains sulphate, but the concentration is too low to be significant, and its concentration in seawater is much lower than the concentration of chloride and therefore has no effect on E_{pit} . As can be seen from the graph, the pitting potential value decreases with the increase in the value of chloride concentration.

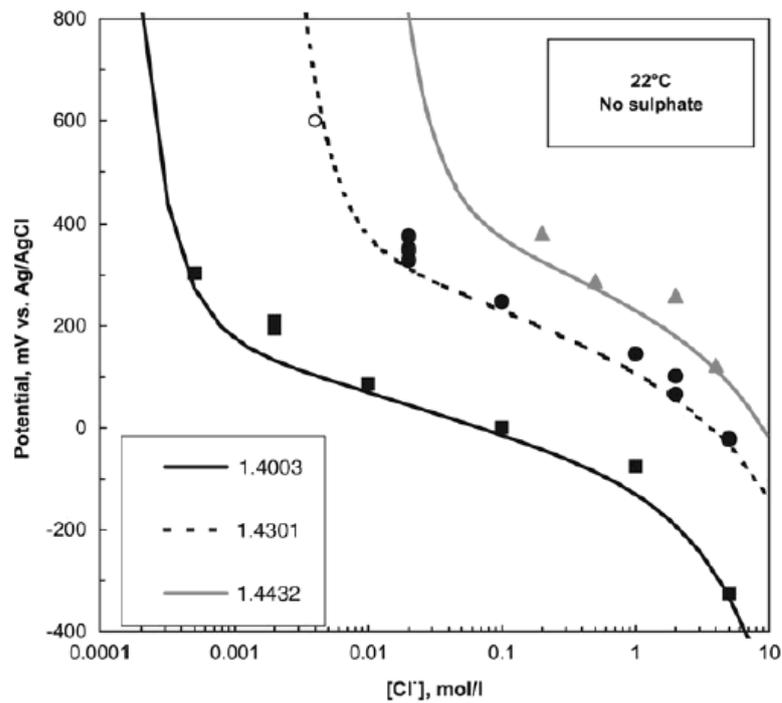


Figure 4.3: Pitting potential as function of chloride concentration at 22 °C from [8]. AISI 316L is equivalent to the curve for 1.4432.

To find the shape of the curve in Figure 4.3, the authors used Equation (4.3). In Equation (4.3) the pitting potential is calculated based on the concentration of chloride, $[Cl^-]$, and the parameters A , k , D , B , n and m . These parameters may be dependent on temperature and the concentration of sulphate[8].

$$E_{pit} = A - k \cdot \log([\text{Cl}^-]) + \frac{D}{([\text{Cl}^-])^n} - B \cdot ([\text{Cl}^-])^m \quad (4.3)$$

For the case of 316L (1.4432) the curve in Figure 4.3 was fitted with only four points, which is not enough to determine the shape of the curve for such a wide range of chloride concentration. Other experiments for different stainless steels with more data points show a similar curve, so it may be likely that this equation can be applied for 316L as well[6-8]. The curve plotted in Figure 4.4 is based on the four data points of the curve for 316L shown in Figure 4.3 using a simpler equation given in Equation (4.4).

$$E_{pit} = A - k \cdot \log[\text{Cl}^-] \quad (4.4)$$

The curve is fitted by Equation (4.4)[8]. Equation (4.5) is found by curve fitting for the plot in Figure 4.4 and it is this equation that is used for further calculations.

$$E_{pit} = -110.06 \cdot \ln[\text{Cl}^-] + 218.99 \quad (4.5)$$

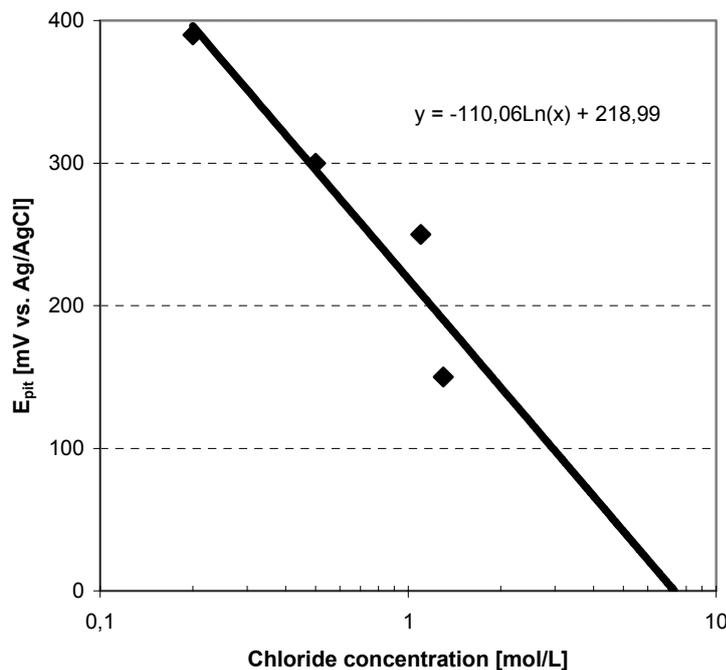


Figure 4.4: The pitting potential as function of the chloride concentration based on the points from the graph in Figure 4.3. The temperature is 22 °C.

It is important to note that the plot in Figure 4.4 is for E_{pit} as a function of temperature at 22 °C. The E_{pit} varies with changes in temperature, so it would be preferable to have several plots of different temperatures between 0 and 100 °C. As discussed earlier, for diluted solutions the value of E_{pit} is dependent upon the value of temperature, but for concentrated

solutions the values of E_{pit} is not significantly dependent upon the temperature[7]. Therefore the plot shown in Figure 4.4 can be considered valid for the procedure shown in this chapter.

4.3.4 Determination of the Possibility of Pitting Corrosion

After E_{pit} has been determined from Figure 4.4, the next step is to compare it to the corrosion potential of the material, E_{corr} . This is done to decide if E_{pit} is sufficiently higher than E_{corr} so that stable pitting corrosion is prevented from occurring. The corrosion potential has to be directly measured on the surface of the pipe, which is not possible to do for all pipes and all locations. This is a very comprehensive task and instead the E_{pit} value is compared to the oxidising capacity of the environment. Table 4.1 shows the potential ranges and corresponding oxidising capacity of the environment.

Table 4.1: Oxidising capacity for different potential ranges from[8].

Potential Range	Oxidising capacity
-300...0 mV	Very low, i.e. oxygen removed
-150...150 mV	Low, i.e. weaker oxidisers than dissolved oxygen present
0...300 mV	Normal, i.e. only dissolved oxygen present
200...550 mV	High, i.e. hydrogen peroxide, dithionite, chlorite present
550...900 mV	Extremely high, i.e. chlorine, chlorine dioxide, chlorite present

The offshore environment is assumed to have normal oxidising capacity, with a potential range between 0 and 300 mV as seen from the table. If the pitting potential is observed to be in this region or lower, there is a possibility of pitting corrosion. How high the possibility can be is discussed in the next section.

If the oxidising capacity used from Table 4.1 is normal, then Table 4.2 can be used to give a quantitative value on the possibility of pitting corrosion, as an integer between 0 and 100 on a linear scale.

Table 4.2 : The possibility of pitting corrosion due to the oxidising capacity of the environment and the pitting potential from[8]. Value of risk is between 0 and 100.

Oxidising capacity	Value 100	Value 100...0	Value 0
Very low	$E_{pit} < -300$ mV	-300 mV $< E_{pit} < 0$ mV	$E_{pit} > 0$ mV
Low	$E_{pit} < -150$ mV	-150 mV $< E_{pit} < 150$ mV	$E_{pit} > 150$ mV
Normal	$E_{pit} < 0$ mV	0 mV $< E_{pit} < 300$ mV	$E_{pit} > 300$ mV
High	$E_{pit} < 200$ mV	200 mV $< E_{pit} < 550$ mV	$E_{pit} > 550$ mV
Extremely high	$E_{pit} < 500$ mV	500 mV $< E_{pit} < 900$ mV	$E_{pit} > 900$ mV

In Figure 4.5, the possibility of pitting corrosion against E_{pit} is plotted as a linear graph between 0 and 300 mV, for the normal oxidising capacity range.

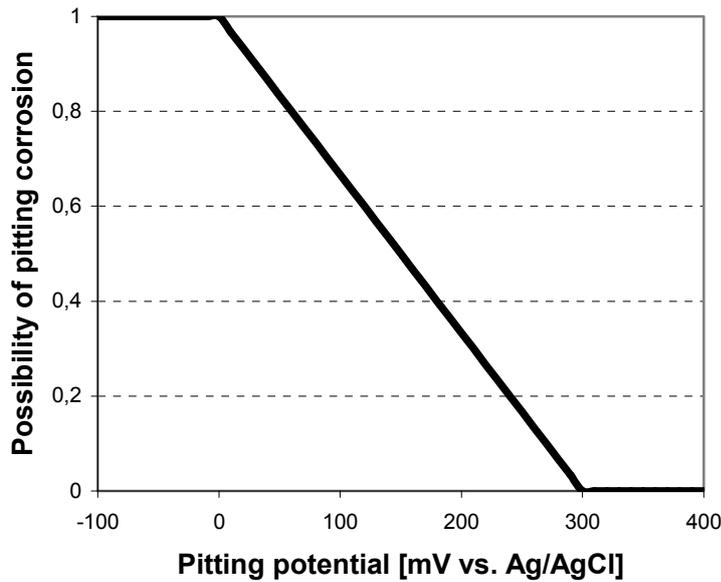


Figure 4.5: The possibility of pitting corrosion as a function of the pitting potential based on the normal range in Table 4.2.

From Figure 4.5 the possibility of pitting corrosion can be determined if E_{pit} is known, or the possibility of pitting corrosion can be found for the normal oxidising capacity of the environment by using Equation (4.6). The potential range is 300 mV for normal oxidising capacity. It is important to note that this equation is only applicable for normal oxidising capacity environment and has to be modified if other oxidising capacities of the environment are to be evaluated.

$$\text{Possibility of pitting} = 100 \cdot \left(1 - \frac{E_{pit}}{300}\right) \quad (4.6)$$

To be able to evaluate the possibility of pitting, a possibility value is calculated which can then be compared with those given in Table 4.3. This gives a qualitative measure on the possibility of pitting corrosion. In Table 4.3, the number intervals are defined as pitting corrosion risks. This expression is not used in this work, as risk in RBI is a combination of probability of failure and consequence of failure. Probability of failure considers the growth of pits and this is not considered here, when assessing the possibility of pitting corrosion. Consequence of failure is not considered at all in this study. This chapter is focused on the possibility of pitting corrosion, so Table 4.3 is used as a measure of possibility of pitting corrosion and not risk.

Table 4.3: Determining the possibility of pitting corrosion from [8]. Pitting corrosion risk is presented as possibility of pitting corrosion in the model used in this chapter.

Numerical value	Pitting corrosion risk
0	Insignificant
1...29	Minor
30...69	Moderate
70...99	High
100	Very high

Figure 4.6 shows a plot of possibility of pitting corrosion against temperature for a saturated chloride solution. It is seen from the graph that for saturated solution the possibility of pitting corrosion is very high from about 0.93 at 0 °C to above 0.97 at 100 °C.

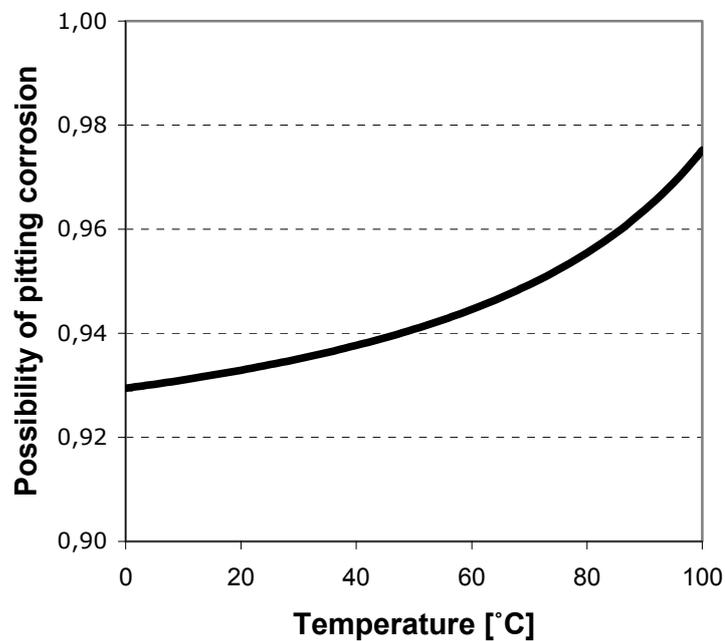


Figure 4.6: The possibility of pitting corrosion as a function of temperature for saturated solution of chloride.

Figure 4.7 shows the possibility of pitting corrosion as a function of the chloride concentration. The plot shows that the possibility of corrosion decreases significantly with the fall in concentration. The red portion of the curve in the plot is based on the values from Figure 4.6. This part is for saturated solutions at different temperatures.

The concentration of chloride in seawater is approximately 24 g/ (Table 2.3), assuming it to be in the form of sodium chloride, the concentration of sodium chloride may be taken as 40 g/L (0.68 mol/L). At that concentration level, according to Equation (4.5), the value of E_{pit} is 261. For a E_{pit} value of 261, Equation (4.6) gives the possibility of pitting corrosion to be 13. This corresponds to a minor possibility of pitting corrosion. While there is a minor possibility

of corrosion, it does not imply that the corrosion may not take place. The possibility of corrosion would be insignificant for salt concentrations less than 25 g/L. Seawater at such low concentrations is therefore not considered as dangerous for the possibility of pitting corrosion, but the actual concentration varies due to conditions on the installation. Thus washing the pipes with rain water or fresh water would significantly reduce the possibility of corrosion.

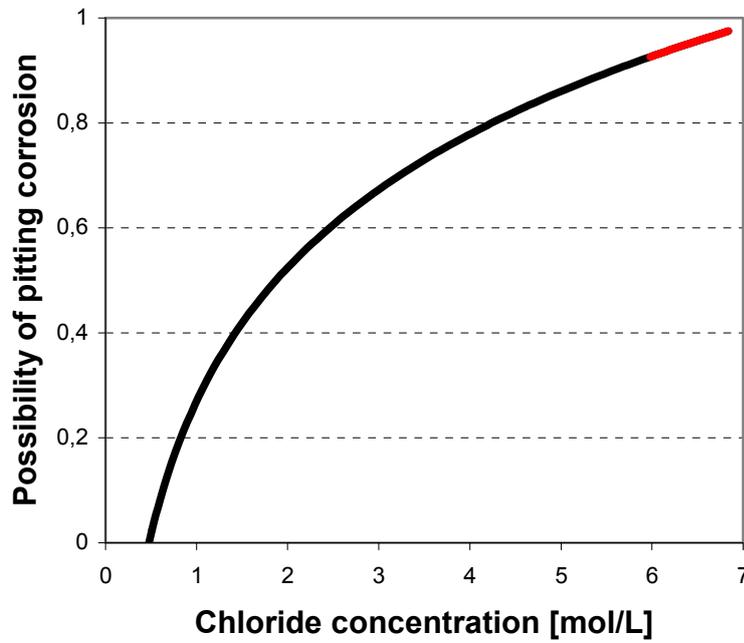


Figure 4.7: Possibility of pitting corrosion as a function of chloride concentration from diluted to concentrated solutions. The red part of the curve uses values from Figure 4.6.

4.4 Example Calculation

This section presents an example of the calculation of the possibility of pitting corrosion using the procedure explained above.

Step 1: Assume that the surface temperature of the pipe is 60 °C.

Step 2: Based on Equation (4.1), at 60 °C the solubility of NaCl in water is 36.8 g NaCl/100g H₂O

Step 3: From Equation (4.2) the chloride concentration is found to be 6.29 mol/L.

Step 3: From Equation (4.5) at 6.29 mol/L concentration, the value of E_{pit} is calculated to be 17 mV.

Step 4: Using Equation (4.6), for E_{pit} value of 17 mV, the possibility of pitting corrosion is 94 %, which according to Table 4.3 corresponds to a high possibility of corrosion.

4.5 Discussion of Presented Procedure

The procedure presented in this chapter contains several assumptions and simplifications. These have been made in order to develop a simple model that can provide guidance to inspection engineers using the limited amount of data that is normally available in the industry. Some of the assumption and simplifications of the procedure that need to be reconsidered and possibly corrected are given in the following paragraphs.

In RBI the media in the pipe is assumed to be at the same temperature as that on the surface of the pipe and this was also followed here. In reality, the external temperature of the pipe surface is dependent on conditions on the installation and changes with the seasons. The air temperature has an effect and solar radiation may also heat the pipe surface up to a higher temperature than the media in the pipe. This installation is assumed to be placed in the North Sea, so the assumption that the temperature is like the media in the pipe is not so far off from what is true. The solar radiation is not very strong, so it is assumed to have little effect. The normal air temperature is low and will probably not increase the temperature on the surface, but this and the wind may lower it further. The use of surface temperature gives conservative results. Overall for concentrated solutions any temperature will give high possibility of corrosion.

As mentioned earlier, the solubility of NaCl in water is not directly comparable to the amount of chloride present on the pipe surface in a real offshore environment. It is normally seawater that reaches the pipe surface, even though evaporation and rainfall may change the composition of the solution. The solution on the surface can therefore vary between diluted solution and a supersaturated brine. There are also other components present that may affect the solubility.

The E_{pit} as a function of chloride concentration plot is valid only for a temperature of 22 °C, so graphs of different temperatures between 0–100 °C should be plotted to give a more accurate picture of how E_{pit} changes—both with temperature and chloride concentration—which are assumed to be the two most important effects on E_{pit} in this environment. This is just to demonstrate the procedure, so if this procedure is to be used then tests should be carried out for different chloride concentrations, for example, representing low, medium and high concentrations. These should be carried out on actual pipes that are located in the offshore environment to obtain more accurate values.

CHAPTER 5

Evaluation of the Structural Integrity of Stainless Steel Piping

5.1 Introduction

This chapter proposes two approaches for estimating the probability that the wall of a pipe is penetrated at time t due to pitting corrosion. The approaches are applicable when the flowcharts in Chapter 3 show that there is a possibility of localised corrosion and when there is a possibility of pitting corrosion based on the value of the E_{pit} as found from Chapter 4.

The estimate of the probability of failure depends on the design and the properties of the material, the coating, and the environmental condition on the external pipe surface. Pitting is the only form of corrosion considered in this approach, and other forms of corrosion that may contribute to the probability of failure are not evaluated. The parameters used when developing the probabilistic models have been explained in Chapters 2 and 3. If a material other than AISI 316/316L is used, the parameters and corrosion rates will change.

When estimating the probability of failure as a function of time, the steps in the flowchart given in Chapter 3 should be considered. Location, walls, and if there is a roof, will give an idea of how much the pipe surface is exposed to the aggressive environment and the concentration of chloride (see sections 3.4.1–3.4.3 for more information). The severity of pitting corrosion increases with increasing chloride concentration, and the location of the pipe is therefore important when assessing how severe the pitting corrosion damage may become. If only a part of the pipe is located in an aggressive environment and the rest is not, the corrosion rate will be different for these two parts. Pitting corrosion also increases with increasing temperature, as shown in section 2.4.1. The current approach deals with the simplified case where the chloride concentration and the temperature are kept constant for the whole length of pipe considered.

The next section presents a mathematical description of the variables that are used as a basis for these approaches. Section 5.3 shows Approach 1 for determining the probability of failure with respect to time. Section 5.4 presents Approach 2 for doing these calculations, while Section 5.5 discusses the proposed approaches.

5.2 Description of the Variables for the Two Approaches for Estimating the Probability of Failure as a Function of Time

This section presents a mathematical description of the different variables needed to develop the approaches for estimating the probability of failure as a function of time. Several assumptions are made as a basis for these different approaches. Due to limitations in the availability of relevant data, the proposed approaches are mainly a guideline that can be used to estimate the probability of failure, when relevant data does becomes available. The theory on statistics used in these approaches are found from Rausand and Høyland[66].

These approaches can be used to provide the input to decision-making related to the determination of inspection intervals. This is essential to ensure that pitting attacks on the pipes are detected and mitigated before the occurrence of pipe failure, which can lead to severe damage to health and safety of people and the environment. Cost and safety are the most important considerations for companies when planning inspections. If the probability of failure is known, inspections can be made at proper time intervals, and thus reduce cost without compromising safety.

The next section presents the mathematical description of the variables used in these approaches. Sections 5.3–5.4 explains how the different probability values are calculated for the two different approaches.

5.2.1 Mathematical Description of the Variables

In order to develop the structural reliability models, the variability of two factors need to be determined: (a) rate of degradation of the coating; and (b) rate of corrosion.

In this thesis the rate of degradation of the coating is based on the recommendation given by DNV-RP-G101[2]. According to the recommendation, the effectiveness of the coating is almost 100 % for the first period and thereafter it falls linearly. A commonly used degradation function is 100 % effectiveness for the first 5 years and a linear degradation to 0 % effectiveness after 15 years. It is represented by Figure 2.14 shown in section 2.4.9.

Determination of the rate of corrosion is a far more difficult task. It can normally be found from inspection data, but unfortunately scientific collection of data for corrosion growth in an offshore environment is generally not available. In this thesis, a detailed analysis has not been carried out to accurately determine the rate of corrosion. Based on industry experience, the rate of corrosion is estimated to be a normal distribution with the mean of 0.38 mm/year and standard deviation of 0.3. It is also assumed that the pits grow vertically through the cross-

sectional area of the pipe and the mean rate and standard deviation values do not change with time. In real life this is not the case, because the corrosion rate varies with time depending upon a number of factors and the pits grow in different directions. While, normal distribution is assumed here, it would be better to use the gamma distribution in order to arrive at a more realistic picture of the actual growth of pits. This distribution would account for the salt film formation that occurs in the pit after some time and mitigates further pit growth. The curve increases slowly in the beginning, then almost linearly and then rounds off after a while. This is similar to the mechanism for corrosion rate where some time is needed to stabilise the environment in the pit, after which the corrosion rate starts increasing until a salt film forms in the bottom of the pit protecting the pipe against further pitting corrosion, and thus lowers the corrosion rate. The lowering of the corrosion rate is not considered when using a normal distribution, which leads to underestimation of the time to perforation of the pipe, T_F . It is determined to be much lower than it actually is and thus is the cause for an unnecessary increase in the number of inspections. The problem with using gamma distribution is that it complicates the calculations tremendously, due to the need to determine an intractable inverted complete gamma function.

Equation (5.1) shows the calculation of the variance, where X and Y are random variables representing corrosion depths. In reality, the depth of a pit increases and is dependent on earlier growth and depth, which means that the mean and standard deviation changes with time, since the depth at any time depends on the depth of the pit at a previous time.

$$Var(X + Y) = Var(X) + Var(Y) + Cov(X, Y) \quad (5.1)$$

In this model, it is assumed that the pit depths are normally distributed and independent of each other, which implies that the last term, $Cov(X, Y) = 0$. This also implies that the standard deviation and mean corrosion depth both are assumed to be independent of previous corrosion depths.

In reality, the pit growth increases fast after initiation but is limited at a later stage by the formation of a salt film that protects the pit surface from further pitting attack.

Time of initiation is unknown, but it is assumed in the calculation of the corrosion rate that pitting corrosion initiates instantaneously after a defect in the coating occurs. The chloride concentration has to be sufficient to penetrate the oxide film to initiate the pitting corrosion on the surface. If the pipe is protected in some way, for example, by walls, it may take a longer time before the pitting corrosion initiates. In the aggressive offshore environment, it is assumed that this does not take a long time, as there are many sources of chloride due to conditions on the installation. The environment, and especially the washing of pipes with sea water, is assumed to eventually promote the development of the necessary aggressive solution on the surface for pitting corrosion.

As an illustrative example, the normal pipe wall thickness in the offshore environment is assumed to be 3.5 mm.

5.3 Approach 1

The time to failure T_F in this context, is the time from the pipe is installed and put into operation at time $t=0$, until the pipe wall is penetrated for the first time due to pitting corrosion. The time to failure is a random variable with a probability distribution. The distribution function is written as $F_{T_F}(t) = P(T_F \leq t)$ and can be interpreted as the probability that the first penetration occurs before time t . The distribution function is therefore sometimes called the failure probability at time t .

In this approach, it is assumed that the pipe has a coating that will prevent corrosion attacks during a certain period. The coating will, however, deteriorate and gradually lose its properties of corrosion prevention. Let T_1 denote the time from the pipe is put into operation at time $t=0$, until the first time the pipe is no longer fully protected by the coating. The time T_1 is a random variable with distribution function $F_{T_1}(t) = P(T_1 \leq t)$.

Following the deterministic model given in DNV-RP-G101, $F_{T_1}(t) = 0$ from $0 < t < 5$ years and $F_{T_1}(t) = 1$ above 15 years. In the time interval $5 < t < 15$ years, T_1 is assumed to have a linear probability density function $f_{T_1}(t)$ and a probability distribution $F_{T_1}(t)$. It is assumed to be a random variable $F_{T_1}(t) \in (0,1)$, where T_1 can be presented as $T_1 = 5 + \sqrt{100 \cdot F_{T_1}(t)}$.

When the coating no longer provides corrosion protection, the pipe material is directly exposed to the corrosive environment and pitting corrosion will commence. Let T_2 denote the time from the instant that the coating fails till the time when the first pit has penetrated the pipe wall. Time T_2 is a random variable with a distribution function $F_{T_2}(t) = P(T_2 \leq t)$.

When the first pit penetrates the pipe wall, leakage takes place and it is said that the pipe has failed. The rate of corrosion is assumed to be normally distributed with mean μ and standard deviation σ .

The time to pipe failure can be written as:

$$T_F = T_1 + T_2 \tag{5.2}$$

The concept of Equation (5.2) is illustrated in Figure 5.2 where the thickness d of the pipe wall is shown as a function of time.

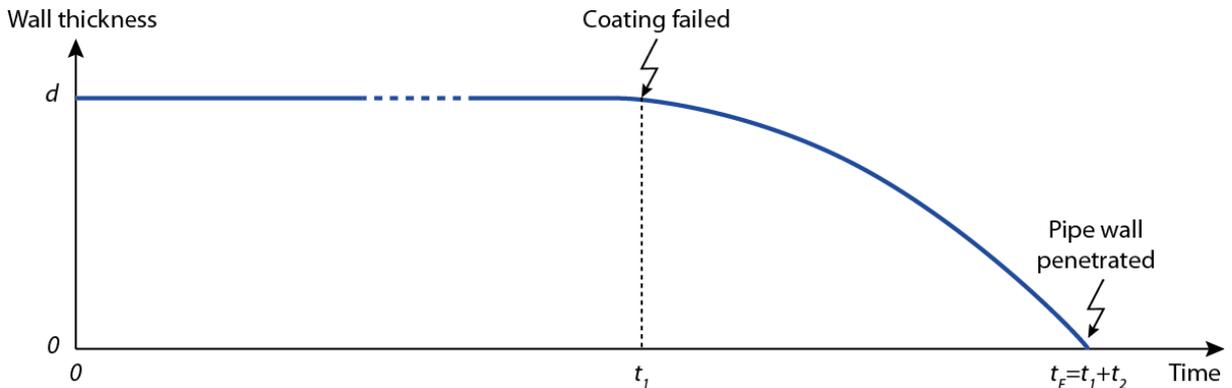


Figure 5.1: Graph representing thickness of pipe wall, d , as a function of time. The time when a hole in the coating occurs is T_1 and $T_1 + T_2$ is where a leakage in the pipe occurs due to perforation of the pipe wall thickness.

Normally there are many pits that can develop into a pit deep enough to penetrate the wall. T_{F_1} , T_{F_2} , T_{F_3} and so on are the time elapsed before Pit 1, Pit 2, Pit 3, and so on penetrate the wall, respectively. Failure occurs when the first pit penetrates the wall at time T_F . This can be presented as $T_F = \min\{T_{F_1}, T_{F_2}, T_{F_3}\}$, which means that the time of failure is when the smallest value becomes T_F .

The probability of failure calculations were done using the Monte Carlo simulation technique in which an i^{th} value was randomly selected from the distribution functions T_1 and T_2 and then an i^{th} output value of $T_F = T_1 + T_2$ was calculated. These steps were repeated a number of times. The set of output values gives the distribution function of the T_F .

Figure 5.2 shows the distribution function $F_{T_F}(t)$ and the probability density function $f_{T_F}(t)$ of T_F . The $f_{T_F}(t)$ is shown as a function of time t in years, which depends on both the coating degradation and the consequent pitting attack, and shows the density of failures that are probable at a point in time t . It shows how many pipes that are assumed to fail at one certain time depending on the number of pipes present initially.

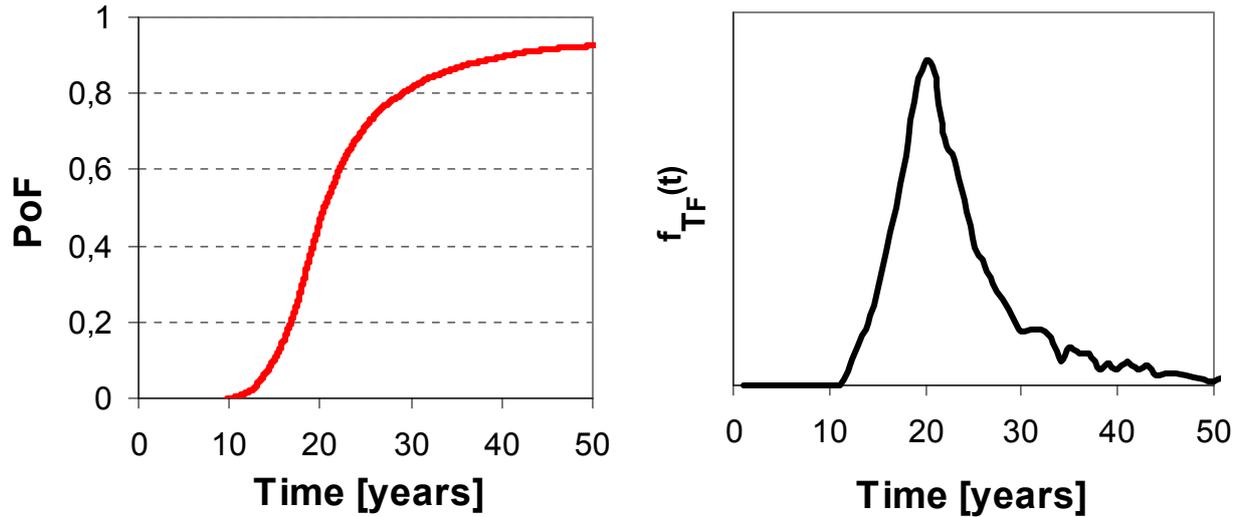


Figure 5.2: The distribution function, $F_{T_F}(t)$ is shown to the left, while the probability density function, $f_{T_F}(t)$ is shown to the right, both as function of time in years.

Equation (5.3) shows the relationship between $f_{T_F}(t)$ and $F_{T_F}(t)$.

$$f_{T_F}(t) = \frac{d}{dt} \cdot F_{T_F}(t) \quad (5.3)$$

The probability density function $f_{T_F}(t)$ is the derivative of the distribution function $F_{T_F}(t)$. The probability density function can be more easily explained by commenting on the shape of the curve. It is assumed that the coating remains intact for five years, so $f_{T_F}(t) = 0$, since no pipes fail during this time. The $f_{T_F}(t)$ increases between 5–15 years, due to increased degradation of the coating and the pit depths grows larger with time due to pitting corrosion. It is more probable for perforation of the pipe to occur if the pipe is exposed longer to the environment. After 15 years the pipes are no longer protected from the environment. Several pit depths becomes large enough to cause perforation of the pipe wall thickness, which means that most pipes will fail at the peak in the curve, which here is after approximately 20 years. The exact year that most pipes fail depends on time of initiation, corrosion rate and pipe wall thickness. After this time period, the rest of the pipes that are still intact will eventually experience pipe failure. The decrease in the curve is due to the fact that fewer pipes remain that have not already failed. When $f_{T_F}(t) = 0$ again, it indicates that all pipes have failed.

5.4 Approach 2

5.4.1 Probability of Coating Failure (PoCF)

The probability of coating failure depends on the preservation of the coating. The probability is based on the time it takes from when the pipe is installed with an intact coating system, until the coating experiences one or several defects. Defects make the pipe surface vulnerable to attack from the aggressive offshore environment. A defect can arise under installation of the pipe, under application, or with time, due to degradation of the coating. The coating surface may also experience a hit. This can be from equipment hitting the pipe, for example, during construction. The coating is assumed to be intact when applied, under installation, and that no hits are experienced, so only degradation rate is considered when determining the probability of coating failure in this model.

It is assumed that the coating is applied according to the DNV-RP-G101[2], where more about this is given in section 2.4.9. The probability of coating failure is found by using this deterministic model, and a sketch of it is shown in Figure 2.14. The coating is considered intact for the first five years after application. This means that the probability of coating failure is zero for this period of time. Between 5–15 years there is coating degradation, which increases the probability of coating failure by 0.1 each year, so after 15 years in service there is zero protection. This means that after 15 years, the probability of coating failure is 1, unless maintenance is carried out to increase the preservation of the coating. If there is no information about the coating, the probability of coating failure should simply be set to 1. This calculation of the probability of coating failure is only applicable for coatings that follow the DNV-RP-G101 and should therefore be modified if this is not valid.

5.4.2 Probability of Pitting Initiation (PoPI)

The Probability of Pitting Initiation (PoPI) depends upon the external corrosive environment. This has been discussed in detail in Chapter 4. The previous chapter presents a method to calculate the possibility of pitting corrosion. Since the possibility value is always greater than the probability value, hence, as a conservative approach the Probability of Pitting Initiation is assumed to be the possibility of pitting corrosion as discussed in Chapter 5. PoPI has been considered to account for the concentration of the chloride in water. At low concentration, the probability of destruction of protective layer is low, consequently the probability of a corrosion pit to form is also low. Without this initiation process the pit growth cannot take place.

5.4.3 Probability of Pipe Failure (PoPF)

The Probability of Pipe Failure (PoPF) is determined using the concepts of structural reliability analysis. In structural reliability analysis, first the limit state function is calculated using Equation (5.4)

$$z = d_s - d_p \quad (5.4)$$

Where,

d_s is the maximum allowed corrosion depth, and in this case equal to the thickness of the wall.

d_p is the predicted corrosion depth.

As the predicted depth of the corrosion pit increases with time, a stage is reached when the complete wall gets perforated and the failure event (Fi) occurs. This happens when the predicted corrosion depth is more than the allowed corrosion depth ($d_p > d_s$). The predicted depth of corrosion can be found using the rate of corrosion and the allowed corrosion is the thickness of the wall.

The calculations can be carried out using Monte Carlo simulation technique. In this technique the i^{th} value of the corrosion rate is selected from the probability density function of the corrosion rate. This value is used to calculate the i^{th} value of predicted depth of corrosion at time t (d_{pt}). If in the i^{th} Monte Carlo simulation, the predicted corrosion depth (d_{pt}) is more than the maximum allowed corrosion depth (d_s), then failure occurs ($Fi = 1$); otherwise the operation is safe ($Fi = 0$). The calculations are carried out many times. The number of failure events divided by the number of Monte Carlo simulations gives the approximate probability of failure.

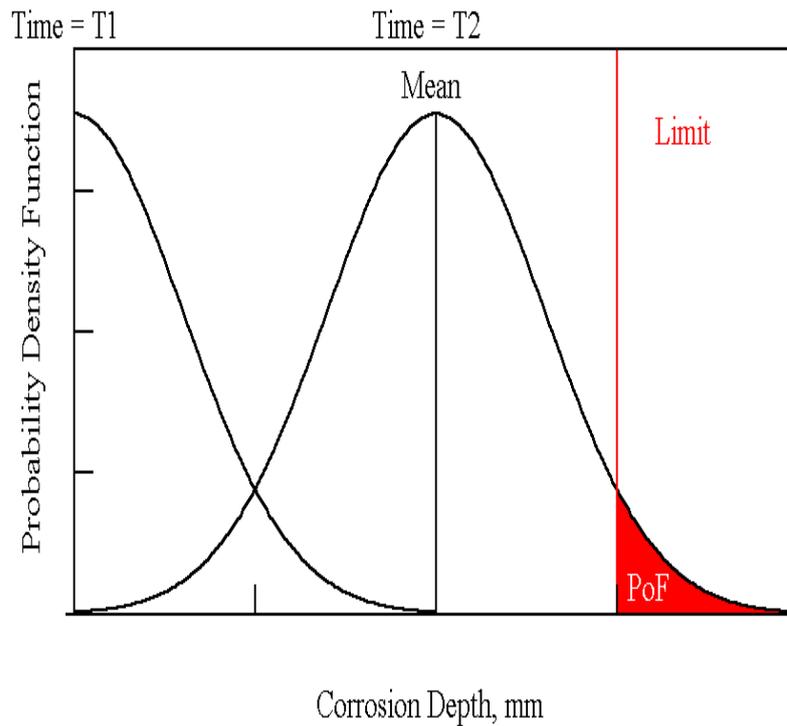


Figure 5. 3: Probability density function plotted against the corrosion depth.

5.4.4 Probability of Failure

The total probability of failure with respect to time is the product of the three probabilities found in sections 5.4.1–5.4.3. Equation (5.5) shows the calculation of the probability of failure with respect to time.

$$Probability\ of\ failure = PoCF \cdot PoPI \cdot PoPF \quad (5.5)$$

5.4.5 Probability of Failure with Respect to Time

A plot of probability of failure (PoF) as a function of time in years for a pipe with and without coating is shown in Figure 5.5. The blue curve is for a pipe without coating, where the probability of coating failure is 1. The black curve is for a pipe with coating, with zero probability of coating failure for the first five years and degradation of the coating from 5–15 years. The probability of coating failure is 1 when the coating exceeds 15 years, as the protection from the coating is lost. The Probability of Pitting Initiation is taken as 1, as that is the most common case.

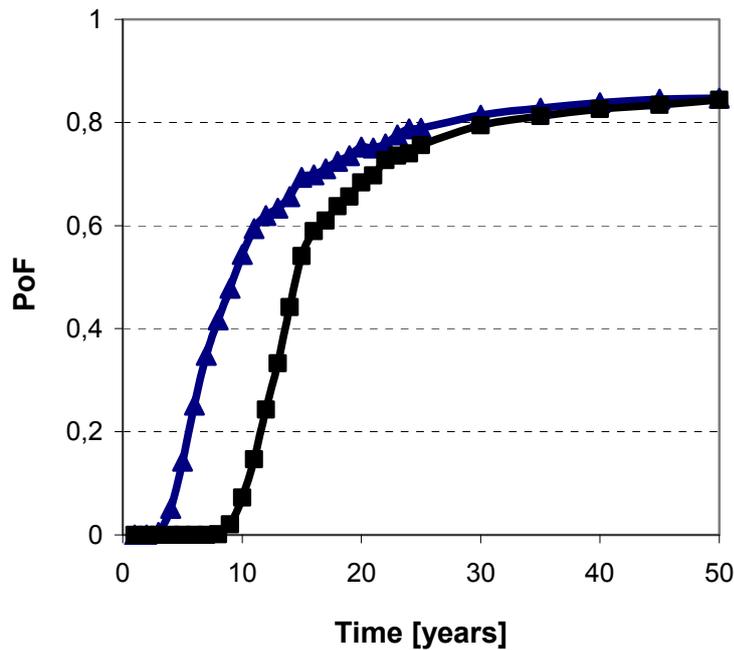


Figure 5.4: Probability of failure with respect to time in years. Black curve is for a pipe with coating, while blue is without coating.

It can be seen from the black curve that the coating has an effect on the probability of failure of a pipe as long as it is intact, that is, for the first five years. Degradation of the coating starts after the fifth year, but there is no probability of failure before the eighth year. For the red curve, which is without coating, there is already a probability of failure as early as the second year.

5.5 Discussion of Presented Approaches

This chapter presents two different approaches for estimating probability of failure as function of time. The models only account for pitting corrosion, so other types of corrosion or damage mechanisms that can contribute to perforation of the pipe are not considered.

The models only account for corrosion on the the external surface of the pipe, so if corrosion from the inside contributes to the damage, failure can happen earlier than that determined in this study.

The use of coating decreases the probability of failure for the model calculations. The coating is assumed to remain intact for the first five years. In reality, the coating is not completely dense and all organic coatings are permeable to oxygen and water. Most coatings have defects which might act as initiation sites for pitting corrosion. Even so, it is an important measure, as shown in Figure 5.4, to reduce the attack of pitting corrosion on AISI 316L pipes.

The models take into account the most important parameters in order to assess the probability of failure of a pipe, which are temperature, chloride content based on location of the pipe, and protection by the coating. The chloride content decides the probability of initiation and the temperature decides the corrosion rate of the pitting attack, but both are assumed constant for this calculation. It is assumed that the temperature of the external surface is the same as that of the media in the pipe, as is normal in RBI.

The salt content is high, as it is assumed that the pipe is shielded from rainfall. This means that salt accumulates on the pipe. Therefore the Probability of Pitting Initiation is 1 in Approach 2 and can be considered to be 1 in Approach 1 also. The first approach is therefore limited as it does not take into account the variations in the chloride contents effect on pitting initiation.

If the salt film forms for some time and then disappears the corrosion rate is lowered for a period of time. This is not considered by either the normal distribution nor the gamma distribution. The initiation of pit growth may take longer than the instantaneous pit growth that is assumed in these models. This is dependent on the location of the pipe and the accumulation of chloride on the pipe. The development of a pit is dependent on the material alignment of grains, which depends on the production method of the material.

It is important to note that pits do not only grow vertically through the cross-sectional area of the pipe. The corrosion rate in these models is determined as an average rate, assuming linear growth. If the pit grows horizontally for some time, then the corrosion rate may be determined to be lower than actual due to no growth promoting penetration during this time.

The approaches for estimating the probability of failure was made for the purpose of providing an input to the choice of inspection intervals, when relevant data does become available in future.

CHAPTER 6

Conclusions

The aim of this study was to identify and evaluate the parameters that affect pitting and crevice corrosion in AISI 316/316L in an offshore environment. The information gained has been used to develop procedures that shall help to: (a) identify the topsides piping that may be prone to pitting and/or crevice corrosion; (b) develop a procedure to evaluate the maximum possibility of localised corrosion; and, (c) develop a procedure to evaluate the probability of failure of AISI 316/316L pipes that may be prone to corrosive attacks.

Based on the literature survey it may be concluded that there is still a need for better understanding of pitting and crevice corrosion of 316/316L under offshore conditions. There is also a need for development of better procedures and models to assess the probability of failure and rate of corrosion.

In this research work, flowcharts have been developed to identify offshore piping that may be prone to pitting and crevice corrosion. The procedure takes into account the location, quality of coating, pipe surface temperature, structure, insulation and presence of external objects for determining the possibility of localised corrosion.

In this work, a procedure for assessing the possibility of pitting corrosion in the offshore topside environment based on E_{pit} has also been developed. This procedure takes into account the surface temperature and solubility of sodium chloride. Based on the concentration of sodium chloride E_{pit} is calculated. The value of E_{pit} is then used to determine the possibility of pitting corrosion.

Finally, two procedures to predict the probability of failure of an offshore piping with respect to time have been developed. The procedures takes into consideration the quality of coating and the rate of pitting corrosion.

This study has shown that in order to be able to assess the possibility of pitting and crevice corrosion and probability of failure with respect to time due to pitting corrosion and coating degradation it is not enough to only consider temperature. It is shown that other parameters are probably as important as temperature. The conditions under which the recommendations of the Norsok M-001 and DNV-RP-G101 standards, about the use of AISI 316/316L, are valid should be carefully considered and adhered to.

CHAPTER 7

Suggestions for Further Work

While some headway has been made in the development of procedures for evaluating the possibility of crevice and pitting corrosion in AISI 316/316L and its possibility of failure, considerably more work needs to be done to develop more usable procedures. This chapter highlights some of the shortcomings of the research and gives recommendations for the future work.

The procedure developed for determining the possibility of pitting corrosion needs some improvements. The chloride content in the thin water film on a pipe surface does not have the same solubility of sodium chloride (NaCl) as pure water. The solubility depends upon the presence of other ions that needs to be accounted for. Additionally, the values of E_{pit} as a function of chloride concentration should be extended to temperatures other than 22 °C, to give a better picture of the E_{pit} at diluted solutions.

In this research only the pitting corrosion has been assessed, while in the offshore environment crevice corrosion is the more severe form of corrosion. Hence, it is important to develop procedures to evaluate the possibility of crevice corrosion and its effect on the probability of failure as a function of time for a pipe.

In this work, the mean and standard deviation of the corrosion rate has been assumed. There is a need to find a better method of estimating the corrosion rate and how it develops with time.

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