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Writer: Hossam El-Mogi (Writer's signature)
Faculty supervisor: Professor Daniel Karunakaran (UiS)	
External supervisor(s):	
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Abstract

Pipelines are an essential part of the oil and gas industry as they are the main means of transportation. As the offshore technology advances, subsea pipelines are being operated in more demanding environments. For the pipelines to operate efficiently, they have to be carefully designed. One of the main threats to the integrity of the pipeline is corrosion, which has caused many failures. Corrosion in subsea pipelines has different forms and understanding their mechanisms is an important step in inhibiting them and decreasing their rate of occurrence. As corrosion is unavoidable, it is beneficial to be able to calculate the corrosion rate and the corrosion allowance. By obtaining the results of the corrosion rate it becomes clearer which type of group of steel to consider for the fabrication of the pipeline.

Different types of steels are used in the manufacturing of subsea pipelines. A part of this report focuses on explain the numbering systems and classification of the steels as they are divided into groups and subgroups. The chemical composition is the main character that separates them from each other, which is why the steel types perform differently when introduced to different corrosive environments. Within the commercial steel types, carbon steel is an attractive option to use for subsea pipelines. However, it is not always possible to use it due to the highly corrosive nature of the reservoirs. In that case corrosion resistant alloys are considered, as they posses higher corrosion resistance than conventional steel.

One of the critical stages of pipeline design is the material selection process. Three projects with different parameters are presented as case studies. A simplified process of identifying wether carbon steel and certain corrosion resistant alloys are qualified for use in those projects is demonstrated. The process is based on corrosion rate calculations and continues to compare the different mechanical and corrosion resistance properties of corrosion resistant alloys.

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Chapter 1 Introduction

Today, pipelines are an indispensable part of the oil and gas industry. They are the veins and arteries through which the daily supply of energy flows and they are essential to the standard of living and economy. It is estimated that there is a total of about 3,500,000 km of pipelines around the world (Hopkins, P. 2007), which transfer different kinds of fluids. They are conduits for water, sewage, oil, gas, and more. That is why they are everywhere, even if they are not always visible, as they are built in trenches, underground, and even under the sea. They connect countries and continents together over thousands of kilometres, whether onshore or offshore (subsea) pipelines. The latter are mainly intended for transfer of hydrocarbons and will be the main focus of this paper.

When operating in harsh subsea environments, corrosion of pipelines becomes one of the main challenges. The pipe has to be protected against inner as well as outer corrosion. The properties of the fluid or hydrocarbon to be extracted have to be identified, as they play a great role in the type of internal corrosion to occur. Not all reservoir environments are the same. They are categorized into sweet, mildly sour, and sour environment. The sweet environment contains no hydrogen sulphide (H_2S). The mildly sour environments contain CO_2 and some amount of H_2S , while the sour environment contains a significant amount of H_2S . Those environments pose different types of corrosion mechanisms, which could lead to the failure of the pipe. This failure has many drastic consequences ranging from simple leakage to explosions that could claim lives. For that reason, some of the most important internal corrosion mechanisms will be presented.

After the nature of the reservoir environment has been identified, engineers go through a process of material selection of the pipeline. There are different design parameters to consider when designing a subsea pipeline, such as internal and outer diameter, wall thickness, weight, and material type. Material selection for hard pipes will be the main design parameter discussed in this paper and the method is based on calculating the corrosion rate and the corrosion allowance. From those calculations it can be decided if carbon steel can be used or if an alloy steel or a corrosion resistant alloy (CRA) has to be used. To be able to reach a sound decision, some parameters have to be known, such as the pH value of the product, the amount of CO_2 , the partial pressure of H_2S (pH_2S), the maximum operating temperature, and other several parameters.

When choosing the material type and specifications, the company and the manufacturer both have to follow certain international standards, such as the International Organization for Standardization (ISO) and Det Norske Veritas (DNV). Those standards are developed based on practical tests and years of experience in, but not limited to, the oil and gas industry. They are guidelines, which must be followed, to make sure that the pipeline material is fabricated and designed in a manner that would qualify it to withstand the harsh environments without failure.



Figure 1.1: Subsea pipelines (Oil States, n.d.)

1.1 Objective and scope

The main scope of the thesis is to conduct three case studies of real projects. The parameters of the well stream will be given and the goal is to reach a decision on which material type to use as pipelines for our projects. The decision is based on calculations, a material selection process, and using the different standards as references. The objective is to show the following:

- Classification of steels and how they are categorized.
- Introduce the different corrosion mechanisms and their effects on the different types of steels.

- To demonstrate how to calculate the corrosion rate of a pipeline.
- To demonstrate how to calculate the corrosion allowance of a pipeline.
- To identify the acceptance criteria for using carbon steel pipeline.
- To introduce alternative materials to carbon steel and evaluate their properties.

The main objective of the thesis is to demonstrate the material selection process considering the different corrosion mechanisms and other factors.

1.2 Background

The basic concept of pipelines to transfer fluids has been there for thousands of years. The use of pipelines could be traced as far back as the ancient Chinese and the ancient Egyptian civilization. The ancient Chinese used hollow bamboo sticks to transfer natural gas to their city. This was recorded transportation of hydrocarbons. The ancient Egyptians used copper pipes for water transportation. Many other civilizations have since relied on the same method for different kinds of pipes (Hopkins, P. 2007).

In the 18th century England used hollow pipes made out of wood as well as cast iron. Later, during the 19th century, pipes were made out of wood, iron, lead, and tin. In the beginning of the 1900s the largest pipe diameter was 400 mm and operated at a pressure of 2 bar (Hopkins, P. 2007).

It was not until the year 1942 that subsea pipelines were manufactured and installed. This project was called "PLUTO", which was short for Pipeline Under The Ocean. The purpose of the project was to connect England and France via the English Channel to supply fuel during World War 2 (O-lay.net, n.d.).

A decade later, the first commercial offshore pipeline was constructed in the Gulf of Mexico in 1954. The depth at which the pipeline was installed was a shallow depth of only 4 to 10 metres and was installed at a rate of 800 metres per day. In 1961 the fixed reel-laying barge was developed, while the first reel lay ship was built in 1975 (O-lay.net, n.d.).

Many technological advances occurred during the 20th century. Some examples are the materials of the pipes, the mechanical properties, the diameter sizes, increase in operating pressures, cathodic protection against corrosion, using pigs for internal inspection of the pipelines, subsea installation of pipelines, and many others.

Furthermore, the standards had begun to be written in this era as well (Hopkins, P. 2007)

In the present time, the oil and gas company “Shell” is setting the record with its new project “Stones” by installing the deepest gas pipeline at a depth of 3200 m below sea level in the Gulf of Mexico with design pressures reaching 15 kpsi (103 MPa) and temperature up to 265°F (129°C) (Offshore technology, n.d.).

Chapter 2 Steels and corrosion mechanisms

It is important to have a good overview of the different types of steels and their classifications, since it helps to better understand the main differences between them. The types of steels have different microstructures, compositions, mechanical and corrosion properties, and are used in different applications accordingly. The reason why many types exist is that the different applications require certain properties to withstand the environmental conditions and loads that the steel will be exposed to. When choosing the type of steel to be used in the desired application, these conditions must be taken into account. Also, cost plays a big role in the selection process. The common goal in any selection process is to reduce costs as much as practicable while choosing the type of steel that fits the purpose of the application.

2.1 Steel classification and numbering systems

2.1.1 AISI/SAE designation system

There are many types of steels and these types are further divided into grades. To distinguish between the types of alloy steels and carbon steels, the American Iron and Steel Institute (AISI) and the Society of Automotive Engineers (SAE) have established a coding system. The system comprises of four digits, where the first digit indicates the category or group of steels. The second digit indicates a major element in percentage, which would have an effect on the properties of the steel. The last two digits show the amount of carbon in the steel. If we take the last two digits and divide them by one hundred we will get the carbon concentration. Figure 2.1 illustrates this system. Stainless steels are indicated by three-digit number, which could start with 2, 3, 4, or 5 (Capudean, B. 2003).

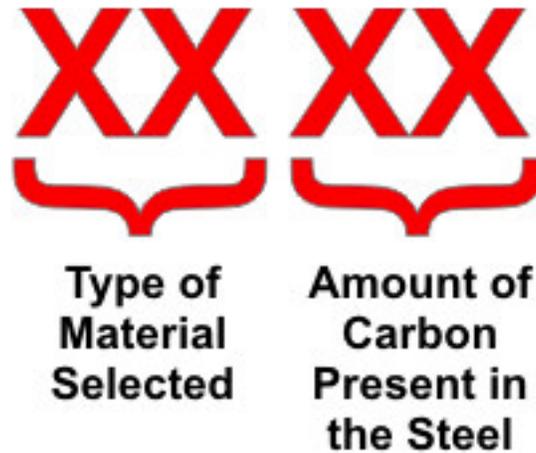


Figure 2.1: AISI/SAE designation system (AZO Materials, 2012)

Table 2.1 (AZO Materials, 2012) shows the groups of carbon steels and alloy steels.

Table 2.2-1: Classification of carbon and alloy steels (AZO Materials, 2012)

SAE designation	Type
1xxx	Carbon steels
2xxx	Nickel steels
3xxx	Nickel-chromium steels
4xxx	Molybdenum steels
5xxx	Chromium steels
6xxx	Chromium-vanadium steels
7xxx	Tungsten steels
8xxx	Nickel-chromium-vanadium steels
9xxx	Silicon-manganese steels

The carbon steel is then divided into grades to show the differences in their chemical compositions. Hence, carbon steel will always start with the number 1 and is followed by three digits to indicate the chemical composition and the designation will look as follows: 1xxx.

From the second group, which is Nickel steels, and all the way to the last group, those are all alloy steels.

To give a quick example, the designation 5130 indicates that we have chromium alloy steel with 1% of chromium and 0.3% of carbon.

Table 2.2 (AZO Materials, 2012) shows the main groups of carbon and alloy steels along with their subgroups.

Table 2-2.2: Material grades (AZO Materials, 2012)

AISI Steel	Specifications
Carbon Steel	10XX Plain carbon steel , Mn 1.00% max
	11XX Resulfurized free cutting
	12XX Resulfurized - Rephosphorized free cutting
	15XX Plain carbon steel, Mn 1.00-1.65%
Manganese Steel	13XX Mn 1.75%
Nickel Steel	23XX Ni 3.50%
	25XX Ni 5.00%
Nickel Chromium Steel	31XX Ni 1.25%, Cr 0.65-0.80%
	32XX Ni 1.75%, Cr 1.07%
	33XX Ni 3.50%, Cr 1.50-1.57%
	34XX Ni 3.00%, Cr 0.77%
Molybdenum Steel	40XX Mo 0.20-0.25%
	44XX Mo 0.40-0.52%
Chromium Molybdenum Steel	41XX Cr 0.50-0.95%, Mo 0.12-0.30%
Nickel Chromium Molybdenum Steel	43XX Ni 1.82%, Cr 0.50-0.80%, Mo 0.25%
	47XX Ni 1.05%, Cr 0.45%, Mo 0.20-0.35%
Nickel Molybdenum Steel	46XX Ni 0.85-1.82%, Mo 0.20-0.25%
	48XX Ni 3.50%, Mo 0.25%
Chromium Steel	50XX Cr 0.27-0.65%
	51XX Cr 0.80-1.05%
	50XXX Cr 0.50%, C 1.00% min
	51XXX Cr 1.02%, C 1.00% min
	52XXX Cr 1.45%, C 1.00% min
Chromium Vanadium Steel	61XX Cr 0.60-0.95%, V 0.10-0.15%
Tungsten Chromium Steel	72XX W 1.75%, Cr 0.75%
Nickel Chromium Molybdenum Steel	81XX Ni 0.30%, Cr 0.40%, Mo 0.12%
	86XX Ni 0.55%, Cr 0.50%, Mo 0.20%
	87XX Ni 0.55%, Cr 0.50%, Mo 0.25%
	88XX Ni 0.55% Cr 0.50% Mo 0.35%
Silicon Manganese Steel	92XX Si 1.40-2.00%, Mn 0.65-0.85% Cr 0.65%
Nickel Chromium Molybdenum Steel	93XX Ni 3.25%, Cr 1.20%, Mo 0.12%
	94XX Ni 0.45%, Cr 0.40%, Mo 0.12%
	97XX Ni 0.55%, Cr 0.20%, Mo 0.20%
	98XX Ni 1.00%, Cr 0.80%, Mo 0.25%

The steel grades have slightly different chemical compositions, which give the steels different mechanical properties. Having a wide range of steel grades to choose from makes the selection process more flexible and more cost efficient.

2.1.2 Unified Numbering System

There is another numbering system for metals and alloys called the unified numbering system (UNS) and it is the one used in ISO 15156-3 (2015). Other numbering systems such as the AISI have been used in this system to avoid confusion. For example plain carbon steel in the AISI system is 1080 and in the UNS system it becomes G10180. In the UNS system each metal is assigned a letter followed by five digits. In total there are nine designations for nine metals and alloys (MatWeb, n.d.)

Figure 2.2 shows an overview the UNS designation system.

- **Axxxxx** - Aluminum Alloys
- **Cxxxxx** - Copper Alloys, including Brass and Bronze
- **Fxxxxx** - Iron, including Ductile Irons and Cast Irons
- **Gxxxxx** - Carbon and Alloy Steels
- **Hxxxxx** - Steels - AISI H Steels
- **Jxxxxx** - Steels - Cast
- **Kxxxxx** - Steels, including Maraging, Stainless Steel, HSLA, Iron-Base Superalloys
- **Lxxxxx** - Low Melting Metals, including Lead and Tin Alloys, Babbit Alloys and Solder Alloys
- **M1xxxx** - Magnesium Alloys
- **Nxxxxx** - Nickel Alloys
- **Rxxxxx** - Refractory Alloys
 - **R03xxx**- Molybdenum Alloys
 - **R04xxx**- Niobium (Columbium) Alloys
 - **R05xxx**- Tantalum Alloys
 - **R3xxxx**- Cobalt Alloys
 - **R5xxxx**- Titanium Alloys
 - **R6xxxx**- Zirconium Alloys
- **Sxxxxx** - Stainless Steels, including Precipitation Hardening Stainless Steel and Iron-Based Superalloys
- **Txxxxx** - Tool Steels
- **Zxxxxx** - Zinc Alloys

Figure 2.2: UNS designation system (MatWeb, n.d)

2.2 Commercial steels

Now that the numbering systems of steels have been explained, the next step is to understand the differences between the types of steels in more detail.

There are three main groups of commercial steels and they are classified as plain carbon steel, low-alloy steel, and high alloy steel. Usually the carbon content in steels does not exceed 0.35%, but in there are steels with carbon content that ranges between 0.35% and 1.86% and in some cases might reach up to 2% (Capudean, B. 2003).

2.2.1 Plain carbon steel

Carbon steel is one of the most common types of steel used in many different industries such as construction industry, fabrication of pipelines, and many other applications. As carbon content increases in the steel, hardness also increases and hardenability is enhanced. But the problem with high content of carbon is that the steel becomes more brittle and the weldability decreases. In most cases, the steel will have to be welded together. For that reason the carbon content must be chosen according to the requirements of the application. There are several elements that could be added to carbon steel in order to improve certain mechanical or physical properties. Such elements could be manganese, phosphorus, sulphur, and silicon. These elements are called alloying elements. However, in plain carbon steels, the main characteristics and the weldability depend on the carbon content. The plain carbon steels are then further divided into low carbon steels, medium carbon steels, high carbon steels, and very high carbon steels (Capudean, B. 2003).

2.2.1.1 Low carbon steels

Also called mild steels, as carbon content could only reach up to maximum 0.3% while the manganese content could reach up to 0.4%. Machining and welding are relatively easy due to their high ductility. They are cheap and used more than the other types of carbon steel (Capudean, B. 2003).

2.2.1.2 Medium carbon steels

The carbon content in this grade ranges from 0.3% to 0.45% and manganese could be around 0.6%. It has increased hardness and less ductility compared to the low

carbon steel and this is due to the increased carbon content. This grade of steel is mostly used in the production of machine components, shafts, axles, gears, crankshafts, coupling and forgings and could also be used in rails and railway wheels (Capudean, B. 2003).

2.2.1.3 High carbon steels

High carbon steels have 0.45% to 0.75% carbon. Weldability decreases and requires preheating and post weld heat treatment. In some cases heating might be required during welding to obtain acceptable weld quality. The manganese content could range from 0.3% to 0.9%. Hardness is higher than the other grades but ductility decreases. High carbon steels could be used for springs, rope wires, hammers, screwdrivers, and wrenches (Capudean, B. 2003).

2.2.1.4 Very high carbon steels

The carbon content in this grade could reach up to 1.5% and welding also needs heating before, during, and after welding in order to maintain the mechanical properties of the steel. This grade of steel could be used for hard steel products, such as truck springs and metal cutting tools (Capudean, B. 2003).

2.2.2 Alloy steels

2.2.2.1 Low-alloy steels

Alloying elements are added to the base material to create low-alloy steels. The alloying elements could be nickel, chromium, molybdenum, manganese, and silicon. These alloys add strength to the steel at room temperature. As for the carbon content, it is below 0,25% and often even below 0.15%.

The role of the alloying elements is not only to increase strength, but also to enhance corrosion resistance. They must be added with care and in certain amounts because they might also increase crack susceptibility (Capudean, B. 2003).

2.2.2.2 High-alloy steels (Stainless steels)

Stainless steels fall under high alloy steels. They can be identified by their three-digit designation, such as the 200, 300, 400, and 500 series. Another way to identify them is by their chromium and nickel percentages. If they have designations such as 18-8, that means that there is 18% chromium and 8% nickel. Stainless steels usually have at least 12% chromium added to the base material. One of the most important properties of stainless steels is their high corrosion resistance, which makes them very suitable for use in harsh environments. Furthermore, stainless steels do not need to be painted or coated, which makes them suitable for use in applications where cleanliness is required, such as hospitals and kitchens.

There are many grades of stainless steels. To date, there are more than 150 different grades and 15 of those grades are the most commonly used. The 304-stainless steel and the 316-stainless steel are two of the most popular and mostly used ones. To further put it into perspective, stainless steels are divided into five main types: ferritic, austenitic, martensitic, precipitation hardening, and duplex. (Worldstainless n.d.)

Ferritic: Ferritic stainless contain less than 0.1% carbon and 12% to 27% chromium with small amounts of alloys that form austenite. Although this type of stainless steel is used in a wide range of applications, its use is somewhat limited since it does not weld to a high standard and cannot be hardened via heat treatment (Worldstainless n.d.)

Martensitic: This type of stainless steel contains the least amount of chromium. It contains up to 1% carbon but it still has a few properties in common with ferritic stainless steels. It has high hardenability and can be tempered and they require preheating and post heating when welding to avoid cracks in the heat-affected zone (HAZ). They are mainly used in applications where the strength of the steel is more critical than the corrosion resistance. This type of stainless steels is use in cutlery.

Austenitic: It accounts for 70% of all stainless steels production and can be readily formed and welded. Elements must be added to act as austenite stabilizers, such as nickel, being the most important alloy. Other elements that could be added to improve some properties of the steel are carbon, manganese, and nitrogen.

Precipitation hardening: Adding certain elements, such as aluminium, copper, and niobium makes this stainless steel type very strong and it can be machined and shaped. As for corrosion resistance, it is on the same level as austenitic stainless

steels.

Duplex: Duplex stainless steel gets its name from having a combination of ferritic and austenitic microstructure. This makes duplex about two times stronger than both them alone. As for toughness and ductility, duplex introduces an improvement compared to ferritic stainless steels, but is still not as tough or ductile as austenitic stainless steels. Duplex stainless steels have a range of corrosion resistance, which depends on the chemical composition and alloying elements. In general it is on the same level of austenitic stainless steels, specifically the 304 and 316 types (Worldstainless n.d.).

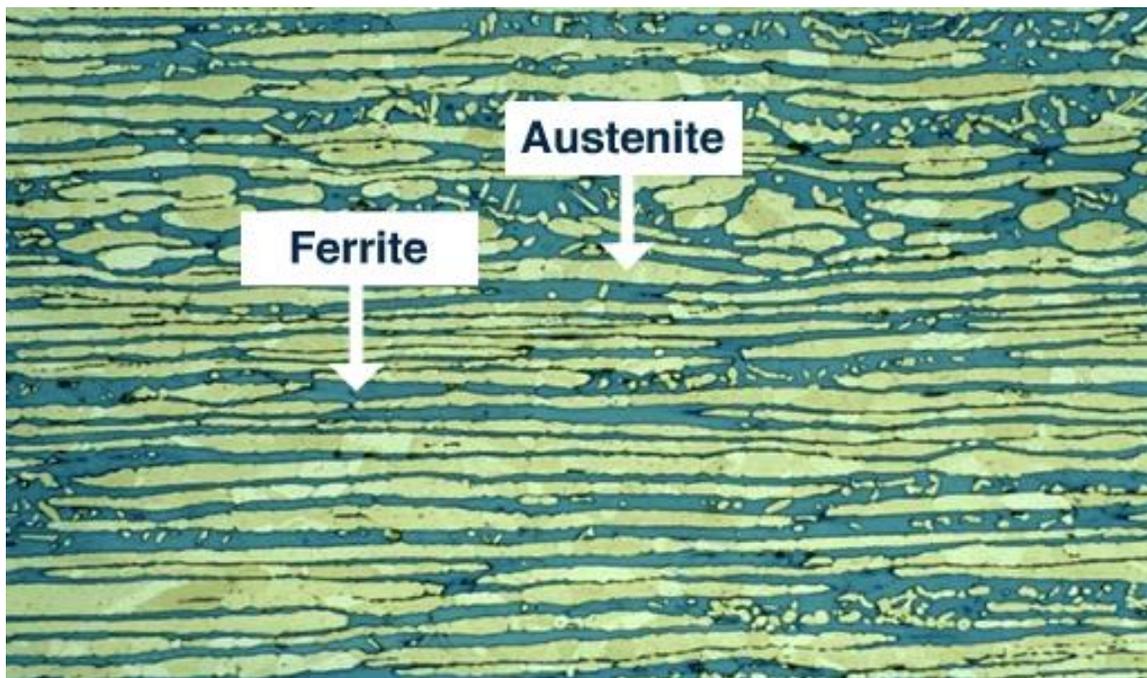


Figure 2.3: Duplex microstructure (International Molybdenum Association, n.d.)

Chromium, molybdenum, and nitrogen are most important for the resistance against chloride pitting and crevice corrosion. Stress corrosion cracking (SCC) resistance is also one of the duplex stainless steels great advantages. This type of corrosion could be a problem for austenitic stainless steels, but duplex stainless steels have good resistance against it because of the ferritic structure. The nickel and molybdenum amounts are less in duplex, yet it still has the same corrosion resistance. Furthermore, duplex stainless steel has higher yield strength than austenitic grades and that allows the reduction of the section thickness, which allows for more cost reduction as well as weight reduction compared to austenitic stainless steels. They can be easily differentiated from austenitic stainless steels in

that they are magnetic. Duplex stainless steels are widely used in the oil and gas industry and in marine applications, but they are also utilized in other applications such as and transport, pollution control, and paper manufacturing (Aalco, n.d.)

Figure 2.4 illustrates the different groups and grades of steels.

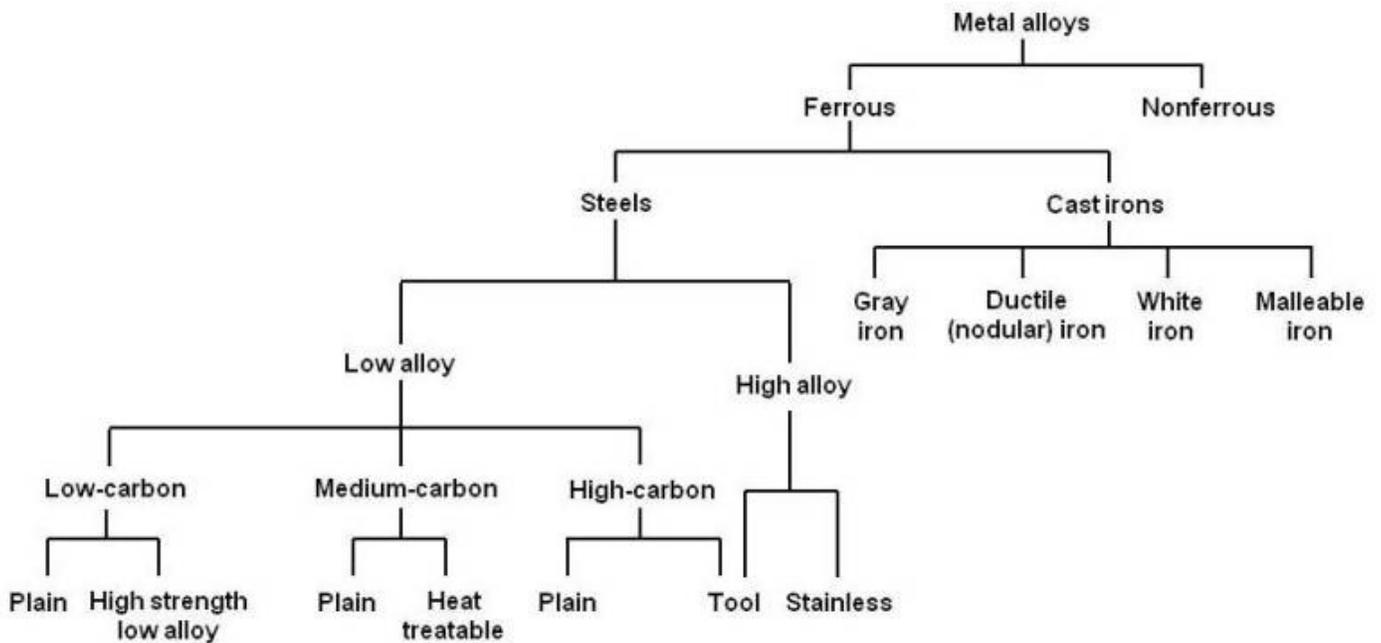


Figure 2.4: Classification of Steels (Shah, K.P., n.d.)

2.3 Corrosion resistant alloys (CRA)

Corrosion resistant alloys (or cracking resistant alloys) are the result of combining certain metals, which could be for example, chromium, cobalt, molybdenum, stainless steel, and nickel. One of their greatest advantages is their higher resistance against corrosion than conventional steels, which makes them convenient for the fabrication of pipelines (Corrosionpedia, n.d.). However, H₂S containing environments have a significant effect on the cracking resistance of CRAs. The following are the main factors:

- Chemical composition, strength, heat treatment, microstructure, method of manufacture, and finished condition of the material.
- Acidity (in situ pH) of the water phase.
- Chloride or other halide ion concentration.
- Presence of oxygen, sulphur, or other oxidants.
- Exposure temperature.
- Pitting resistance of the material in the service environment.
- Galvanic effects.
- Total tensile stress (applied plus residual).
- Exposure time.

(BS EN ISO 15156-3, 2015).

The reason why the following corrosion resistant alloys are presented and discussed is that there is a lot of experience in dealing with them in the oil and gas industry and they have been used many times before with successful results. They are available by the manufacturers and they have the required properties at affordable prices.

2.3.1 C-Mn steel lined with 3mm AISI 316L (UNS S31603)

The 316 steel grade is an austenitic stainless steel. The letter “L” that comes after 316, indicates that the steel contains low carbon concentration. In low temperatures, it has very high toughness due to its austenitic structure. If it is compared to chromium-nickel austenitic stainless steels, it has better creep resistance, higher stress to rupture, and higher tensile strength in high temperatures (Azo Materials, Feb. 18, 2004). Table 4.1 shows the chemical composition of 316L austenitic stainless steel according to ISO 15156-3 (2015).

Table 2-3: Chemical composition of austenitic stainless steel 316L grade (ISO 15156-3, 2015)

UNS	C	Cr	Ni	Mn	Si	P	S	Mo	N	Ni + 2Mo
S31603	0.03	16 to 18	10 to 14	2	1	0.045	0.03	2 to 3	-	14 to 20

Austenitic stainless steel 316L has improved corrosion resistance against crevice and pitting corrosion in chloride environments due to the amounts of molybdenum it contains. However, crevice and pitting corrosion resistance decreases in the warm chloride environments. According to table B1 in ISO 15156-3 (2015), austenitic stainless steels are subject to stress corrosion cracking, especially at temperatures above 60°C. The condition in which the 316L grade suffers from SCC is chloride containing environments, residual tensile stresses and temperatures above 49°C. Those stresses could result from thermal cycles due to welding or from cold deformation. (stal.com.cn, n.d.)

The 316L grade has very good weldability using fusion and resistance methods. Also, this grade specifically does not need post-weld annealing, even when heavy welding is involved. The 316L grade is easy to machine if compared to the 316 grade due to its low carbon content. It can also be hot and cold worked, although it requires post work annealing in order to eliminate residual stresses.

If we look at table A.2 from BS EN ISO 15156-3 (2015) in the appendix A, we can see the limiting conditions for the use of 316L grade stainless steel.

2.3.2 13% Cr stainless steel

The 13% chromium supermartensitic stainless steel (SMSS) is the only CRA presented in this report, which is not an ISO standard CRA. However, it has very good corrosion resistance and is used in some pipelines in the North Sea. Its properties and requirements for use are stated in DNV-OS-F101(2013). A slight disadvantage might be that welding requires preheating and post weld heat treatment (PWHT) due to its high carbon content. More recently, super 13% Cr

stainless steel has been developed. The main difference in the chemical composition is that the carbon content is lower, which makes the chromium much more effective and also the concentrations of nickel and molybdenum are increased. As a result the corrosion resistance is improved and the weldability is improved even without post-weld heat treatment (Kondo, K. et al, 1999)

Furthermore, 13% Cr stainless steel has improved resistance against general and localized corrosion and against sulphide stress cracking. According to table B.1 in ISO 15156-3(2015), the primary corrosion mechanism for martensitic stainless steels is sulphide stress cracking, which is caused by hydrogen embrittlement. This is true for a typical martensitic stainless steel despite the high chromium content; and low alloy steels have had better corrosion resistance against SSC. A paper written by Konde et al presents some practical tests made to investigate the corrosion resistance of 13% Cr stainless steel (Kondo, K. et al, 1999). It was found that lowering the carbon content is very important since it decreases chromium carbide precipitation and increases the amount of effective chromium. Furthermore, the SSC corrosion rate decreased significantly when the molybdenum content was increased. When the steel contained 2% Mo it did not suffer from SSC corrosion at 0.001MPa H₂S, whereas at lower Mo contents, SSC corrosion did occur.

The paper also showed that martensitic stainless steels with low carbon content showed much higher corrosion resistance compared to conventional 13% Cr steel. The test was conducted in a CO₂ environment at a temperature of 150°C and it confirmed that the addition of molybdenum and/or nickel did indeed improve the corrosion resistance of martensitic stainless steels.

Table 2-4: Chemical compositions of two 13%Cr stainless steels. (Konde et al. 1999, p.5)

	C	Cr	Ni	Mo	Ti
13Cr-S	Max. 0.03	11.5-13.5	4.5-6.5	1.5-3.0	0.01-0.5
13Cr-M	Max. 0.03	11.5-13.5	4.0-6.0	0.5-1.0	0.01-0.5

Table 4.3 shows the chemical compositions of two types of 13% Cr stainless steel. The first type designated with “S” was tested in an environment with CO₂ and H₂S. The molybdenum content in that sample was 2.5% to resist SSC corrosion due to the presence of H₂S. This test was successful, as the sample did not show any signs of SSC corrosion.

The second sample designated by “M” was tested in an environment containing only CO₂, that’s why the molybdenum content was only 0.7%. This sample also showed resistance to CO₂ corrosion. (Kondo, K. et al, 1999)

The yield strength of both types was also tested at different temperatures ranging from room temperature to more than 250°C. Both types showed only a small decline in the yield strength compared to duplex steels, which are very much favoured for flowlines at temperatures around 100°C (Kondo, K. et al, 1999).

Koichi Nose and Hitoshi Asahi (2000) conducted another experiment where they investigated the corrosion properties of the weld portions of martensitic stainless steels in mild sour environments. This was an important test because the SSC occurs in this area when it comes to pipelines, as the heat affected zone (HAZ) is normally weaker than the base material. From the microstructure point of view, it was found that generally, martensitic stainless steels that contained 10% or more retained austenite showed better resistance to SSC corrosion. However, the effect of microstructure is beyond the scope of this paper and will not be discussed in detail. The different samples of martensitic stainless steels showed high resistance against CO₂ corrosion, regardless of their microstructure. The test conditions and the results could be seen in the tables 4.4 and 4.5.

Table 2-5 Test conditions of SSC test for a martensitic stainless steel (Nose, K. and Asahi, H. 2000, p.6)

Temperature	Gas partial pressure		Test solution, chemical content		Applied stress	Estimated pH	Test duration
	CO ₂	H ₂ S	NaCl	NaHCO ₃			
25 °C	0.1 MPa	0.01 MPa	5 wt%	0.002 wt%	606MPa	4.0*	720 hours
25 °C	0.1 MPa	0.004 MPa	5 wt%	0.002 wt%	606MPa	4.0*	720 hours
25 °C	0.1 MPa	0.001 MPa	5 wt%	0.002 wt%	606MPa	4.0*	720 hours

*: 0.1MPa CO₂ partial pressure, 5wt%NaCl+0.002wt%NaHCO₃

Table 2-6 Test results of the SSC test of a martensitic stainless steel (Nose, K. and Asahi, H. 2000, p.7)

Heat treatment		T-300	T-500	T-600	T-630	T-660	T-720	As N
H ₂ S in MPa and result	0.01	SSC, SSC	SSC, SSC	SSC, NC	NC, NC	NC, NC	SSC, SSC	SSC, SSC
	0.004	NC	SSC	NC	-	-	SSC, NC	NC
	0.001	NC, NC	NC	NC, NC	-	-	NC, NC	NC, NC
TM /%		99.8	99.9	94	53	15	0	0
RA /%		0.2	0.1	4	18	13	3	0.1
FM /%		0	0	2	29	72	97	99.9
YS /MPa		853	959	893	793	698	807	842
TS /MPa		1043	1084	925	904	1007	1116	1043

N: normalized at 950 °C, T: tempered at indicated temperature in °C after normalized.

Result: SSC; failed in SSC, NC: no crack., -: not tested.

TM: tempered martensite, RA: retained austenite, FM: fresh martensite.

Table 4.4 shows that a pH value of 4 and at 1 kPa of pH₂S there was no cracking in the martensitic stainless steel samples. These conditions are very similar to the conditions of Project B and Project C, which are being investigated in this paper.

The chemical compositions of the 13% Cr martensitic stainless steels in Kondo et al. (1999) tests are very much in line with the requirements stated in DNV-OS-F101. According to the standard the chemical compositions of the two types of 13% Cr should be as follows:

Table 2-7: Chemical compositions for 13% Cr stainless steels according to DNV-OS-F101 standard (2013)

Element	Grade 13Cr - 2 Mo wt.%	Grade 13Cr - 2.5 Mo wt.%
C	0.015 max	0.015 max
Mn	-	-
Si	-	-
P	0.025 max	0.025 max
S	0.003 max	0.003 max
Ni	4.50 min	6.00 min
Cr	12.0 min	12.0 min
Mo	2.00 min	2.50 min
N	-	-

The DNV-OS-F101 (2013) also states the mechanical properties, which should be as follows:

- Specified minimum yield strength (SMYS): 550 MPa
- Specific minimum tensile strength (SMTS): 700 MPa

This applies to both types of 13% Cr stainless steel. Knowing the mechanical properties is important when comparing it to other materials.

Table A.18 in ISO 15156-3 (2015) shows the environmental and materials limits for martensitic stainless steels used for any equipment or components. The types mentioned in this table can be used at any combination of temperature and chloride concentration as long as pH_2S does not exceed 10 kPa and the pH value is greater than 3.5.

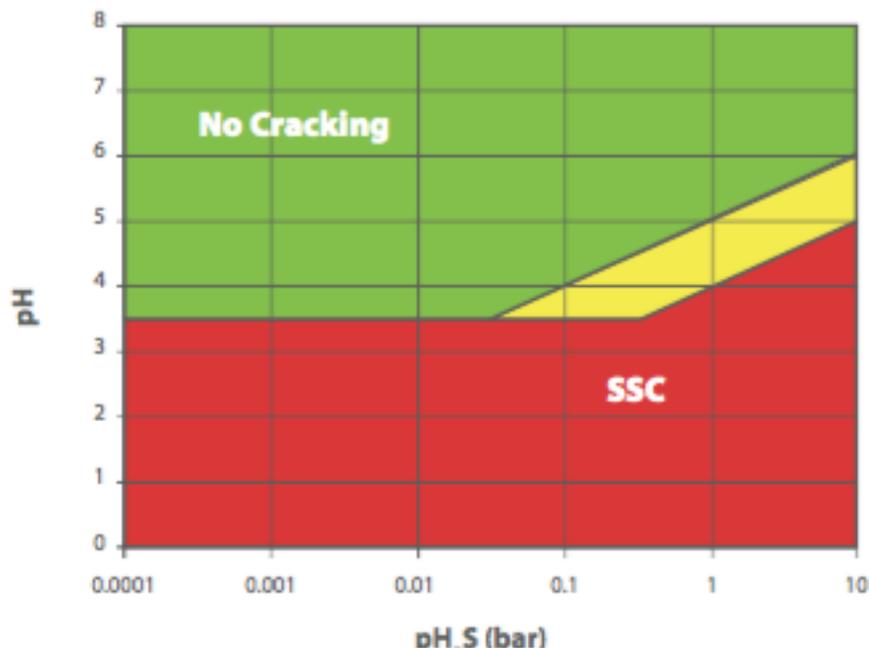


Figure 2.5: Limits for 13% Cr in sour service (Nickel Institute. Craig, B.D. and Smith, L. September 2011).

In

Figure 2.5 the environmental limits considering pH_2S and pH value of the 13% Cr are shown. The green area means that 13% Cr is resistant to SSC and the red area means it is prone to suffer SSC. The yellow area shows the conditions for which further investigation is warranted.

2.3.3 22% Cr and 25% Cr Duplex stainless steels

Two of the most common duplex stainless steels are the 22% Cr stainless steel and the 25% Cr stainless steel. One of the great advantages of duplex stainless steels is that they are extremely corrosion resistant. They are not as resistant to stress corrosion cracking (SCC) as ferritic stainless steels, but all grades of duplex stainless steels are more resistant to that form of corrosion than the 316 grade of the austenitic stainless steel. In general, they have very high resistance to SCC in environments that contain chloride and sulphide. The high amount of chromium is one of the main reasons of the high corrosion resistance. (Otukumpo 2205 Code Plus Two data sheet, n.d.)

The 22% Cr steel has the UNS number S31803. There are two types of 25% Cr stainless steels and they have different UNS designations, which are S32750 and S32760. They are very similar but have minor differences in their chemical compositions.

Table 2-8: Chemical compositions of 22% Cr and 25% Cr according to ISO 15156-3 (2015)

UNS	C max w _C %	Cr max w _{Cr} %	Ni max w _{Ni} %	Mn max w _{Mn} %	Si max w _{Si} %	Mo max w _{Mo} %	N max w _N %	Cu max w _{Cu} %	W max w _W %	P max w _P %	S max w _S %
S31803	0.03	21 to 23	4.5 to 6.5	2	1	2.5 to 3.5	0.08 to 0.2	-	-	0.03	0.02
S32750	0.03	24 to 26	6 to 8	1.2	0.8	3 to 5	0.24 to 0.32	-	-	0.035	0.02
S32760	0.03	24 to 26	6 to 8	1	1	3 to 4	0.2 to 0.3	0.5 to 1	0.5 to 1	0.03	0.01

2.3.3.1 22% Cr Duplex stainless steel (S31803)

The 22% Cr duplex stainless steel is the most widely used stainless steel and it has a microstructure comprising of roughly 50% austenite and 50% ferrite. The yield strength of the 22% Cr grade is double that of the standard austenitic stainless steel grades and has good fatigue strength. It is used in many applications, such as rotors and fans, food processing equipment, pressure vessels, heat exchangers, and cargo tanks. In the oil and gas industry it is used in pipes as well as x-mas trees, manifolds, pumps, valves, bolting, any several other applications (Accura.co.uk, n.d.)

This stainless steel grade has excellent pitting and crevice corrosion, but it might suffer from crevice corrosion in seawater related applications and in that case regular maintenance has to be done. The good resistance to pitting and crevice corrosion is due to the high chromium, molybdenum, and nitrogen content. The resistance against stress corrosion cracking is excellent when dealing with the 22% Cr steel grade (Accura.co.uk, n.d.).

Table 2-9: : S31803 SCC test results vs other steel grades (Outokumpu data sheet, n.d)

Grade	Boiling 42% MgCl ₂	Wick Test	Boiling 25% NaCl
2205 Code Plus Two®	F	P	P
254 SMO®	F	P	P
Type 316L	F	F	F
Type 317L	F	F	F
Alloy 904L	F	P or F	P or F
Alloy 20	F	P	P

(P = Pass, F = Fail)

The above table shows that the 22% Cr steel grade (designated here as 2205 Code Plus Two) has passed the SCC test in a chloride-containing environment. The specifics of the tests were not given but the duplex stainless steel grade did not suffer from stress cracking corrosion, while the two austenitic stainless steel grades 316L and 317L did suffer from that type of corrosion in the same exact test. That proves that duplex stainless steels are superior austenitic stainless steels when it comes to SCC resistance.

In a test conducted by the company “Outokumpu” (n.d.), a 22% Cr stainless steel specimen was placed in a chloride-acetic acid solution saturated with hydrogen sulphide. The specimen completed 500 hours without cracking while it was subject to uniaxial stress. This was the NACE Standard Test Method TMO177, which is equivalent to ISO 15156 (2015). The conclusion was that this grade of steel could be used in a sulphide-containing environment to a temperature of up to 232°C if the partial pressure of H₂S is not higher than 2 kPa. In table A.24 in ISO 15156-3 this steel grade can be used in environments with a maximum temperature of 232°C and a maximum partial pressure of H₂S of 10 kPa. If these conditions are satisfied then the chloride concentration and the pH value don't really matter.

The machinability and forming of the 22% Cr grade is difficult due to its high strength and needs high power and very sharp tools to go through these processes. As for weldability, the 22% Cr stainless steel has good weldability. A filler metal should be used in the welding process, but preheating and post-weld heat treatments are usually not necessary.

2.3.3.2 25% Cr Duplex stainless steel (S32750 & S32760)

The S32750 and S32760 grades contain 25% chromium and are considered super duplex stainless steels. Their chemical compositions are very similar except that the S32760 contains copper and tungsten. Just like the 22% Cr duplex stainless steel (or S31803) they have a combination of ferritic and austenitic microstructure, but they have higher chromium content and are considered higher grades. The 25% Cr grades have higher strength and can withstand higher stresses in addition to the high tensile and high yield strength. Furthermore, they have high ductility and very good impact strength at room temperature as well as sub-zero temperatures and that is one of the reasons why this grade is very suitable for oil and gas applications, especially for subsea equipment (Langley Alloys, n.d.)

There is a lot of experience in using the 25% Cr grades in both, the oil and gas industry and the marine industry. In the oil and gas industry they are used in pumps, pipes, valves, wellhead equipment, and other subsea equipment. In the marine and shipbuilding industry they are used in propellers and shafts, bolts and fasteners, and oil and chemical tankers. They are also widely used in other applications, such as seawater desalination plants and sewage treatment (Langley Alloys, n.d.)

According to table B.1 in ISO 15156-3 (2015), the main form of corrosion for duplex stainless steels is stress corrosion cracking (SCC). The 25% Cr super duplex

stainless steels have excellent resistance against general and uniform corrosion. They are also very resistant against SCC in environments containing chlorides as well as excellent resistance against pitting and crevice corrosion, which makes them excellent candidates for the use in sweater related applications. However, DNV-OS-F101 (2013) states that the 25% Cr duplex stainless steel should be regularly inspected for pitting corrosion. They are also suitable for use in the sour environments where hydrogen sulphide (H₂S) is present, which is why they are used in the most corrosive and most aggressive environments. The duplex stainless steels can withstand high temperatures as high as 298°C (570°F) and also have high resistance against erosion corrosion, which is very important for pipelines due to the continuous friction of the fluid particles. The S32760 and S32750, for example, are used in heat exchangers.

The weldability of the duplex stainless steels is very good and preheating and post-weld annealing is not necessary.

Due to the high strength and excellent mechanical properties, thinner sheets can be used to withstand the same amount of stress as austenitic or nickel-based steels. This leads to an overall reduction in the costs.

2.3.4 Nickel-based alloys

The two types of nickel-based alloys to be investigated are N06625 and N08825. Their chemical compositions are shown in the following table.

Table 2-10: Chemical composition by w% Of N06625 and N08825 according to ISO 15156-3

UNS	C max	Cr	Ni	Fe max	Mn max	Si max	Mo	Cu max	P max	S max	Ti max	Nb max	Al max
N06625	0.1	20 to 23	Bal.	5	0.5	0.5	8 to 10	-	0.015	0.015	0.4	3.15 to 4.15	0.4

N08825	0.05	19.5 to 23.5	38 to 46	Bal.	1	0.5	2.5 to 3.5	1.5 to 3	-	0.03	0.6 to 1.2	-	0.2
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“Bal.” in the table is the balance of composition up to 100% as defined in the ISO standard. For N06625 the Ni concentration is usually minimum 58% according to different manufacturers.

The nickel-based alloys are austenitic alloys with the addition of molybdenum and titanium, and in the case of the 825-alloy, copper. Those alloys were developed to have excellent resistance against corrosive environments and they do have higher corrosion resistance than the 316 austenitic stainless steels.

2.3.4.1 Nickel alloy N06625

The addition of niobium together with molybdenum gives the nickel-based alloy 625 very high strength and toughness as well as fatigue strength. It has excellent oxidation resistance and has outstanding resistance to stress corrosion cracking in chloride-containing environments and has also very high resistance against pitting and crevice corrosion due to the presence of molybdenum. The combination of nickel and chromium enhances resistance to oxidizing chemicals, while the combination of nickel and molybdenum improves resistance against non-oxidizing elements. The ability of this alloy to function in a temperature range from cryogenic up to 982°C gives it a big advantage. The weldability is also good and post-weld heat treatments are not required. All those advantages lead the alloy 625 to be used in different industries, such as aerospace, chemical processing, nuclear, as well as the marine and oil and gas industry (Special Metals data sheet Inconel alloy 625, n.d.)

2.3.4.2 Nickel alloy N08825

The chemical composition of the 825-alloy is somewhat similar to the 625 alloy in that it contains nickel, chromium, and molybdenum. For that reason it also has high resistance against oxidizing acids and excellent resistance against stress corrosion cracking and pitting and crevice corrosion. The addition of higher concentrations of titanium gives good resistance against intergranular corrosion. It is known to be especially resistant to sulphuric acids and phosphoric acids. It can function in very

high temperatures and has good weldability. Since it is similar to the 625-alloy, it is more or less used in the same applications (Megamex.com – Inconel 825, n.d.)

The 825-alloy had good mechanical properties and can serve in a wide range of temperatures from cryogenic temperatures and up to 540°C. It can retain its strength at the cryogenic temperatures. (Sandmeyer steel company data sheet, n.d.)

2.3.5 Comparison of the candidate CRAs

Their main properties are highlighted in the following table.

Table 2-11: The properties of the different material candidates

Material	Resistance to SCC	Resistance to SSC	Resistance to pitting and crevice corrosion	Other forms of corrosion	Tensile strength [Mpa]	Yield strength [MPa]	Weldability	Temp. range [°C]
316L (S31603)	SCC occurs above 60°C	Might be sensitive to SSC	Pitting occurs in seawater and pipe needs protection	-	485	170	Excellent	60-149
13% Cr	Secondary corrosion form	Primary corrosion form	Pitting occurs in seawater and pipe needs protection	High resistance to CO ₂ corrosion	700	550	Good	140-156
22% Cr (S31803)	Excellent	Very high (better than martensitic steels)	Pitting occurs in seawater and pipe needs protection	-	620	450	Good	Up to 232
25% Cr (S32750)	Excellent	Resistant to SSC	Excellent	High resistance to intergranular corrosion	750	550	Good	Up to 232

25% Cr (S32760)	Excellent	Resistant to SSC	Excellent	High resistance to intergranular corrosion	750	550	Good	Up to 232
625-Alloy (N06625)	Excellent	Excellent	Excellent	High corrosion fatigue strength, excellent uniform corrosion resistance	827	300-530	Good	270-450
825-Alloy (N08825)	Excellent	Excellent	Excellent	Excellent against general and intergranular	772	441	Good	270-450

The table above gives a rough indication of the corrosion resistance, mechanical properties, and weldability of the different metals. It makes it easier to see and compare their performance. The exact specifications will have to be discussed with the manufacturers before going through with the purchases because the figures and details might somewhat differ from one manufacturer to the other.

316 Austenitic stainless steel

This type of stainless steel has been used a lot in the oil and gas industry and there is a lot of experience in its behaviour. The most important parameters to look out for are the chloride concentration and the pH₂S as they are the limiting factors for that type of steel. The combination of those two factors can lead to SSC or SCC, and in some cases, both forms of corrosion.

It must be noted that oxygen has a significant effect on the corrosion resistance of the 316-alloy. When the pipeline is exposed to seawater, which contains oxygen, the allowable service temperature decreased. Figure 2.6 shows the range at which it can be used, where sodium chloride (NaCl) represents the chloride concentration. It shall be noted, however, that this is in the condition where there is no oxygen in the atmosphere. So, the allowable service temperature decreases to 60-90°C when the pipeline is exposed to seawater. This is to show the significant effect of oxygen on the allowable service temperature. It explains why it is subject to pitting corrosion

in warm chloride environments and why it is subject to SCC at temperatures above 60°C.

Nonetheless, the 316 stainless steels are still considered very good corrosion resistant alloys and that's why they are widely used in the marine industry. In addition, they have excellent toughness, even at cryogenic temperatures. They have higher creep, stress to rupture, and tensile strength at elevated temperatures than chromium-nickel austenitic steels. However, the industry is slowly shifting to super-austenitic steels when it comes to continuous exposure to seawater (Azo materials, 2004)

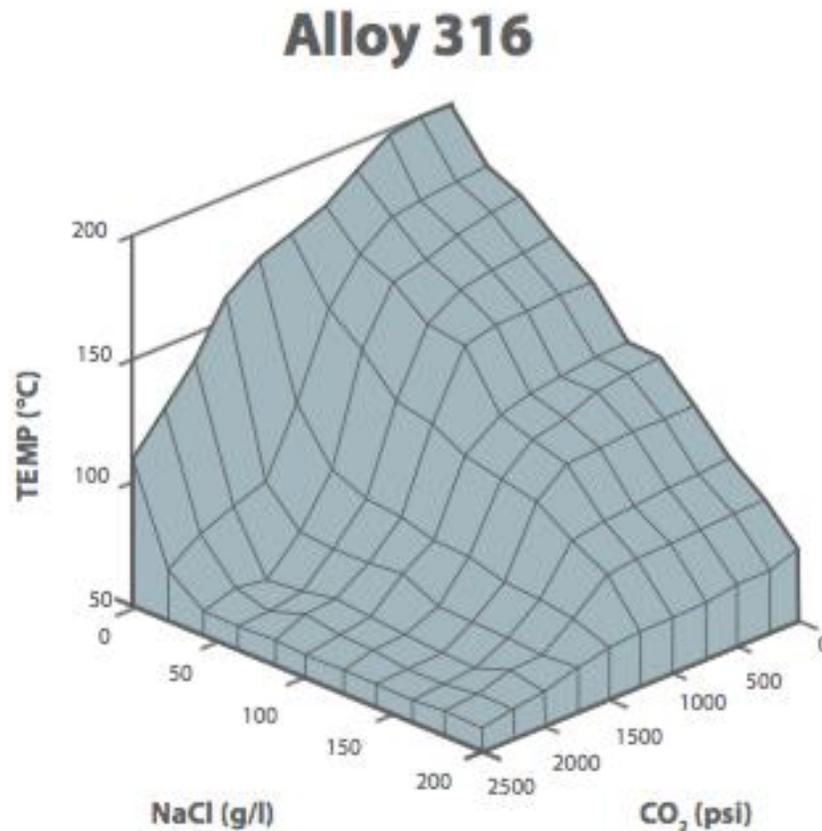


Figure 2.6: Limiting conditions of temperature and chlorides and CO₂ for the 316-alloy (Nickel Institute. Craig, B.D. and Smith, L. September 2011)

13% Cr stainless steel

This type of stainless steel is not registered as an ISO standard stainless steel and testing is always required before using it. The acceptable limit of H₂S to avoid SSC is yet not very clear.

The high amount of chromium and the addition of molybdenum have rendered the 13% Cr highly resistant to SSC and CO₂ corrosion. Pitting can occur in the presence of oxygen and chlorides. The modified type of today's 13% Cr has better properties than the standard 13% Cr and is already in use in several locations, such as the North Sea.

22% and 25% Cr duplex stainless steels

The 22% Cr has higher chromium concentration and is therefore more corrosion resistant than 13% Cr and 316 stainless steels and can be used in higher service temperatures. The 25% are even more corrosion resistant and are called super duplex stainless steels. They have higher resistance to pitting corrosion than the 22% Cr and could be generally used in service temperatures higher by 30°C, although ISO 15156-3 (2015) recommends the same service temperature for both steels. They have been both used successfully in sour environments.

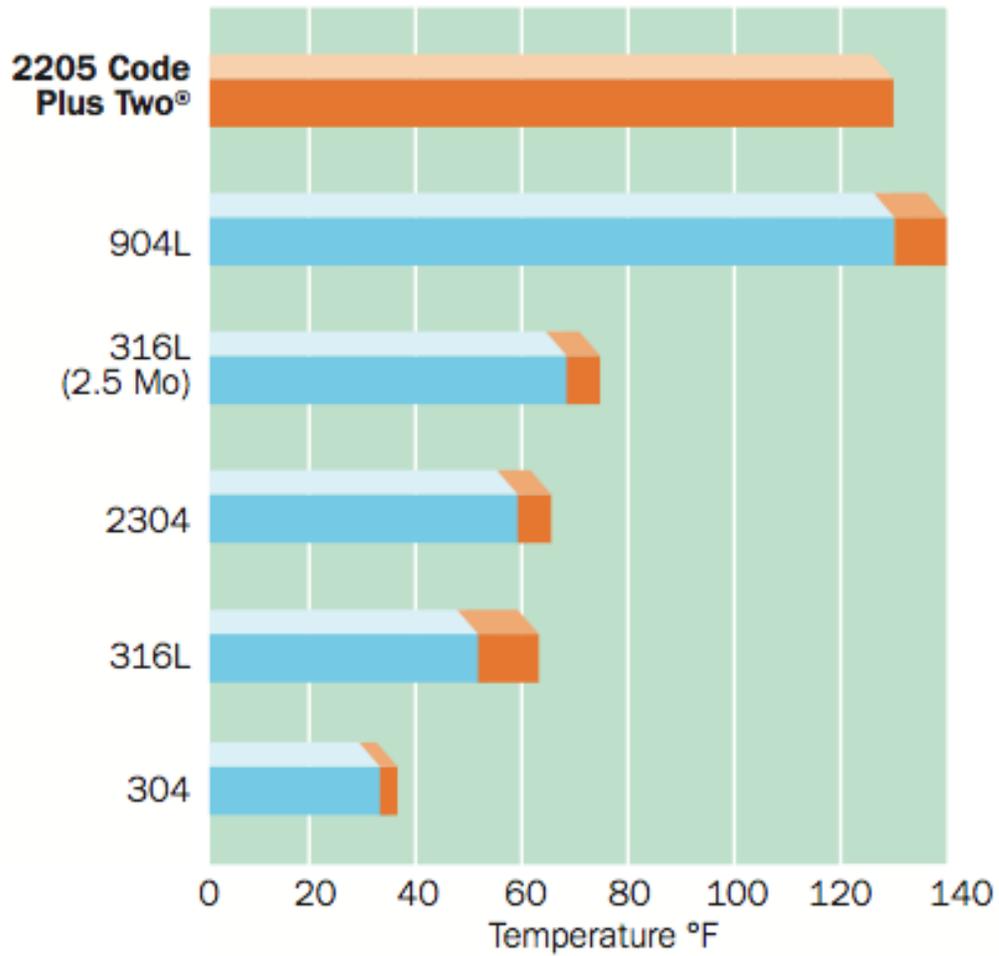


Figure 2.7: Critical pitting temperature in NaCl. (Outokumpo, n.d)

Figure 2.7 shows the critical pitting corrosion temperature for the 22% Cr, the 316L, and the 316L with 2.5% molybdenum. The 22% Cr has a higher critical temperature.



Figure 2.8: Critical crevice corrosion temperature (Outukumpu, n.d.)

This figure 2.8 shows that the 22% Cr has a higher critical temperature than 316L, at which crevice corrosion occurs.

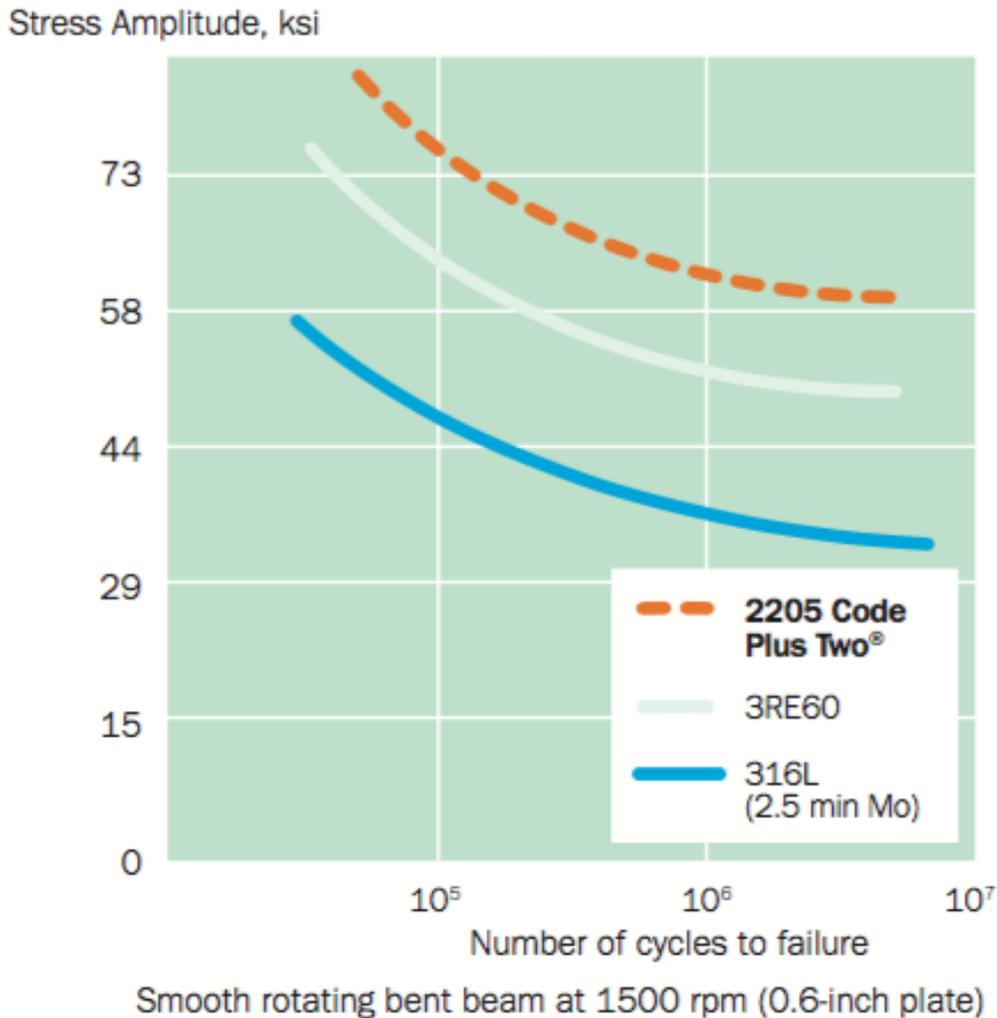


Figure 2.9: Corrosion fatigue in synthetic seawater. (Outokumpo, n.d.)

Figure 2.9 shows that 22% Cr duplex stainless steel can withstand higher stress amplitudes than the 316L austenitic stainless steel in synthetic seawater.

625 and 825 nickel-based alloys

Those alloys have excellent resistance to several forms of corrosion including SSC and SCC, even at elevated temperatures. CO₂ does not affect those types of steels, while H₂S is the main threat at high temperatures. Their corrosion resistance is even superior to the 22% Cr and 25% Cr super duplex stainless steels. The high cost of the nickel-based alloys is why they are not chosen for all the projects. They are only chosen when facing the harshest environments.

ALLOY 625

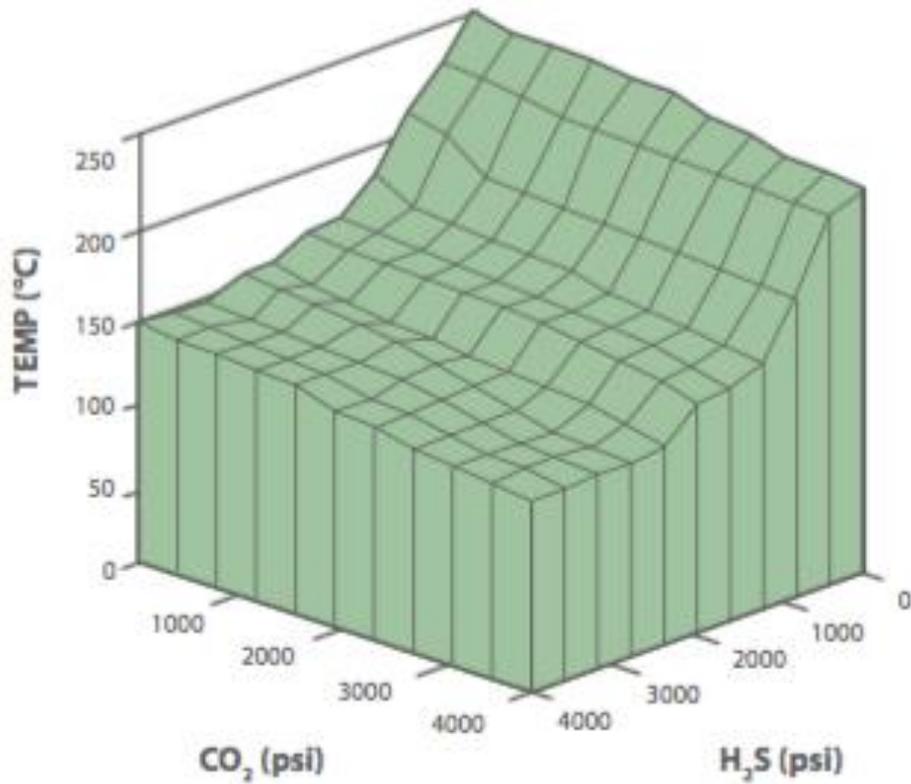


Figure 2.10: The applicable range of the 625-alloy (Nickel Institute. Craig, B.D. and Smith, L. September 2011)

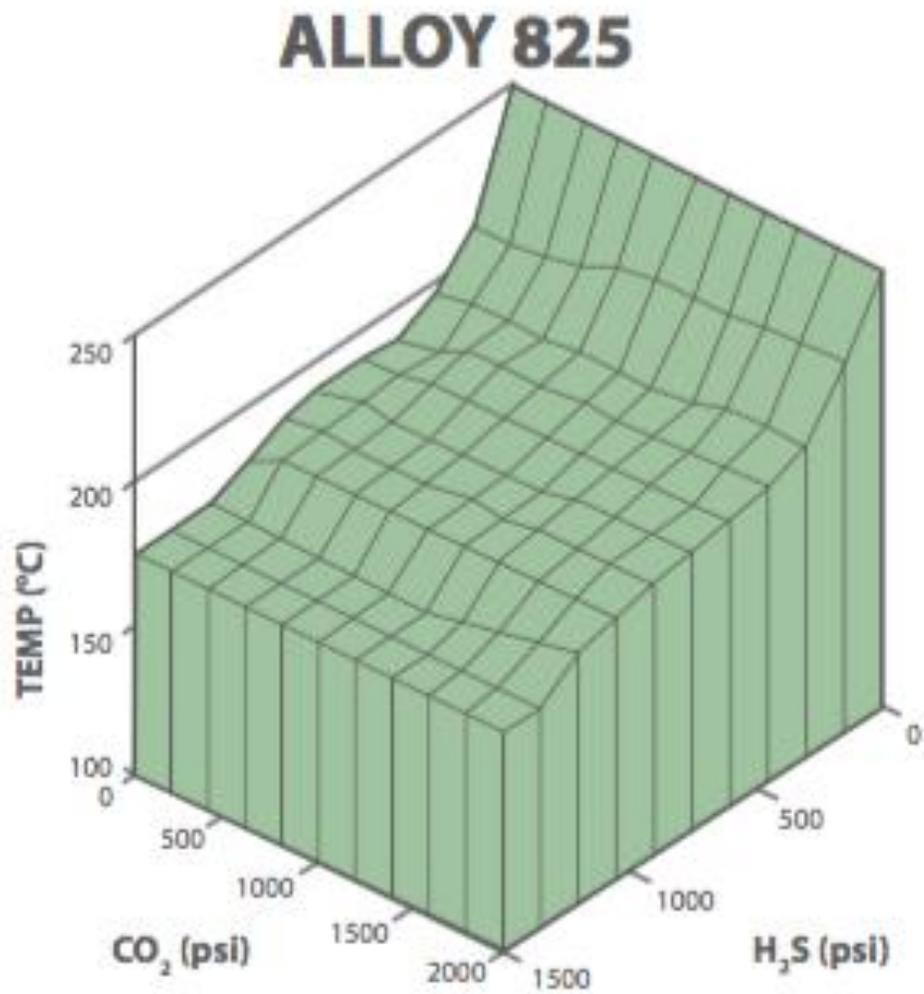


Figure 2.11: The applicable range of the 825-alloy (Nickel Institute. Craig, B.D. and Smith, L. September 2011).

Figures 2.10 and 2.11 illustrate the conditions under which the 625 and 825 alloys can be used.

2.3.6 Cost

It is difficult to know the exact cost of the different materials because the suppliers usually give this information to the customers when discussing business deals. This kind of information is not publicly available like how much a car costs, for example. However, as a rule of thumb, the more alloying elements the steel contains, the more expensive it is. Based on that rule, it is logical to assume that the 316L austenitic stainless steel and the 13% Cr martensitic stainless steel will cost less than the 22% CR and the 25% Cr duplex stainless steels. The Nickel-based steels would probably cost at least around the price of the duplex stainless steels.

In the case, where several types of steel are technically and environmentally qualified for the project, usually the choice is set on the type of steel with the lowest price.

2.4 Corrosion mechanisms

Corrosion is one of the root causes behind oil and gas pipeline failure and a lot of studies and research have been made on this topic. It occurs due to several reasons, such as the presence CO₂, H₂S, oxygen, sulphides, chlorides, and water (seawater or production water). Other factors have an effect on the corrosion process, like temperature and the pH value. The pH is a measure of hydrogen ion concentration, or in other words, the measure of the acidity or alkalinity of a solution. It is an abbreviation for “power of hydrogen”. In general, the lower the pH value the more acidic the solution is, hence, more corrosive (About Education May 2016). The pH value must be considered in two types of water, which are formation and condensed water. Formation water is the water found in the reservoir and lies under the oil, while condensed water is the water vapour present in the gas (usually in gas reservoirs) and condenses later in the production process. Formation water contains more chlorides and condensed water is sourer.

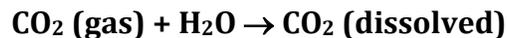
Corrosion of a pipeline could be internal or external. Both are very dangerous because a failure in a pipeline could lead to a disaster. The consequences could range anywhere from a simple leak, that could be contained, to a massive oil spill with catastrophic environmental pollution or even an explosion and loss of lives. The different types of corrosion and their mechanisms must be studied and understood in order to be able to avoid them or at least decrease the rate of corrosion as the cost of repairing pipelines or replacing them is very high. Some of the corrosion mechanisms are explained in this section.

2.4.1 Carbon dioxide (CO₂) corrosion

This type of corrosion occurs in carbon steel pipes due to the CO₂ present in the oil, gas and water that reside in the well. The main driving factors are:

- CO₂ partial pressure
- pH value of the water phase in the well
- Temperature
- Acids
- Flow rate

Carbon dioxide gas dissolves in the water and forms carbonic acid (H₂CO₃), which then dissociates to form the bicarbonate ion, which in turn dissociates to form the carbonate ion. The chemical process is presented in the following equations:



According to de Waard and Milliams, the corrosion rate of mild steels is directly related to the concentration of the non-dissociated H₂CO₃ and to the CO₂ partial pressure.

When CO₂ comes in contact with the steel surface the following electrochemical reaction takes place:

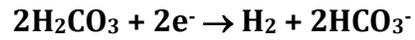


Where FeCO₃ is the corrosion product

The anodic reaction is the dissolution of iron:



And the cathodic reaction could be one or both of the following reactions. It is till not quite determined which of the two reaction actually occur:



(Koteeswaran, M., June 2010)



Figure 2.12: Internal CO₂ corrosion. (Liberty corrosion, n.d)

2.4.2 Sulphide Stress Cracking (SSC)

According to the National Association of Corrosion Engineers (NACE), the definition of sulphide stress cracking is: “cracking of a metal under the combined action of tensile stress and corrosion in the presence of water and H_2S (a form of hydrogen stress cracking)”. The agreed upon mechanism is hydrogen embrittlement and it is one of the main challenges when using stainless steel pipes in harsh environments. Several factors have to be present for SSC to occur, which are:

- A susceptible material
- Tensile stress
- Hydrogen sulphide
- Water

(Ogden, B.L., 2005)

The environments where SSC occurs are called sour environments. There are other variables that affect the SSC process, such as pH, partial pressure of H_2S (p_{H_2S}), and temperature. The lower the pH value and the temperature are, the more susceptible the material is to SSC; and the higher the p_{H_2S} is the higher the potential is for SSC to occur.

Sulphide stress cracking is considered one of the most dangerous forms of corrosion because it could lead to other forms of corrosion, such as pitting corrosion. Furthermore, the release of H_2S can be fatal to the workers in the area (Ogden, B.L., 2005).

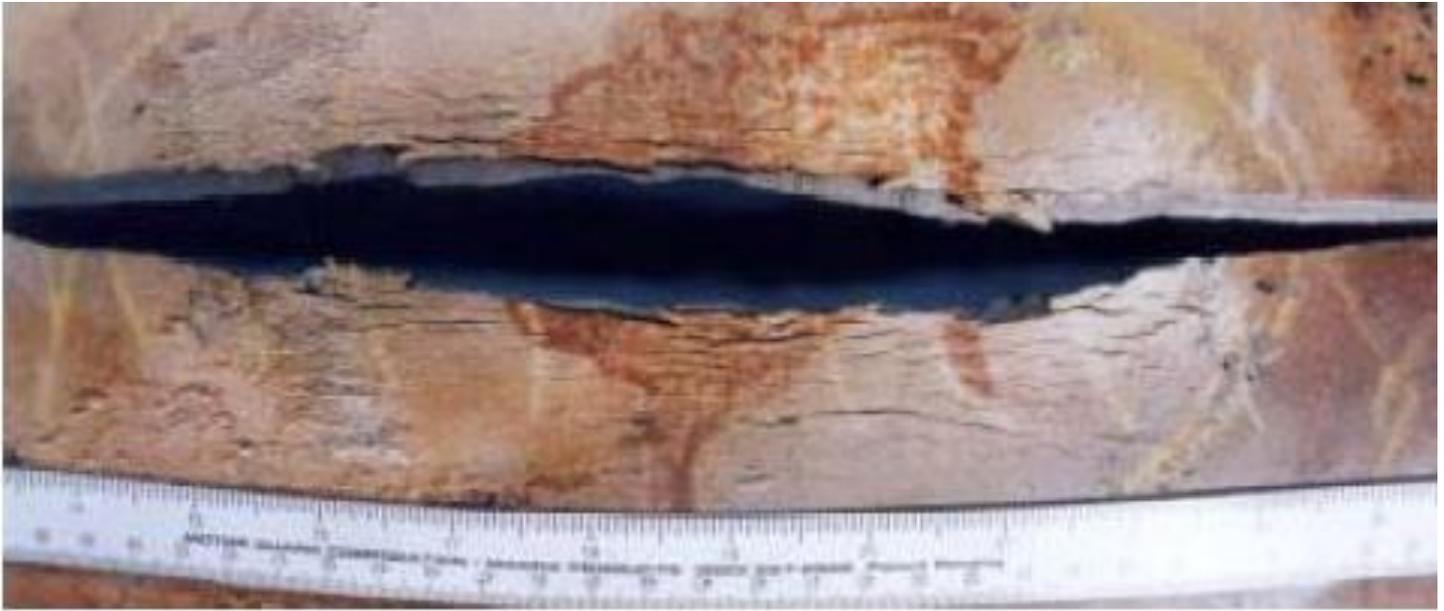


Figure 2.13: Sulphide stress cracking (Metropolitan Engineering Consulting and Forensics, n.d.)

2.4.3 Stress corrosion cracking (SCC)

Stress corrosion cracking (SCC) is a combination of corrosion and mechanical stress that results in cracking that leads to the failure of the pipe. According to Jones, R.H. et al, the term “stress corrosion cracking” is used to describe any type of environmentally induced or assisted crack propagation. For SCC to occur, three conditions must be true:

- A susceptible material
- An environment that causes SCC for that material
- Tensile stress

(National Physical Laboratory, n.d.)

A very important fact to know is that a certain critical value of stress concentration must be reached before cracking can occur. So mechanical and chemical factors have to exist at the same time for SCC to occur. If only one of those factors is present without the other, the SCC cannot occur. The stresses that cause SCC are tensile stress and they could be applied externally or could be residual stresses. One of the properties of SCC is that it depends on the combination of alloy and environment. There is a specific environment for each type of alloy, for SCC to occur in that alloy.

When the crack occurs it usually propagates at a very slow rate. It could be 10^{-9} m/s to 10^{-6} m/s. According to Jones, R.H. et al, the SCC process goes through three stages:

1. Crack initiation and stage 1 propagation
2. Stage 2 or steady state crack propagation
3. Stage 3 crack propagation or final failure

One of the reasons why this type of corrosion is dangerous is that the cracks area is very difficult to detect through simple inspection. It is difficult to determine when exactly a pit is considered a crack and when intergranular corrosion turns into SCC. It causes a big loss of mechanical strength with only a small loss of material. The result is a catastrophic failure of structures.

The corrosion process comprises of cathodic and anodic processes and there are different mechanisms of SCC. The first mechanism is called “active path dissolution”, where material is removed from the crack tip. Usually that path is along the grain boundary. The second mechanism is hydrogen embrittlement and the third mechanism is called “film-induced cleavage”. Many factors affect the crack propagation rate. Some of those factors are temperature, pressure, and pH value (Jones, R.H. and Ricker R.E., 1992).



Figure 2.14: Intergranular stress corrosion cracking (NACE international, n.d)



Figure 2.15: SCC in a 316 stainless steel chemical processing pipe.
(NACE international, n.d.)

2.4.4 Uniform corrosion

This type of corrosion is uniformly distributed over a surface area. This is the most form of corrosion that leads to tonnage waste, where thinning process of the metal takes place until failure occurs. It is easily predicted and detected so only in rare cases does failure occur due to this form of corrosion (Nace Internatoinal, n.d.).

2.4.5 Pitting corrosion

Pitting corrosion is more dangerous than uniform corrosion because it is more difficult to predict and detect. This type of corrosion creates cavities or holes in the material. It could occur due to chemical or mechanical damage, low dissolved oxygen, and high concentrations of chloride. The presence of non-metallic particles in the material and damage to the protective coating are also enough reasons to initiate pitting corrosion. The pits are dangerous because they act as stress risers and from there, fatigue corrosion and stress corrosion cracking could be initiated (Nace Internatoinal, n.d.).

Figure 2.16 illustrates the different types of pitting corrosion.

Trough Pits



Sideway Pits



Figure 2.16: Types of pitting corrosion (NACE International, n.d)

2.4.6 Crevice corrosion

According to NACE international, crevice corrosion is associated with a stagnant solution on the micro-environmental level. This occurs in small openings or tight spaces, such as under gaskets, washers and fasteners. It is initiated by:

- Depletion of inhibitor in the crevice
- Depletions of oxygen in the crevice
- A shift to acid conditions in the crevice

- Build-up of aggressive ion species in the crevice, such as chloride

(Nace Internatoinal, n.d.).

2.4.7 Intergranular corrosion

This form of corrosion occurs along the grain boundaries of the material. It could occur due to precipitation of impurities on the grain boundaries, which reduces corrosion resistance. When corrosion attacks the grain boundary, the grain boundary becomes anodic relative to the rest of the material. The form of corrosion significantly affects the mechanical properties of the material.

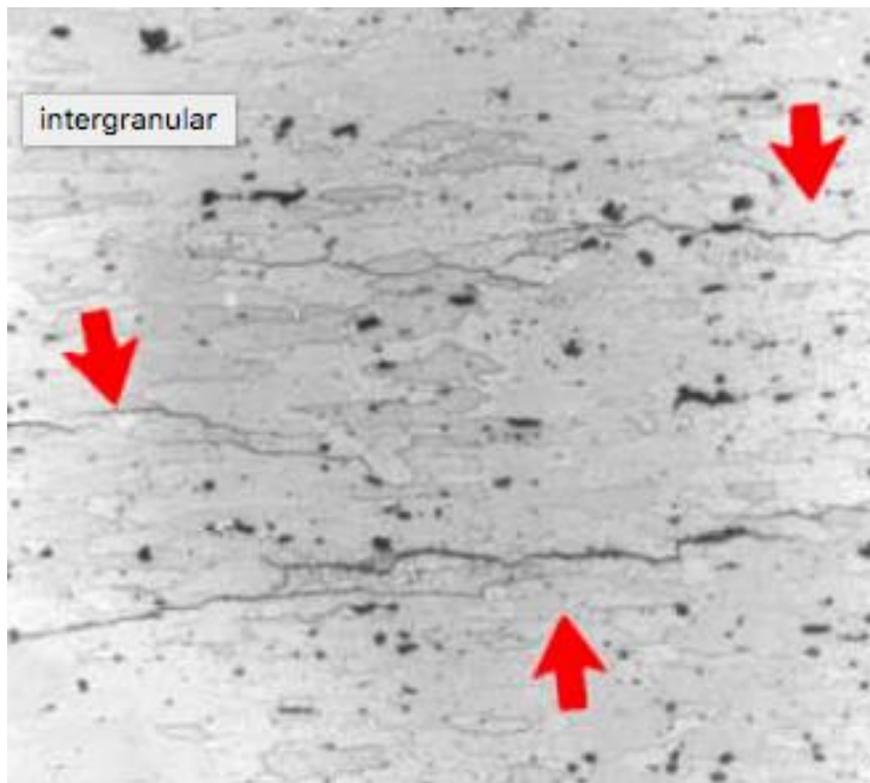


Figure 2.17: Intergranular corrosion. (NACE International, n.d.)

The above-mentioned corrosion forms are the forms experienced most in the oil and gas pipelines. There are many other types of corrosion but they will not be covered in this paper (Nace Internatoinal, n.d.).

2.4.8 Temperature vs. concentration of corrosive elements

As the service temperature increases, the line pipe material has to be tougher, have better mechanical properties, and higher corrosion resistance because the corrosive environment gets harsher. It can be seen in the ISO 15156-3 (2015) tables in appendix A, for example, that when the environmental limits for materials are stated in terms of temperature, pH_2S , chloride concentration, and pH value. For a certain operating temperature, the maximum allowed H_2S pressure and chloride concentration are identified. At a higher operating temperature for that same material, the maximum allowed H_2S pressure or the chloride concentration have to decrease.

The company “Outokumpu” conducted a test on 22% Cr stainless steel (denoted 2205 Code Plus Two) and the 316-stainless steel. Figure 2.18 shows that the maximum allowed operating temperature decreases as sulphuric acid (H_2SO_4) concentration increases in order to maintain a corrosion rate of 0.1mm/year.

Isocorrosion Curves 4 mpy (0.1 mm/yr), in pure sulfuric acid solution

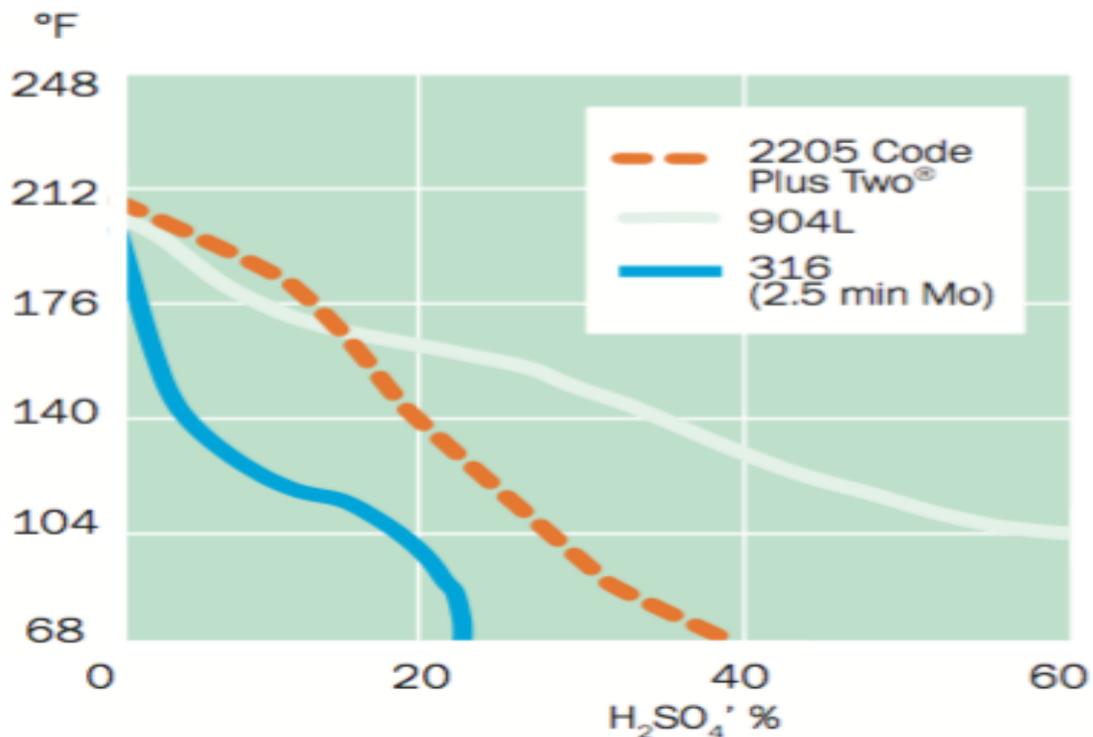


Figure 2.18: Temperature vs. H₂SO₄ (Outokumpo, n.d)

At a concentration of 20% of H₂SO₄ the allowed operating temperature for 22% Cr is 140°F (60°C). When the concentration increases to almost 40%, the allowed temperature decreases to 68°F (20°C).

The case is the same for oil and gas pipelines. As pH₂S and chloride concentrations increase, the operating temperature, which the pipeline can sustain without failing due to corrosion, decreases. Therefore, if a certain material cannot sustain the combination of temperature, pH₂S and chloride concentration, then a different material has to be chosen (Outokumpu Code Plus Two data sheet, n.d.)

Chapter 3 Calculation method of corrosion rate

When it comes to choosing a suitable material for fabricating a pipeline, usually one of the first things the engineers or companies want to know is if carbon steel can be used because it is the more economic option. In order to reach the conclusion that carbon steel is suitable, two steps have to be done:

1. Calculate the carbon dioxide (CO_2) uninhibited corrosion rate (CR_u).
2. Calculate the corrosion allowance (CA).

This first step could be done using the NORSOK M-506 computer program. The required parameters are inserted and the program calculates the CR_u .

If the corrosion allowance in step 2 is within the appropriate limits, then carbon-manganese (C-Mn) steel could be used under the condition that a suitable corrosion inhibitor will be used as well. The limits and steps will be explained in greater detail, by looking at the three case studies (Project A, Project B, and Project C), which were supplied by "Subsea 7".

3.1 Analysis

The corrosion calculations methods and material selection process presented in this report are based on the following assumptions for the sake of simplification. "Subsea 7" provided the assumptions along with the case studies.

- The pipelines are single bore hard pipes.
- The flow conditions are constant throughout the lifetimes of the pipelines.
- The temperatures and pressures vary along the pipeline.
- The amount of condensation water in "Project A" was too little to be considered effective in the final decision making process.
- C-Mn steel cannot be used for "Project C" because internal corrosion inhibitor is not allowed due to operational considerations.
- No sulphur is present in the reservoir.
- No acetic acid is present in the reservoir.

The boundary conditions are the parameters of the three case studies and all the calculations and material selection are based on those parameters.

It is important to note that the calculations and the material selection process presented in this thesis are only simplified illustrations of how material selection is

carried out for pipeline design and could be regarded as the screening stage. It is also one of the many approaches that are applied nowadays. The detailed process is more complicated and includes simulation programs and different aspects beyond the scope of this thesis.

Although the material selection approach differs from one company to another, the target in the end is the same, which is to know whether carbon steel can be used or not. If the answer is yes, then usually no further considerations for other types of steel have to be made. If the answer is no, then CRAs have to be considered and a longer process is initiated until the most reasonable solution is found.

In Project A, a method of corrosion rate calculation will be demonstrated. Furthermore, a worst-case scenario will be investigated by calculating the corrosion rates at different temperatures, pH values, and pressures in order to see how much they affect the corrosion rate.

In Projects B and C it will be shown how other materials are considered when carbon steel is not an option.

3.2 Project A

The parameters of project A are shown in table 3.2.

Table 3-1: Project A parameters

Parameter	Value
Maximum design temperature [°C]	113
Operating pressure [barg]	55-90
CO ₂ content [mole%]	1.1
Bicarbonate concentration [mg/L]	238
Chloride content [mg/L]	147000
TDS/Salinity [g/L]	175
pH ₂ S [kPa]	0.70
Liquid flow rate [Sm ³ /d]	4858
Gas flow rate [MSm ³ /d]	0.385
Water cut [%]	20
Pipe ID [mm]	238.1
Design life [years]	11

Note: In this project specifically, it was shown by flow assurance engineers that the amount of condensed water was not large enough to be separated from the oil phase

and precipitate on the pipe wall. This information was given along with the case studies and these calculations are beyond the scope of this thesis and will not be presented here. Hence, the corrosion rate due to condensed water can be ignored and will not be used for the calculation of the corrosion allowance and only formation water will be considered.

It is still important to demonstrate the corrosion rate can be calculated based on the different types of water to show the difference between them and how to estimate the worst-case scenario.

Step 1: Calculating the uninhibited CO₂ corrosion rate for Project A

The uninhibited corrosion rate can be calculated using the NORSOK M-506 computer program. First, the pH value is calculated using the given pressure and CO₂ content. The results are listed in **the table below**.

Table 3.2: Calculated pH values for Project A

Pressure [bar]	Type of water	Calculated pH
55	Condensed	4.4
90	Condensed	4.3
55	Formation	5.7
90	Formation	5.5

Next, shear stress needs to be calculated. The only variable here is the pressure, since a pressure range has been given instead of an absolute value. The calculation is done only twice, using the minimum and maximum pressure values. The results are listed in the following table.

Table 3.3: Calculated shear stresses for Project A

Pressure (bar)	Shear stress (Pa)
55	8
90	6

Finally, the uninhibited corrosion rate is calculated now that all the needed parameters are obtained. By inserting them in the program the corrosion rate is calculated. To find out the worst-case scenario, the process is repeated several times

because there are two variables, which are the pressure and the pH value. The following table shows the different corrosion rates for the different scenarios.

Table 3.4: Calculated corrosion rates for Project A

Pressure (bar)	pH	Shear stress (Pa)	Corrosion rate (mm/year)
55	4.4 (condensed water)	8	4.3
55	5.7 (formation water)	8	0.61
90	4.3 (condensed water)	6	6
90	5.5 (formation water)	6	0.87

Now, different uninhibited corrosion rates for the different scenarios are obtained. The uninhibited corrosion rate in that case is 6 mm/year.

It is important to note that the temperature given for the project is the maximum design temperature. This does not mean that the pipeline will operate at a constant temperature of 113°C. In fact, there will most likely be fluctuations in the temperature along the pipeline.

Below are graphs 3.1 and 3.2 showing the effect of temperature on the corrosion rate at fixed pH values. The corrosion rates were calculated at a temperature range of 5°C to 113°C, with an increment of 5°C.

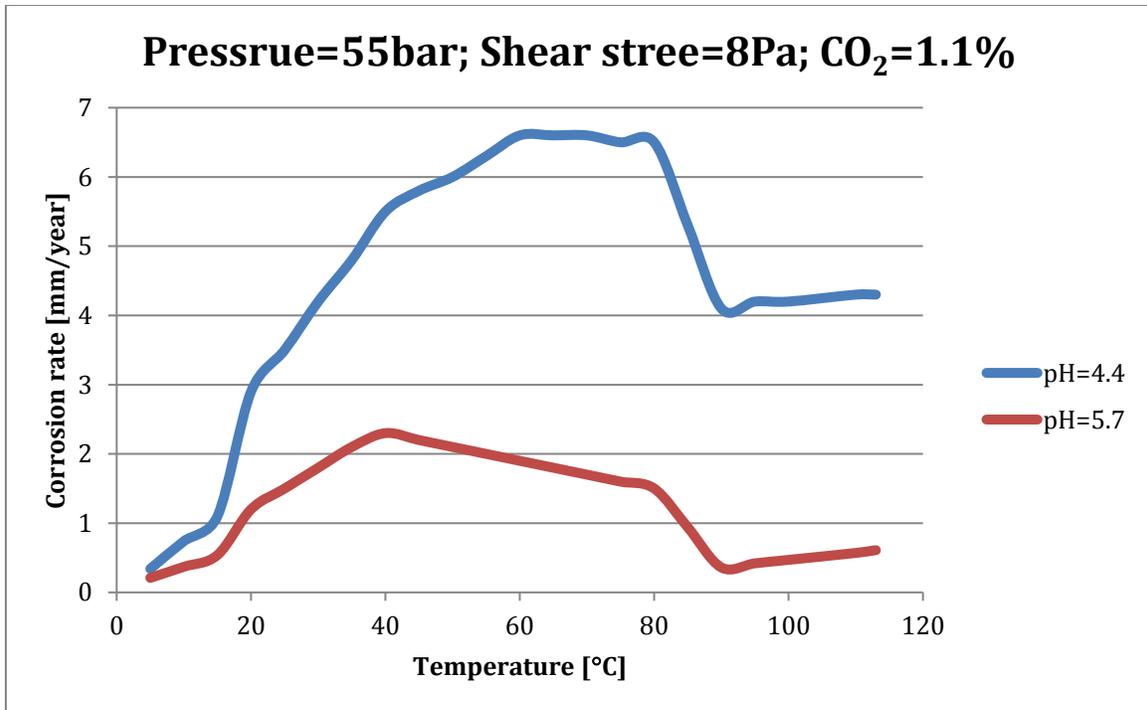


Figure 3.1: Corrosion rate vs temperature with different pH values and 55 bar

The corrosion rate at 55 bar and pH value of 4.4 in condensed water could reach up to 6.6 mm/year when the temperature is between 60°C and 70°C. As for a pH value of 5.7 in formation water, the highest corrosion rate is 2.3 mm/year when the temperature reaches 40°C. Those corrosion rates are significantly higher than the corrosion rates obtained in table 3.4, which were calculated under the assumption that the temperature was constant at 113°C. When temperature fluctuations were taken into account, new corrosion rates appeared.

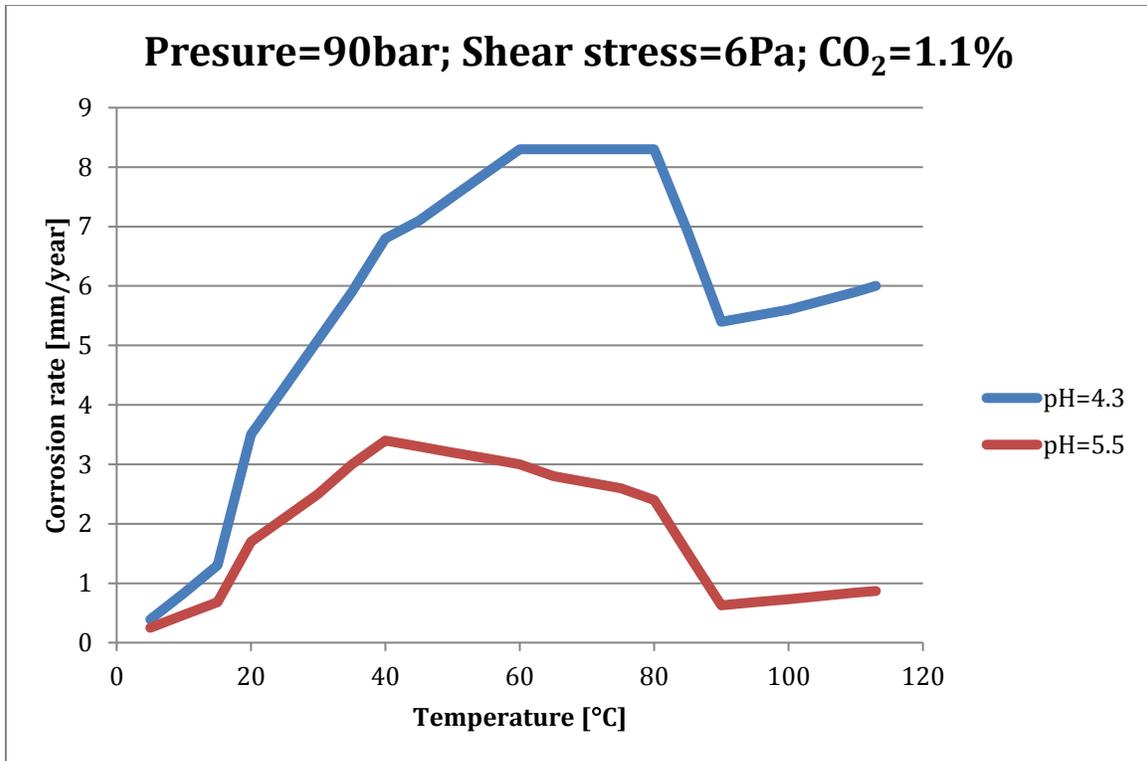


Figure 3.2: Corrosion rate vs temperature with different pH values and at 90 bar

The same is observed at a pressure of 90 bar. Now that temperature fluctuations are taken into account the corrosion rate could reach up to 8.3 mm/year in the case of a pH value of 4.3 in condensed water. This is noticeably higher than 6 mm/year at a temperature of 113°C obtained in table 3.4. And in the case of formation water with a pH value of 5.5, the corrosion rate increases to 3.4 mm/year as the temperature reaches 40°C as a result of temperature fluctuations along the pipeline.

Furthermore, it can be seen in graphs 3.1 and 3.2 above that the corrosion rate does not always increase with increasing temperature. There is a temperature range from 60°C to 80°C at which the corrosion rate is at a peak in the case of condensed water. In the case of formation water the highest corrosion rate is observed at 40°C.

This makes us consider how much the temperature can affect the corrosion rate. Since the goal is to figure out the worst-case scenario, it is important to fine-tune the results. This could be done by investigating the effect of the temperature on the pH value, since it is one of the main factors that directly affect the corrosion rate. In graphs 3.1 and 3.2 above we take into account the temperature changes, but it is assumed that the pH value is constant at all the different temperatures. Graphs 3.3

and 3.4 show the effect of temperature on the pH value. Again, the results were plotted carried out using the M-506 program.

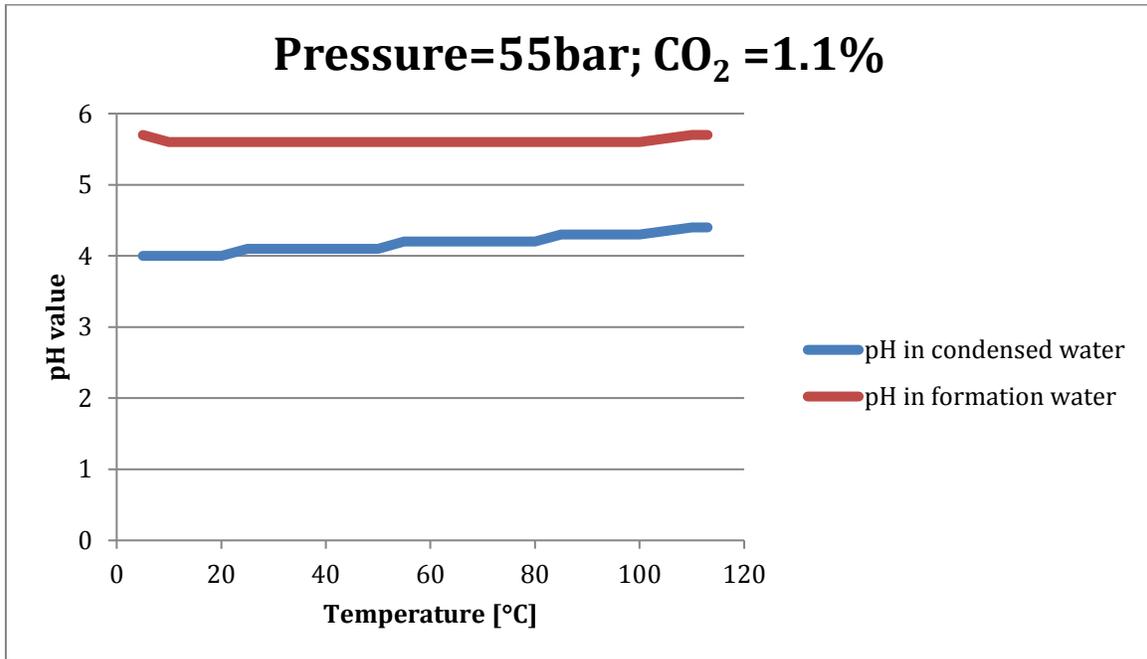


Figure 3.3: Temperature effect on pH value at 55 bar

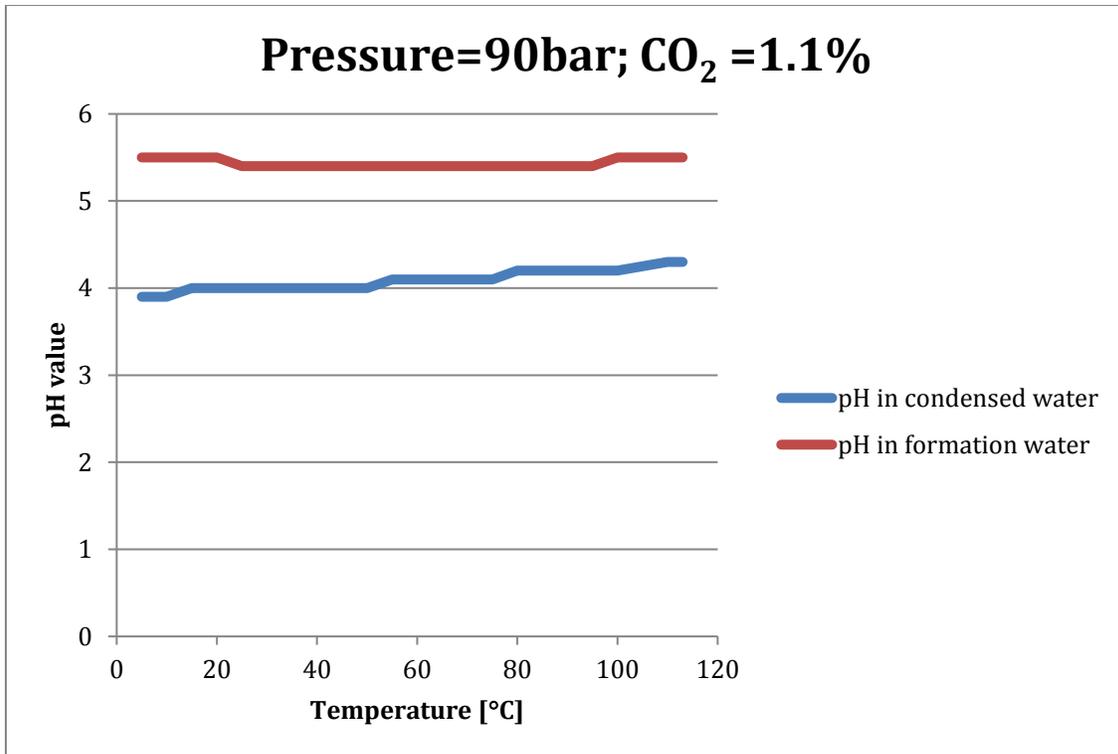


Figure 3.4: Temperature effect on pH value at 90 bar

As shown in graphs 3.3 and 3.4, the temperature does not have a significant effect on the pH value. However, if accurate results are to be obtained then the proper pH value should be inserted according to the temperature when calculating the corrosion rate.

The following tables show the corrosion rates calculated at the different temperatures and their corresponding pH values in condensed water. The results were calculated using the M-506 program and then plotted in the tables 3.5 – 3.8. The corrosion rates are calculated at a pressure of 55 bar to compare it with the corrosion rates at 90 bar.

At pressure = 55 bar and CO₂ = 1.1%

Table 3.5: Corrosion rates for Project A at different temperatures and pH values in condensed water at 55 bar

Temperature [°C]	pH in condensed water	Corrosion rate [mm/year]
5	4	0.37
10	4	0.8
15	4	1.2
20	4	3.1
25	4.1	3.7
30	4.1	4.4
35	4.1	5.1
40	4.1	5.8
45	4.1	6.1
50	4.1	6.4
55	4.2	6.6
60	4.2	6.8
65	4.2	6.9
70	4.2	6.9
75	4.2	6.9
80	4.2	6.9
85	4.3	5.5
90	4.3	4.3
95	4.3	4.4
100	4.3	4.5
110	4.4	4.7
113	4.4	4.7

It is observed from the table that the calculated corrosion rate increases even more. At a pressure of 55 bar the calculated corrosion rate is 6.9 mm/year compared to 6.6 mm/year in Figure 3.1.

At pressure = 90 bar; CO₂ = 1.1%

Table 3.6: Corrosion rates for Project A at different temperatures and pH values in condensed water at 90 bar

Temperature [°C]	pH in condensed water	Corrosion rate [mm/year]
5	3.9	0.42
10	3.9	0.9
15	4	1.4
20	4	3.7
25	4	4.6
30	4	5.4
35	4	6.3
40	4	7.2
45	4	7.6
50	4	7.9
55	4.1	8.2
60	4.1	8.5
65	4.1	8.6
70	4.1	8.7
75	4.1	8.8
80	4.2	8.6
85	4.2	7.1
90	4.2	5.6
95	4.2	5.7
100	4.2	5.8
110	4.3	5.9
113	4.3	6

From this table it is observed that the highest corrosion rate at 90 bar pressure has increased to 8.8 mm/year compared to 8.3 mm/year when it was assumed that the pH value was constant at different temperatures in graph 3.2.

The same calculations are carried out to obtain the corrosion rates considering the pH values of formation water and the results are plotted in tables.

At pressure = 55 bar and CO₂ = 1.1%

Table 3.7: Corrosion rates for Project A at different temperatures and pH values in formation water at 55 bar

Temperature [°C]	pH in formation water	Corrosion rate [mm/year]
5	5.7	0.21
10	5.6	0.4
15	5.6	0.58
20	5.6	1.3
25	5.6	1.6
30	5.6	1.9
35	5.6	2.3
40	5.6	2.6
45	5.6	2.5
50	5.6	2.3
55	5.6	2.2
60	5.6	2.1
65	5.6	2
70	5.6	1.9
75	5.6	1.8
80	5.6	1.7
85	5.6	1.1
90	5.6	0.4
95	5.6	0.46
100	5.6	0.51
110	5.7	0.57
113	5.7	0.61

At pressure = 90 bar and CO₂ = 1.1%

Table 3.8: Corrosion rates for Project A at different temperatures and pH values in formation water at 90 bar

Temperature [°C]	pH in formation water	Corrosion rate [mm/year]
5	5.5	0.25
10	5.5	0.47
15	5.5	0.68
20	5.5	1.7
25	5.4	2.3
30	5.4	2.8
35	5.4	3.2
40	5.4	3.7
45	5.4	3.6
50	5.4	3.5
55	5.4	3.4
60	5.4	3.3
65	5.4	3.2
70	5.4	3
75	5.4	2.9
80	5.4	2.7
85	5.4	1.8
90	5.4	0.78
95	5.4	0.81
100	5.5	0.73
110	5.5	0.84
113	5.5	0.87

After going through the method of calculating the corrosion rates for the different types of water and different temperatures, a good estimate of the corrosion rates is acquired, upon which the pipeline designs can be based.

The corrosion rate calculated in the case of condensed water was just a demonstration as mentioned above and will not be considered when calculating the corrosion allowance. Hence, the highest corrosion rate is 3.7 mm/year in the case of formation water.

Step 2: Calculating corrosion allowance for Project A

Step one is complete and the corrosion allowance can now be calculated. This can be done by using the formula given in NORSOK M-001 Materials Selection (2014). The formula is as follows:

$$CA = \sum_{i=1}^n \left[\frac{A}{100} \cdot CR_{in} + \left(\frac{100 - A}{100} \right) \cdot CR_u \right]$$

Where:

CA: corrosion allowance [mm]

A: availability of corrosion control [%]

N: number of periods with constant conditions

CR_{in}: corrosion rate with corrosion control [mm/year]

CR_u: corrosion rate without corrosion control [mm/year]

According to NORSOK M-001 (2014) the availability of corrosion inhibitor should be 0.9 (90%), unless otherwise defined, and the inhibited corrosion rate for pipelines should be 0.1 or 0.2 mm/year.

Since the worst-case scenario is considered, the parameters will be chosen as follows:

A= 90%

N=11 years

CR_{in}=0.2 mm/year

CR_u=3.7 mm/year (corrosion rate due to formation water)

This gives the following corrosion allowance:

$$CA = [(0.9 \times 0.2) + (0.1 \times 3.7)] \times 11 = 6.05 \text{ mm}$$

According to NORSOK M-DP-001 (1994) the upper limit of the total corrosion allowance for a submarine pipeline should be 10mm. Furthermore, carbon steel may be used in pipelines if the calculated inhibited annual corrosion rate is less than 10mm divided by the design life, which in this case is 0.9mm/year. Also, the recommended minimum internal corrosion allowance for carbon manganese (C-Mn) pipelines should be 3mm according to DNV-OS-F101 (2013), where C-Mn is a type of carbon steel. These conditions are satisfied and carbon steel can be used for Project A.

Based on the obtained pH values, Figure 1 in ISO 15156-2 (2015) is investigated, which shows the regions of environmental severity with respect to the stress corrosion cracking (SCC) of carbon and low-alloy steels. At the design stage, it is preferable to assume the worst conditions, which in this case is a pH value of 4.3. The lower the pH value the more corrosive it is. Taking into account the pH value and the partial pressure of H₂S, it is observed that it is just on the limit between region 1 and region 2. To be on the safe side, region 2 is considered. This is defined as sour service and leads to the below conclusions.

Conclusion:

- According to the Figure-1 in ISO 15156-2, Project A lies in region 1, which means that it is possible choose the steel from either section A.2, section A.3 or section A.4 of ISO 15156-2.
- The more economic solution should be chosen based on availability and ease of securing the materials.

3.3 Project B

The parameters of project B are shown in the following table.

Table 3.9: Parameters of Project B

Parameter	Value
Maximum design temperature [°C]	90
Operating pressure [barg]	50-90
CO ₂ content [mole%]	4.38
Bicarbonate concentration [mg/L]	541
Chloride content [mg/L]	38200
TDS/Salinity [g/L]	63.3
pH ₂ S [kPa]	FW: 0.8; CW: 0.31
Liquid flow rate [Sm ³ /d]	6413
Gas flow rate [MSm ³ /d]	1.6
Water cut [%]	10
Pipe ID [mm]	305.2
Design life [years]	20

Step 1: Calculating the uninhibited corrosion rate for Project B

The same steps as in project A are done and the same NORSOK M-506 program is used.

The first step is to calculate the different pH values taking into account the range of the operating pressures.

The results of the pH values are shown in the following table:

Table 3.10: Calculate pH values for Project B

Pressure [bar]	Type of water	Calculated pH
50	Condensed	4
90	Condensed	3.9
50	Formation	5.7
90	Formation	5.4

In the case of condensed water at 90 bar pressure and p_{H_2S} of 0.31 kPa the lowest pH value is 3.9.

The next step is to calculate the shear stresses. Again, the required parameters are inserted in the program and the following results are obtained and listed in table

Table 3.11: Calculated shear stresses for Project B

Pressure [bar]	Shear stress [Pa]
50	13
90	9

The uninhibited corrosion rate is then calculated and the results are listed in table:

Table 3.12: Calculated corrosion rates for Project B

Pressure [bar]	pH	Shear stress [Pa]	Corrosion rate [mm/year]
50	4	13	11
50	5.7	13	0.86
90	3.9	9	15
90	5.4	9	1.9

The highest corrosion rate is 15 mm/year. This is already too high compared to the corrosion rate of 3.7 mm/year obtained in project A. To save time, the corrosion allowance is directly calculated using the corrosion rate of 15 mm/year to see if it is

still within the specified limits. If it is within the limits, or at least close to it, then the corrosion rate can be fine tuned like in Project A, but if it is too far from the limit then it is unnecessary.

Step 2: Corrosion allowance for project B

The corrosion allowance is calculated with a corrosion rate of 15 mm/year. The same formula used for calculating the corrosion allowance in Project A is used here again, but with the following parameters:

$$A = 90\%$$

$$N = 20 \text{ years}$$

$$CR_{in} = 0.2 \text{ mm/year}$$

$$CR_u = 15 \text{ mm/year}$$

Hence, the following corrosion allowance is calculated.

$$CA = [(90 \times 0.2) + (0.1 \times 15)] \times 20 = 33.6 \text{ mm}$$

This corrosion allowance is too high, since it should be less than 10 mm, which is the upper limit according to NORSOK M-DP-001 (1994). It is more than three times as much. In this case carbon steel cannot be used and it is not even necessary to fine-tune the results for the corrosion rate as was done in Project A. CRA materials presented in chapter 2 should be considered and this will be discussed in the next chapter.

3.4 Project C

The parameters of this project are listed in the below table 3.13.

Table 3.13: Parameters of Project C

Parameter	Value
Maximum design temperature [°C]	130
Operating pressure [barg]	50-100
CO ₂ content [mole%]	3.8
Bicarbonate concentration [mg/L]	
Chloride content [mg/L]	175000
TDS/Salinity [g/L]	276
pH ₂ S [kPa]	0.2
Liquid flow rate [Sm ³ /d]	-
Gas flow rate [MSm ³ /d]	-
Water cut [%]	-
Pipe ID [mm]	151.3
Design life [years]	15

For Project C, it is mentioned in the assumptions at the beginning of chapter 3 that internal corrosion inhibitor is not permitted due to operational considerations and therefore C-Mn steel is eliminated as a viable option. In this case it is unnecessary to calculate the corrosion rate or the corrosion allowance as these calculations are mainly done to know if carbon steel can be used or not. In this case CRA materials are immediately considered.

However, it is still important to obtain the pH values, as they are important when choosing the CRA materials.

Table 3.14: Calculated pH values of Project C

Pressure [bar]	Type of water	Calculated pH
50	Condensed	4.2
100	Condensed	4
50	Formation	5.6
100	Formation	5.3

The pH values were calculated at a temperature of 130°C.

The calculations show that it is not possible to use carbon steel in Project B and it is stated in Project C that C-Mn is not qualified as a candidate material; we have to look at some alternatives. Those alternatives are:

- C-Mn steel lined with 3mm AISI 316L
- 13%Cr stainless steel
- Duplex 22%Cr stainless steel and duplex 25%Cr stainless steel
- C-Mn steel lined with 3mm nickel-based alloys 625 and 825

The C-Mn steel lined with 3 mm AISI 316L and the C-Mn steel lined with nickel based alloys are normal C-Mn steel pipes with a 3 mm layer of corrosion resistant material on the inside. The properties of the materials will be discussed in detail in chapter 4.

Chapter 4 Results and material selection

4.1 Results

The following results are based on following the guidelines and recommendations of the ISO 15156-3 standard, which defines the allowable environmental and material limits.

- C-Mn steel can be used in Project A because the calculated corrosion allowance is within the limits specified by Norsok M-DP-001 and DNV-OS-F101.
- C-Mn steel can't be used for Project B because the calculated corrosion allowance exceeds 10mm, which is the allowable limit. CRAs have to be considered for this project.
- C-Mn lined with 3mm 316L is qualified for Project B, but it is not qualified for Project C.
- The other CRA candidates presented in this thesis are qualified for both Project B and Project C.

The qualified steels and their grades for Project B and Project C have been identified and presented. Table 4.1 gives an overview of the materials discussed earlier.

Table 4-1: Steels and steel grades qualification for the projects

Material	Project B	Project C
316L (S31603)	Qualified	Not qualified
13% Cr	Qualified	Qualified
22% Cr (S31803)	Qualified	Qualified
25% Cr (S32750)	Qualified	Qualified
25% Cr (S32760)	Qualified	Qualified
625-Alloy (N06625)	Qualified	Qualified
825-Alloy (N08825)	Qualified	Qualified

4.2 Material selection

C-Mn lined with 3mm AISI 316L

Project B

The maximum operating temperature in project B is 90°C and the chloride content is 38,200 mg/l, which is less than 50,000 mg/l. Since the chloride level stated in the table is so high, then we are talking about formation water, because the chloride content in condensed water usually does not go above 600 mg/l. The partial pressure of H₂S in Project B is 0.8 kPa in formation water, which is less than 1 kPa stated in the table. Our previously calculated pH value in formation water is 5.7 at 50 bar pressure and 5.4 at 90 bar pressure. In both cases we have pH values greater than 4.5. So, all the conditions are met for the use of 316L stainless steel grade in project B.

Project C

The C-Mn steel lined with 3mm 316L grade can't be used in project C because the maximum design temperature is 130°C and at that temperature the maximum allowable chloride content is 1000 mg/l, while the actual amount of chloride present in project C is 175,000 mg/l. This is enough to eliminate 316L grade steel as a possible candidate for that project.

Supermartensitic 13% Cr stainless steel

Supermartensitic 13% Cr martensitic stainless steels have excellent resistance against CO₂ corrosion in environments that contain low amounts of H₂S. It might be susceptible to SCC corrosion but it is not the primary failure mechanism, according to ISO 15156-3 (2015). Sulphide stress cracking is the primary threat to martensitic stainless steels, but a lot of research has been conducted to improve the corrosion resistance against SSC and significant progress has been made in that field.

Project B

The p_{H₂S} in Project B is 0.8 kPa in formation water and 0.31 kPa in condensed water, so in both cases it is under the limit stated in ISO 15156-3 (2015). As for the pH value, according to the calculations above the pH is always greater than 3.5. Those are the two main conditions for the selection of martensitic stainless steel for pipelines, so 13% Cr is qualified as a potential candidate for this project.

Project C

The same conditions apply here as well, since the p_{H_2S} in this project is only 0.2 kPa and the pH value is above 3.5, then 13% Cr stainless steel is also qualified for this project.

22% Cr and 25% Cr duplex stainless steels

Project B

The environmental and material limits for 22% Cr stainless steel are stated in ISO 15156-3 in table A.24. The 22% Cr (S31803) can be used in temperatures up to 232°C and can withstand a partial pressure of H_2S of 10 kPa. Those conditions are much higher than what we have in project B and that renders the 22% Cr steel as a qualified candidate.

The 25% Cr stainless steel has higher strength and higher mechanical properties and can be used harsher environments than the 22% Cr stainless steel and can be used in project B as well.

Project C

Since the parameters of project C do not exceed the limits of table A.24 in ISO 15156-3, then 22% Cr and 25% Cr stainless steels are qualified for use in this project.

Nickel based alloys N06625 and N08825

Project B

The table A.14 in ISO 15156-3 shows the environmental and materials limits annealed and cold-worked, solid solution nickel-based alloys. If we look at the different combinations of parameters, we see that both alloys can be used in of the cases, since the parameters of project B will never exceed any of the conditions stated in the table.

Project C

The parameters of project C do not exceed the conditions stated in table A.14 in case, and we can be used the 625-alloy and the 825-alloy in that project as well.

Chapter 5 Discussion

By using the NORSOK M-506 computer program, different corrosion rates were calculated as the different temperatures, pH values and pressures were inserted. The obtained results were then plotted in graphs and tables and the following was observed:

- The corrosion rate increases as pressure increases.
- The corrosion rate increases as the temperature increases.
- The corrosion rate increases as the pH value decreases.
- The temperature does not have a significant effect on the pH value.

Pipelines will experience temperature fluctuations throughout its lifetime. The flow rate is also not constant and will change over time, which will have an effect on the internal pressure. Those factors alone are capable of affecting the corrosion rate significantly and their different combinations have to be investigated to take every corrosion rate possible into account. Hence the corrosion rate itself is not constant.

It has been demonstrated how materials are selected based on the parameters of the projects and based on the standards' requirements, as has been demonstrated how those materials are compared based on the main properties, such as mechanical properties and corrosion resistance.

In general, it is not an easy process and the material selection process for pipeline design is much more complicated and could take up to several months to reach a conclusive decision. The different companies and individual engineers approach this challenge from different points of view. Furthermore, there is a lot of testing involved in the process along with computer simulations. Lab tests aid in reaching the best decisions, but that is an extensive topic in its own right, which needs to be addressed separately.

Nevertheless, the process presented in this thesis is still very much in line with the actual process. By referring to ISO 15156-3 (2015), valid conclusions were reached. For example, 316L stainless steel is qualified for Project B, but not Project C, and the other CRAs are qualified for both projects B and C. Knowing the exact cost of the steels would have helped narrowing down the list even more. Furthermore, many other design aspects need to be addressed, such as external and internal pressures, submerged weight of the pipeline and wall thickness.

As a general rule, the more alloying elements are added to the steel the better mechanical properties the steel will have and the more corrosion resistant it will get. On the other hand, it will become more expensive.

It might be argued that choosing the material based on literature and experience could be a time and money saving solution. However, this method lacks practical data to support it. Every project is carried out in a different environment with different conditions, and one must be sure about his selection by conducting tests. There is a great chance of failure if the selection is based on theory only, and this is not acceptable, since failure in the pipelines in the oil and gas industry could lead to loss of life and environmental catastrophes. Materials selection is a very critical process, which if done correctly, ensures the safety of the people and the environment. The candidate CRAs must be tested in simulated environments to ensure safety.

It should also be noted that the standards are there as guidelines and to show the minimum requirements. There are still a lot of uncertainties and unclear conditions. For example, the limits of the combinations of H₂S and temperature is still not very clear for certain alloys. In some cases there is not enough data to make conclusive decisions and further tests need to be made.

Reaching the exact decision on which type of steel to use requires a lot more information than that was available in this thesis, and also needs the experience of engineers who have worked for a few years in this field.

Chapter 6 Conclusion and recommendations

6.1 Conclusion

Pipelines are a crucial part of any oil and gas project. They are the main means of transporting hydrocarbons across long distances. This method of fluid transportation has existed for centuries and is still being used and improved until today. As the oil and gas industry continues to explore new and more remote areas, the environments get harsher and pose more difficult challenges for pipelines to operate in these environments. Corrosion remains to be one of the main challenges, and although it can't be avoided, researches and tests conducted over the years have helped gain a better understanding of the problem and how to contain it to a high degree. Thanks to the technological advances, pipelines are now able to operate for years without failure. The mechanical properties and corrosion resistance of the different types of steels are being enhanced, which renders them fit for operating in the harshest conditions. It's a big step forward in exploring new territories while ensuring the safety of the people and preserving the environment. The standards are being continuously updated and they make the material selection process safer and more secure.

6.2 Recommendations

When approaching a new project the following points have to be considered:

- The parameters of the reservoir have to be studied and identified.
- Know which corrosion mechanisms are to be expected based on the nature of the reservoir.
- Corrosion rate prediction models could be used to get a better understanding of the situation and to be well informed for the material selection process.
- Follow the standards, such as ISO, DNV, and NORSOK in the design stage.
- Simulation programs have to be used to model the pipeline in the specified environment.
- Integrity of the pipeline has to have a priority over cost, as safety comes first.

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Appendix A ISO 15156-3 (2015) Tables

A.2.2 Environmental and materials limits for the uses of austenitic stainless steels

Table A.2 — Environmental and materials limits for austenitic stainless steels used for any equipment or components

Materials type/ individual alloy UNS number	Temperature max °C (°F)	Partial pressure H ₂ S <i>p</i> _{H₂S} max kPa (psi)	Chloride conc. max mg/l	pH	Sulfur-resistant?	Remarks
Austenitic stainless steel from materials type described in A.2 ^a	60 (140)	100 (15)	See "Remarks" column	See "Remarks" column	No	Any combination of chloride concentration and <i>in situ</i> pH occurring in production environments is acceptable.
	See "Remarks" column	See "Remarks" column	50	See "Remarks" column	No	These materials have been used without restrictions on temperature, <i>p</i> _{H₂S} , or <i>in situ</i> pH in production environments. No limits on individual parameters are set, but some combinations of the values of these parameters might not be acceptable.
S31603 ^b	60 (140)	1 000 (145)	50 000	≥4,5	NDS ^d	
	90 (194)	1 000 (145)	1 000	≥3,5	NDS ^d	
	90 (194)	1 (0,145)	50 000	≥4,5	NDS ^d	
	93 (200)	10,2 (1,5)	5 000	≥5,0	NDS ^d	
	120 (248)	100 (14,5)	1 000	≥3,5	NDS ^d	
	149 (300)	10,2 (1,5)	1 000	≥4,0	NDS ^d	
S20910 ^c	66 (150)	100 (15)	See "Remarks" column	See "Remarks" column	No	Any combination of chloride concentration and <i>in situ</i> pH occurring in production environments is acceptable.

Table A.14 — Environmental and materials limits for annealed and cold-worked, solid-solution nickel-based alloys used as any equipment or component^a

Materials type	Temperature max °C (°F)	Partial pressure H ₂ S P _{H2S} max kPa (psi)	Chloride conc. max mg/l	pH	Sulfur- resist- ant?	Remarks
Cold- worked alloys of types 4c, 4d and 4e	232 (450)	200 (30)	See "Remarks" column	See "Remarks" column	No	Any combination of chloride concentration and <i>in situ</i> pH occurring in production environments is acceptable.
	218 (425)	700 (100)	See "Remarks" column	See "Remarks" column	No	
	204 (400)	1 000 (150)	See "Remarks" column	See "Remarks" column	No	
	177 (350)	1 400 (200)	See "Remarks" column	See "Remarks" column	No	
	132 (270)	See "Remarks" column	See "Remarks" column	See "Remarks" column	Yes	Any combination of hydrogen sulfide, chloride concentration, and <i>in situ</i> pH in production environments is acceptable.
Cold- worked alloys of types 4d and 4e	218 (425)	2 000 (300)	See "Remarks" column	See "Remarks" column	No	Any combination of chloride concentration and <i>in situ</i> pH occurring in production environments is acceptable.
	149 (300)	See "Remarks" column	See "Remarks" column	See "Remarks" column	Yes	Any combinations of hydrogen sulfide, chloride concentration, and <i>in situ</i> pH in production environments are acceptable.

Table A.24 — Environmental and materials limits for duplex stainless steels used for any equipment or component

Materials type/ individual alloy UNS number	Temperature max °C (°F)	Partial pressure H ₂ S PH ₂ S max kPa (psi)	Chloride conc. max mg/l	pH	Sulfur-resistant?	Remarks
$30 \leq F_{PREN} \leq 40,0$ Mo $\geq 1,5$ %	232 (450)	10 (1,5)	See "Remarks" column	See "Remarks" column	NDS ^a	Any combination of chloride concentration and <i>in situ</i> pH occurring in production environments is acceptable
S31803 (HIP)	232 (450)	10 (1,5)	See "Remarks" column	See "Remarks" column	No	
$40,0 < F_{PREN} \leq 45$	232 (450)	20 (3)	See "Remarks" column	See "Remarks" column	NDS ^a	
$30 \leq F_{PREN} \leq 40,0$ Mo $\geq 1,5$ %	See "Remarks" column	See "Remarks" column	50	See "Remarks" column	NDS ^a	These materials have been used without restrictions on temperature, pH ₂ S or <i>in situ</i> pH in production environments. No limits on individual parameters are set, but some combinations of the values of these parameters might not be acceptable.
$40,0 < F_{PREN} \leq 45$	See "Remarks" column	See "Remarks" column		See "Remarks" column	NDS ^a	

Table B.1 — Cracking mechanisms that shall be considered for CRA and other alloy groups

Materials groups of Annex A	Potential cracking mechanisms in H ₂ S service ^{a, b}			Remarks
	SSC	SCC	GHSC	
Austenitic stainless steels (see A.2)	S	P	S	Some cold-worked alloys contain martensite and can therefore be sensitive to SSC and/or HSC.
Highly-alloyed austenitic stainless steels (see A.3)	—	P	—	These alloys are generally immune to SSC and HSC. Low-temperature cracking tests are not normally required.
Solid-solution nickel-based alloys (see A.4)	S	P	S	Some Ni-based alloys in the cold-worked condition and/or aged conditions contain secondary phases and can be susceptible to HSC when galvanically coupled to steel. In the heavily cold-worked and well-aged condition coupled to steel, these alloys can experience HSC.
Ferritic stainless steels (see A.5)	P	—	P	—
Martensitic stainless steels (see A.6)	P	S	P	Alloys containing Ni and Mo can be subject to SCC whether or not they contain residual austenite.
Duplex stainless steels (see A.7)	S	P	S	Cracking sensitivity can be highest at a temperature below the maximum service temperature and testing over a range of temperatures shall be considered.
Precipitation-hardened stainless steels (see A.8)	P	P	P	—
Precipitation-hardened nickel base alloys (see A.9)	S	P	P	Some Ni-based alloys in the cold-worked condition and/or aged conditions contain secondary phases and can be susceptible to HSC when galvanically coupled to steel.
Cobalt-based alloys (see A.10)	S	P	P	—
Titanium and tantalum (see A.11)	See “Remarks” column			Cracking mechanisms depend upon the specific alloy. The equipment user shall ensure appropriate testing and qualification is carried out.
Copper and aluminium (see A.12)	See “Remarks” column			These alloys are not known to suffer from these cracking mechanisms

Appendix B Screenshots from NORSOK M-506 program and excel tables

The screenshot displays the NORSOK M-506 pH Menu dialog box, which is used for calculating the pH value. The dialog is titled "NORSOK M-506 pH Menu" and is divided into several sections:

- Input:** Fields for Project (Projcet A), Equipmen, Identifier, Temperature (113 °C), Pressure (90 bar), Mole percent CO2 in gas (1.1 mole%), Bicarbonate (238 mg/l), Ionic strength (147 g/l), and a Comment field.
- Option:** Radio buttons for "Condensed water" and "Formation water" (selected).
- Run:** A "Calculate" button.
- Output:** A field for "Calculated pH" showing the value 5.5.

The background shows an Excel ribbon with "Merge", "0%", and "Conditional Formatting" options.

Figure B.1: Calculating pH value for Project A at 90 bar pressure and in formation water

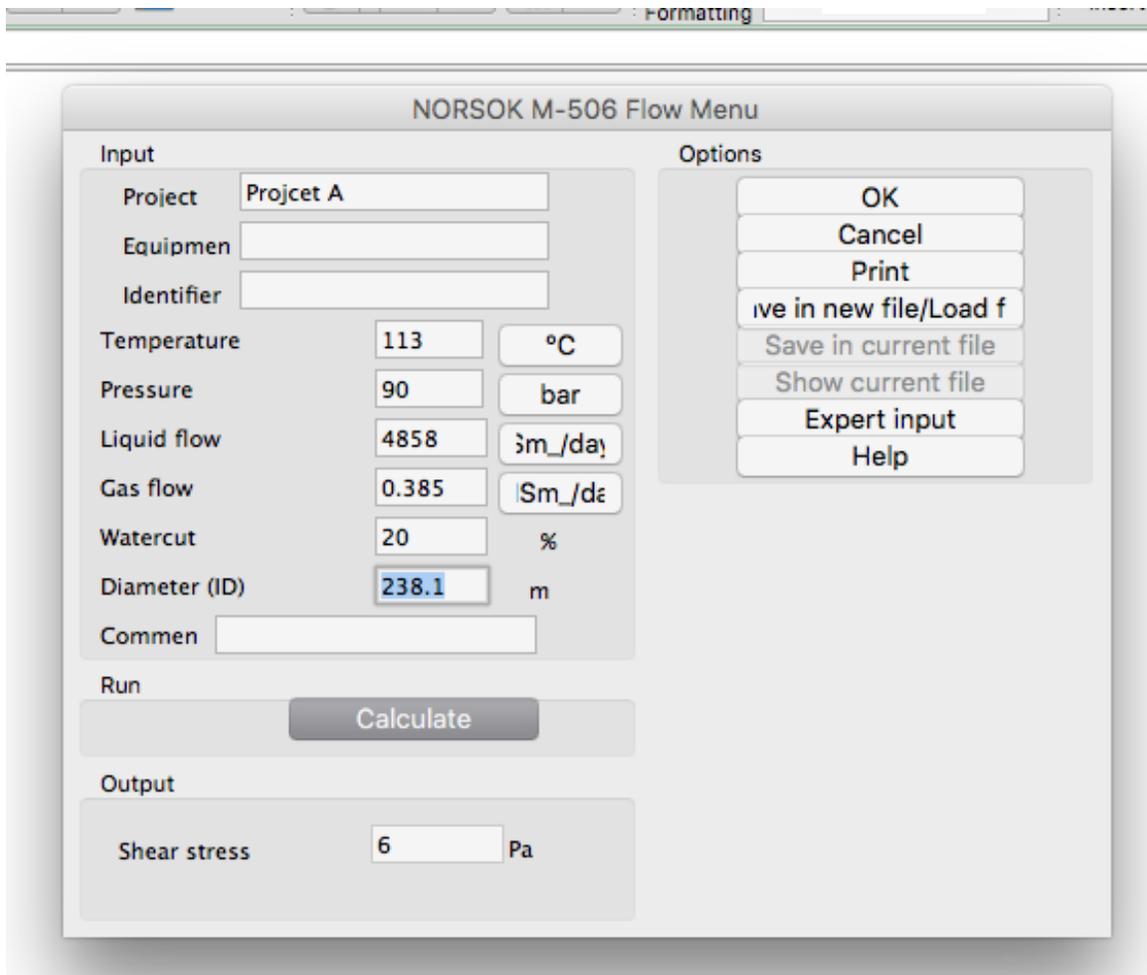


Figure B.2: Calculating shear stress in Project A

NORSOK M-506 Main menu

Input

Project

Equipmen

Identifier

Temperature °C

Pressure bar

Mole percent CO2 in mole%

Shear stress Pa

pH

Glycol concentration %

Inhibitor efficiency %

Commen

CO2 fuqacity bar

Run the corrosion rate model

Calculate corrosion rate

Options on input

Use as CO2 pressure
 CO2 fugacity

Calculate shear stress

Calculate pH

Options

Parameter study

Accumulated corrosion

Calculate humidity

Print

Save in new file / Load file

Save in current file

Show current file

Help

Exit

Output

Corrosion rate without inhibitor mm/year

Figure B.3: Calculating corrosion rate for Project A

NORSOK M-506 Main menu

Input

Project

Equipmen

Identifier

Temperature °C

Pressure bar

Mole percent CO2 in mole%

Shear stress Pa

pH

Glycol concentration %

Inhibitor efficiency %

Commen

CO2 fuqacity bar

Run the corrosion rate model

Calculate corrosion rate

Options on input

Use as CO2
 pressure
 CO2 fugacity

Calculate shear stress

Calculate pH

Options

Parameter study

Accumulated corrosion

Calculate humidity

Print

Save in new file / Load file

Save in current file

Show current file

Help

Exit

Output

Corrosion rate without inhibitor mm/year

Figure B.4: Calculating corrosion rate for project B