Modeling of Corrosion Rate Inside a Pressure Vessel

Titel page

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Abstract

The idea of creating a digital twin that predicts the state of the inner wall of pressure vessels in the oil and gas industry, has been presented by Rambøll. This study investigates the possibility of creating a model in Matlab, that can determine the corrosion rate on this inner wall, where CO_2 is the cause of the corrosion. The model in which has been developed, are based on an already developed corrosion rate model developed by de Waard-Milliams. Since the de Waard-Milliams model is developed for corrosion in pipelines and wellhead corrosion. The model is then compared for use of pressure vessel, with some additional assumptions. Rambøll has provided inspection data for three different pressure vessels, where each vessel has different content flowing through the vessel. This data is used in the model, as the model is used to predict the corrosion depth as detected during inspections. The model proved to some extent capable to determine the corrosion rate due to CO_2, however, it did not prove to describe the corrosion depth to its fullest extent. In order for the model to be a fully predictor of corrosion in a pressure vessel, several other factors needs to be included in the model e.g., Corrosion due to H_2S, and water containing some sort of salts.

Reading Guide

To distinguish between figures, equations, and citations, [] is used for referring to citations and numbers used for referring to figures and equations.

Contents

Nomenclature

d Diameter of the pressure vessel

F_g Effect of CO_2 fugacity

F_{H_2S} Scale formed due to H_2S

F_{oil} Presence of crude oil on the corrosion rate

P Operation pressure of the pressure vessel

p_{H_2S} partial pressure of H_2S

U_{liq} Liquid flow rate

V_m dependent flow contribution for mass transfer rate

V_r Independent flow contribution for rate of reaction

V_{cor} CO_2 corrosion rate

x_{CO_2} Molar fraction of CO_2

T   Temperature given in degrees Celsius

Chapter 1

Introduction

The idea of this project is given by the engineering- and consulting company Rambøll, which is working on producing a digital twin for determining the state of a pressure vessel, which should predict when the opportune moment for inspection of pressure vessels are needed. The main goal is to try and see if the expected inspection date can be delayed, or if the vessels need inspection sooner than this date. Rambøll is a large and global company that was founded in 1945, with presence in various countries as Denmark, Great Britain, North America, and more [?].

The oil and gas industry is one of the largest industries in the world, spreading over almost every country on the planet. It is essential for every part of the oil and gas industry to run at all times with minimum interruption in production e.g., oil. When a piece of production fails or has to be stopped for other reasons, the money lost throughout downtime can be significant. One of the largest causes for production shutting down is unscheduled maintenance, where one of the leading causes of this is due to corrosion damage on the inside of pressure vessels.

For a better understanding of how the oil and gas production functions figure 1.1
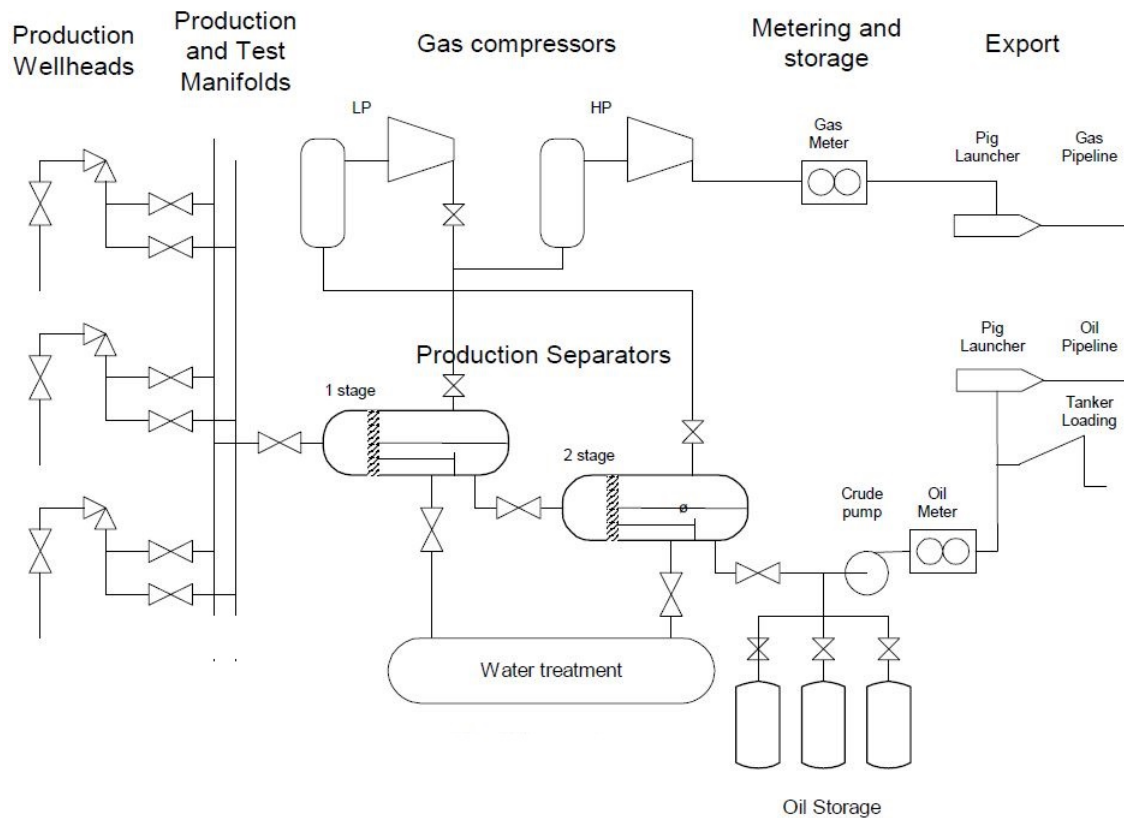
Figure 1.1: simple Illustration of how oil and gas production looks like[1]

Figure 1.1 shows how the oil, gas, and water enters a three-phase separator, from the well. The three-phase separator separates oil, gas, and water from each other, and often, this process is done more than once in order to get the most complete separation of the three phases. In figure 1.1, the three-phase separator, the water treatment chamber, and the two compartments before the compressors are all some sort of pressure vessel and are essentials for the production in the oil and gas industry[1].

This project will use pressure vessels as the equipment for investigation of the corrosion leading to fatigue or failure of these vessels. Pressure vessels have a wide range of usage in different industries. In the oil and gas industry pressure vessels are used in the separation phase, where the pressure vessel can be used in both the gas and liquid phase. A pressure vessel is in its basic form a tank that operates at a higher pressure than ambient pressure. These pressure vessels can vary in size but are often large, which means that the downtime of the production since they take longer time to inspect for corrosion damage. An illustration of a pressure vessel is seen in figure 1.2.

Figure 1.2: Illustration of how large pressure vessels can be [2]

There are two main ways that a pressure vessel can corrode, and be determined out of shape to be used for production, this is due to either internal or external corrosion.

Internal corrosion is where corrosion occurs due to the inner transported material. This can be due to the gas being transported inside the vessel.

The external corrosion is where the corrosion is caused by the outside environment of the vessel. This type of corrosion is highly affected upon the location of the pressure vessel, but where the vessel is exposed to rain, wind and varying temperatures is often a course for the pressure vessel to corrode external.

When talking about corrosion of a pressure vessel in the oil and gas industry, it is often the inside of the vessel, which is interesting to know the state of. Since these pressure vessels are made of metal of various sorts(usually carbon steel), and the fact that the content of these vessels can be highly corrosive, corrosion of the inside wall of the vessel is a significant and continuous problem. Looking at the gas inside a pressure vessel, two types of gases are often of interest, namely CO_2 and H_2S because these gas compounds are the primary corrosive components of the gas.

Corrosion is in its fundamental form deterioration of metal over time, often due to electrochemical reactions between the metal and the content inside of the pressure vessel. When corrosion of metal happens inside a pressure vessel, it can cause severe problems to the integrity of the metal structure depending on the type of corrosion, and the rate in which the corrosion takes place. If corrosion is not inspected closely in a pressure vessel it can course to leakage of gas or oil, an in some instances the

vessel can explode[3] [4] because of the pressure inside the vessel is larger than the external pressure. The explosion is in rare cases, so is not a common factor, and are only for high-pressure vessels.

1.1 Problem definition

One of the essential parts of the oil and gas industry is the separation process. This process can be both for gas-liquid phase and for purely the gas phase. For this process, a pressure vessel is used of different types. However, one common problem with the use of pressure vessels is that they are rather difficult to inspect for internal damage, generally in the form of corrosion. For this reason, the time between inspections is set with fixed intervals. In this period, there are no assessment tools of how the inside wall conditions of the vessel are, so there is no way of knowing how the state of the inner wall is if it is critical or not. When inspection of a pressure vessel is done, it takes a long time to go through all the parts that need an inspection, and in the oil and gas business, it is preferred that the production is ongoing all the time with the least amount of downtime possible. For a better understanding of what can be done in this area, the following questions will be asked.

- What can be done to predict the state of the inside of the pressure vessel

- Which existing models are there to assess the rate of corrosion

- What is the dependence of these models

As mentioned in the introduction the idea is given by Rambøll, that if possible, the creation of a digital twin of a pressure vessel during operation, in which can predict the state of the inside wall. This digital twin is set to run alongside the operating pressure vessel so that it can predict whether or not the vessel needs to be inspected inside the fixed time period, or if it can wait. This project will, however, mainly look into the rate of corrosion and will not be a complete digital twin of a pressure vessel.

Chapter 2

Corrosion and Scaling Theory

In this section, the theory of corrosion will be explained. Since both of these are a disadvantage and a problem in the oil and gas industry, a closer look at the theory behind corrosion. Since corrosion due to CO_2 is the main focus of this project.

2.1 Corrosion

The corrosion process for metallic materials is normally due to electrochemical reactions. The chemical reaction is when there is a transport of electrons between two chemical species, from one to the other. Atoms of metallic material characteristically lose or give up electrons, this is called an oxidization reaction. An example of this is defined in 2.1 where a hypothetical metal M, which has the valence of n electrons can experience oxidation reaction.

$$M \rightarrow M^{n+} + ne^- \tag{2.1}$$
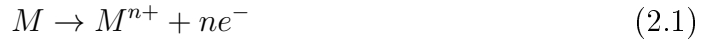
M then becomes positively charged with $n+$ ion, and at the same time, it loses its n valence electrons ne^-. The site where the oxidization happens is referred to as the anode, this is why oxidization also can be called an anodic reaction[5]. The free electrons cannot just be electrons on its own, so they will always transfer to other chemical species and be a part of this species, this is called a reduction reaction. An example of this is the corrosion of metals in acid solution, where there is a high concentration of hydrogen ions (H^+)[5]. The reaction of how the hydrogen ions are reduced is given in equation 2.2.

$$2H^+ + 2e^- = H_2 \tag{2.2}$$

Metals ions can also be reduced, where ions can exist a having more than one valance state, this is called multivalent ions. This means that by accepting an electron, the metal ion decreases its valance state, represented in equation 2.3

$$M^{n+} + ne^- \rightarrow M^{(n-1)+} \tag{2.3}$$

The metal can also be reduced to a complete neutral metal state from an ionic state, equation 2.4.

$$M^{n+} + ne^- \rightarrow M \tag{2.4}$$

The place where this reduction occurs is referred to as the cathode.

For a visual showing of how the corrosion occurs, figure 2.1 is illustrated. It shows how the oxidation of metal happens at the anode and that the reduction occurs in the cathode.
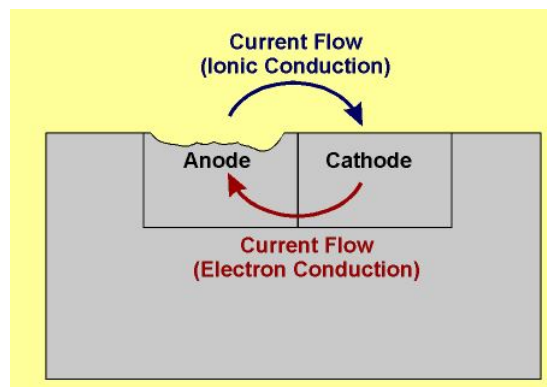

Figure 2.1: Basic showing of how corrosion on a metal surface happens [6]

Pitting

Pitting is a common but destructive form of localized corrosion. Pitting occurs when aggressive anionic chemical species combine with the metal. Here it is often seen that chloride ion(CL^-) the course of the pitting. Chloride is usually found as the anion is strong acids and many metal cations exhibit solubility in chloride solutions. Chloride is a relatively small anion with a high diffusivity, which means it interferes with passivation, which means that it interferes with the protective film that can be created on the inner wall that otherwise would protect the surface from corrosion[7].

Pitting can be seen as an autocatalyst, since when a pit starts to grow, the conditions that are developed in the pit, are favorable for further growth. When a pit is formed, it acts like a fixed anode, where the rest of the passive surface is a cathode[8]. The anodic and cathodic electrochemical reactions that can comprise corrosion spatially separate during pitting. The environment in the pit will be depleted of cathodic reactants e.g., oxygen. This shifts the cathodic reaction to the exposed surface where the reactant is plentiful. The environment inside the pit becomes rich in metal cations, where an anionic species like chloride will migrate into the pit to maintain the charge neutrality by balancing the charge associated with the cation concentration[7].

There are many different ways a pit can grow, this can be seen in figure 2.2 below.
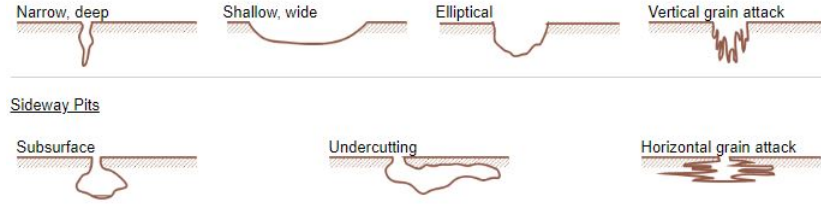

Figure 2.2: Different forms of pitting corrosion can take[9]

Corrosion due to CO2

The models in which are used in this project all mainly investigate corrosion due to CO_2, where different parameters are a factor. It is important to understand which electrochemical reactions that happen when CO_2 reacts with metal in order to start corroding.

The most common form for corrosion reaction is when iron carbonate($FeCO_3$) is formed. Before iron carbonate is formed, the chemical reactions that can happen between the ions involved. First, a look at the reaction when CO_2 is in an aqueous state, this reaction is shown in equation 2.5 and forms carbon acid. [10]

$$CO_2 + H_2O \rightarrow H_2CO_3 \tag{2.5}$$

The following reaction that happens is divided into three cathodic reactions and one anodic reaction. The first cathodic reactions are for the carbon acid into bicarbonate ions shown in equation 2.6.

$$2H_2CO_3 + 2e^- \rightarrow H_2 + H_2CO_3^- \tag{2.6}$$

The second cathodic reaction is from bicarbonate ions into carbonate ions, the reaction is shown in equation 2.7.

$$2H_2CO_3^- + 2e^- \rightarrow H_2 + H_2CO_3^{2-} \tag{2.7}$$

The third cathodic reaction is the reduction of hydrogen ions, reaction shown in equation 2.8.

$$2H^+ + 2e^- \rightarrow H_2 \tag{2.8}$$

The anodic reaction is the oxidation of iron to ferrous(Fe^{2+}) ions, this reaction is shown in equation 2.9

$$Fe \rightarrow Fe^{2+} + 2e^- \tag{2.9}$$

These reactions can lead to corrosive environments where the chemical environment promotes iron carbonate($FeCO_3$) formation. $FeCO_3$ can be formed in a couple of different reaction paths. The first reaction path is the direct formation of iron carbonate with ferrous ions and carbonate ions, as shown in equation 2.10.

$$Fe^{2+} + CO_3^{2-} \rightarrow FeCO_3 \tag{2.10}$$

The second path is divided into two steps in order to form iron carbonate. When ferrous ions react together with bicarbonate ions, it forms ferrous iron bicarbonate, which is shown in equation 2.11. The ferrous iron bicarbonate can subsequently be dissociated into iron carbonate, carbon dioxide, and water, reactions are shown in equation 2.12

$$Fe^{2+} + 2HCO_3^- \rightarrow Fe(HCO_3)_2 \tag{2.11}$$

$$Fe(HCO_3)_2 \rightarrow FeCO_3 + CO_2 + H2O \tag{2.12}$$
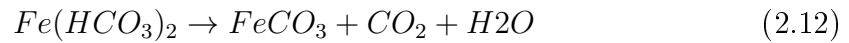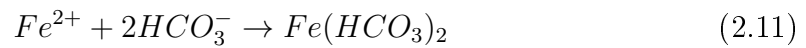
Chapter 3

State of the art for corrosion modeling

This study in the rate of corrosion on the inner surface of a pressure vessel is essential for the inspection phase of the pressure vessel in the oil and gas industry. There are several ways of determining the rate of corrosion on metal surfaces in various operations in the oil and gas industry. In this section, state-of-the-art of different corrosion models for predicting the rate of corrosion is presented and explained. Here the development of the models, and what they primarily contain, are described. Most of the models are empirical, meaning that some sort of experimental data is necessary for them to be solved.

The models in which will be mentioned in this state of the art section are all models in which has been used for other purposes than corrosion on the inside of a pressure vessel, mainly in pipelines. However, these models are all state-of-the-art for determining the corrosion rate of metal in the oil and gas industry and is seen as what is used for the purpose of predicting the corrosion on the equipment regardless.

De Waard Model

This model is developed by de Waard(hereafter denoted as Model DW) and different coworkers, was first published in 1975 where it was based on the dependence of temperature and P_{CO_2} [11][6]. For several years this model was the most widely used CO_2 corrosion used, it has however been revised several times since, where the model from 1995 is seen as the best fit for a large number of the data in which has been generated from laboratory data [6]. Model DW was calibrated for test data between 80-90 degree Celsius and did not take the formation of protective corrosion film into account. This Model DW also includes oil wetting as a factor, which is an on/off factor. It assumes oil wetting and no corrosion when the water cut is below 30 percent and with a liquid velocity higher than 1 m/s [12].

De Waard and Milliams model as it is first published looked like the following in equation 3.1

$$log(V_{cor}) = 7.96 - \frac{2320}{T + 273} - (5.55 \cdot 10^{-3})T + 0.67log(p_{CO_2}) \qquad (3.1)$$

Where

- V_{cor} is the corrosion rate given in $\frac{mm}{year}$

- T is temperature given in degrees Celsius

- p_{CO_2} is CO_2 partial pressure given in mPa

As mentioned the model was then revised later on due to experimental results found, later on, the revised model is shown in equation 3.2

$$log(V_{cor}) = 5.8 - \frac{1710}{T + 273} + 0.67 \cdot log(p_{CO_2}) \tag{3.2}$$

The partial pressure of CO_2 is calculated by taking the total operation pressure and multiplying it with the mole fraction of CO_2 in the content within the pressure vessel.

$$p_{CO_2} = x_{CO_2}P \tag{3.3}$$

Where

- x_{CO_2} is the mole fraction of CO_2

- P is the operation pressure of the pressure vessel

For further validation of this model, it was tried to model the corrosion rate with respect to the velocity, and the absence of surface scales, which resulted in equation 3.4

$$\frac{1}{V_{cor}} = \frac{1}{V_r} + \frac{1}{V_m} \tag{3.4}$$

Where in this instant the V_{cor} is the rate of corrosion, V_r is the independent flow contribution denoting the rate of reaction, and V_m is the flow-dependent contribution denoting the mass transfer rate. V_r can be found using equation 3.5

$$log(V_r) = 4.93 - \frac{1119}{T + 273} + 0.58 \cdot log(p_{CO_2}) \tag{3.5}$$

where V_m can be found from equation 3.6.

$$V_m = 2.45 \cdot \frac{U_{liq}^{0.8}}{d^{0.8}} \cdot p_{CO_2} \tag{3.6}$$

Where U_{liq} is the liquid flow rate, and d is the diameter of the pipe. This also indicates that this model is primarily made for determining the rate of corrosion done by CO_2 in pipelines.

Corporate corrosion models

In this section several, but not all corporate models will be described. A common denominator for all the following models are all complete software that predicts the corrosion rate fitted for each companies own benefit and own experience from working in the field.

The Norsok model (denoted Model NO) is an empirical model developed by a string of Norwegian oil companies(Statoil, Norsk Hydro, and Saga Petroleum). This model is fitted from much of the same experimental data as Model DW, however where Model DW only is for temperatures between 80-90 degree Celsius, Model NO as additional an more recent experimental data for 100-150 degree Celsius. Model NO takes more of the protective corrosion film into account that several other models do, including Model DW. [12] [13]

The Hydrocor model was developed by Shell in order to combine corrosion and fluid flow modeling. CO_2 corrosion models are coupled with models for multiphase flow, pH calculation, and iron carbonate prediction. This model has a simplified model of corrosion due to H_2S and corrosion due to organic acids. [12] [13]

CORPLUS model(denoted Model CO) is developed by Total, and is a combination of two older models that is no longer in use, because they are replaced with Model CO. Model CO is based on detailed analysis of water chemistry, effects of CO_2, organic acids, calcium, and a large amount of field data, primarily collected from wells. [12] [13]

Cassandra model(denoted Model CA) is a model by BP and is BP's implementation of Model DW from there own experience in working with the model. Compared with Model DW, a pH calculation module is included, meaning that the pH value is calculated from the CO_2 content, temperature, and water chemistry. Model CA can include or exclude the effect of the protective corrosion film by choosing the scaling temperature. The rate of corrosion is seen as being constant above the scaling temperature, instead of being reduced when the temperature is increased, as is does in Model DW. oil wetting effects are not included in this model. [12] [13]

As mentioned, these are all software developed to some extent by the companies themselves, and for this reason, the model in which they use as a corrosion rate predictor is not easily available for public use. This is the reason for not showing

the function as is possible for de Waard-Milliams model.

Chapter 4

Modeling

In this chapter, the modeling of the corrosion rate on the inner wall of a pressure vessel described. The chapter will follow how the different steps in the model are set up.

In order to simplify the model, the pressure vessel is seen as only having one inlet flow, and one outlet flow, where there often are multiple inlet and outlet flows in an actual pressure vessel. The reason for not having the various inlets and outlets is that the specific content of each species entering has to be known from each inlet, also given different flow velocities in the pressure vessel.

For this modeling of corrosion rate due to CO_2 inside a pressure vessel, Rambøll has provided three different pressure vessels, where specifications for each vessel is provided. The year of production start, with the inspection year and what has been measured in corrosion depth on the inner wall are also provided. The goal is to run the model for each of the three pressure vessels.

The model which is created in this chapter is based on a model in which predicts the corrosion rate in a pipeline [14]. Since the pressure vessel is set to have an inlet in one end and outlet in the other end, the pressure vessel can be seen as a part of a pipe. There are not found any models in which is based on the corrosion rate in pressure vessels, for this reason, this assessment is seen as valid.

For a better understanding of how the different values for the model are found, look at the Appendix, where the specifications for each of the three pressure vessels are located. Furthermore, the component list of the content within the pressure vessels is given in mole fractions.

There are several factors that need to be taken in to account when modeling the corrosion of any metal. In this model, the corrosion due to CO_2 is in priority, this leads to some factors not being taken into account, and only the ones most affected by the CO_2 corrosion. These are the factors of corrosion due to H_2S, the factor of the protecting coating in which vessels are typically coated with, the chance of there

being any form of salt in the water which is corrosive, and the formation of scale in the vessel due to CO_2. The complete line of factors are set to be multiplied with each other to get the correct corrosion rate, and this is displayed in equation 4.1

$$CR = V_{cor} \cdot F_g \cdot F_{H_2S} \cdot F_{oil} \tag{4.1}$$

Where

- V_{cor} is the CO_2 corrosion rate

- F_g is the effect of CO_2 fugacity

- F_{H_2S} is the scale formed due to H_2S

- F_{oil} is the presence of crude oil on the corrosion rate

V_{cor} is described earlier in the state-of-the-art section, therefore, this will not be shown once more, but is still a part of the model, this is the de Waard-Milliams model from 1995 that should be considered.

In this model, x_{CO_2} is the factor in which changes over time and taking vessel 2 as an example, the starting point is the first time the pressure vessel was inspected in 1997. A piece of important information is that the change in x_{CO_2} in the model is set to be linear from 1997-2010, where the step size is each year between the two inspections. The linear progression of the mole fraction of CO_2 is displayed as a graph for all three vessels
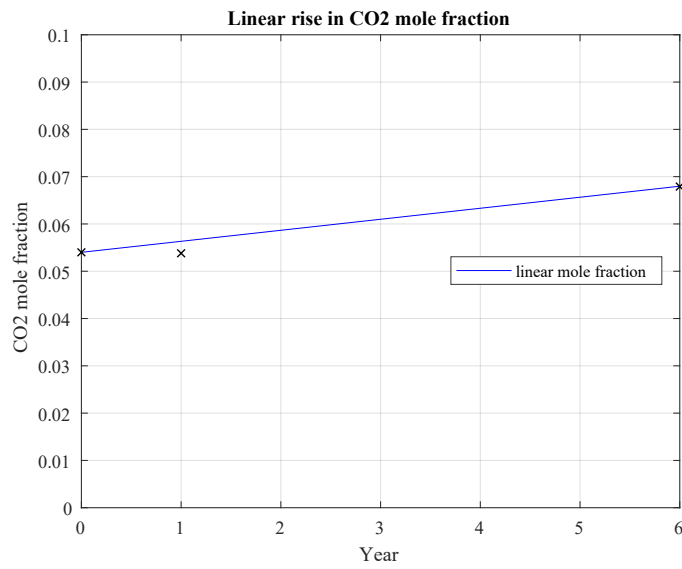
Figure 4.1: Graph that shows the linear progress of the CO_2 mole fraction for vessel 1
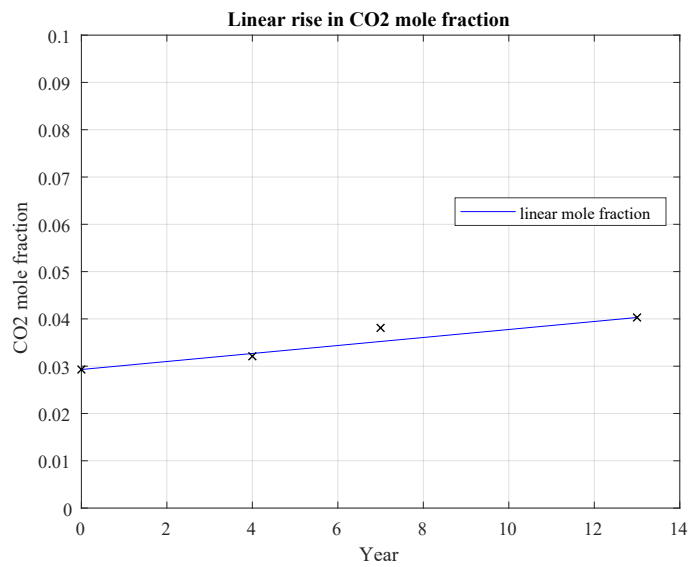

Figure 4.2: Graph that shows the linear progress of the CO_2 mole fraction for vessel 2
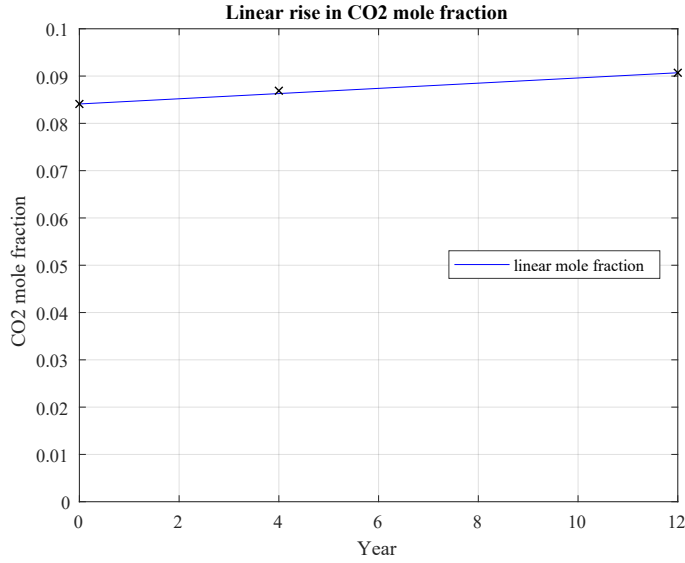
Figure 4.3: Graph that shows the linear progress of the CO_2 mole fraction for vessel 3

The dotted points in these graphs are the data from the inspections done of each of the pressure vessels found in the Appendix. By saying that the mole fraction of CO_2 is linear, it is seen that the mole fraction for the inspections does not hit the linear line. The effect of this will be discussed later in the project, for the purpose of the model, the linear line is used.

For the purpose of getting a better understanding of the rate of corrosion, the fugacity of CO_2 is necessary to be a factor. The fugacity is found by means of equation 4.2.

$$log(F_g) = 0.67(0.0031 - \frac{1.4}{T + 273})P \qquad (4.2)$$

Since H_2S also is a component of what passes through the pressure vessel, the prospect of the formation of a protective scale in the form of FeS is also a factor that needs to be taken into account, this factor is found in equation 4.3.

$$F_{H_2S} = \frac{1}{1 + 1800\frac{p_{H_2S}}{p_{CO_2}}} \qquad (4.3)$$

where p_{H_2S} is the partial pressure of H_2S.
In the case that crude oil is present in the pressure vessel this factor needs to be described in the model, however, since the velocity of the liquid in all vessels are

under 1 $\frac{m}{s}$ the factor of crude oil in the pressure vessels are set to be $F_{oil} = 1$

4.0.1 Further Development

Since this model is set to be a predictor of how the corrosion inside a pressure vessel will look like in the future, there are more factors in which it should be taken into account, these are mentioned earlier in this chapter.

A great deal of time in this project was spent on incorporating flash calculations in Matlab or known as a PTFlash function. The debt of the PTFlash function will not be explained. However, the PTFlash function is in its basic, a function in which compute the split in vapor and mole fraction, in a vapor-liquid compartment, or in another way, the PTFlash function explains the vapor-liquid equilibrium. This would especially benefit vessel 3, which is a mix of gas and liquid in the form of crude oil and water [15].

Furthermore, the time should be changed from year basis to monthly bases, this would make the model better as a predictor tool, which could be used in the oil and gas industry.

4.1 Results

This section the results of the model will be shown. The model has been fitted with the different specifications for each of the three pressure vessels, and the corrosion rate is calculated for each of the vessels. The way the results will be displayed is by putting the corrosion rate into a graph. This graph will then also contain the measured thickness of the pressure vessel wall from all the three vessels.

Vessel 1

The measured thickness of the wall of vessel 1 is found in table 4.1, which is the data provided from Rambøll

Table 4.1: Shows the detected corrosion inside vessel 1 during inspection

year	2010	2011	2016
Corrosion detected	0.3 [mm]	0.37 [mm]	0.79 [mm]

After each inspection, the pressure vessel has been coated again in places where corrosion has been detected. In order to see if the model describes the corrosion of

the vessel the model calculated corrosion rate, will be compared with the detected corrosion from the inspections done on vessel 1, this is done in figure 4.4.
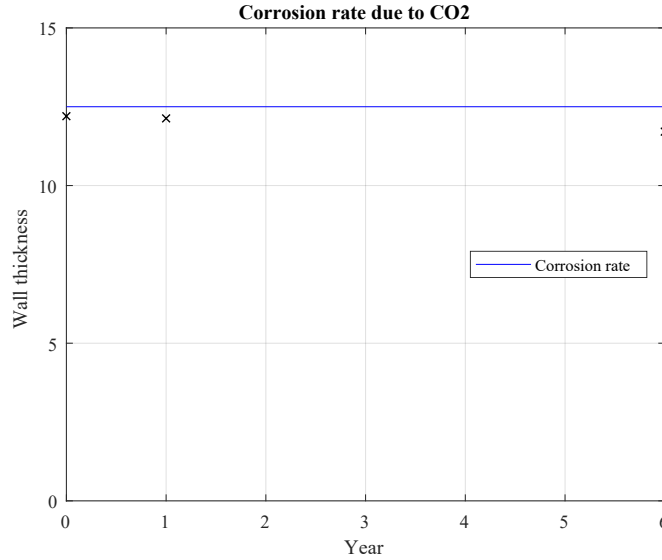

Figure 4.4: Shows the corrosion rate calculated by the model for vessel 1

The line in figure 4.4 is the corrosion rate over years calculated by the model, where the marks in the figure represent the measured corrosion depth given in table 4.1. Since the temperature for this vessel is ambient and that the content of the vessel is NGL gas, both the scale factor and the crude oil factor is neglected in the model. The corrosion rate due to CO_2 for vessel 1 is $0.1065e^{-5} \frac{mm}{year}$.

Vessel 2

Table 4.2: Shows the detected corrosion inside vessel 2 during inspection

year	1997	2001	2004	2010
Corrosion detected	1.5 [mm]	no data	1.7 [mm]	4.2 [mm]

In order to see if the model describes the corrosion of the vessel the model calculated corrosion rate, will be compared with the detected corrosion from the inspections done on vessel 2, this is done in figure 4.5.
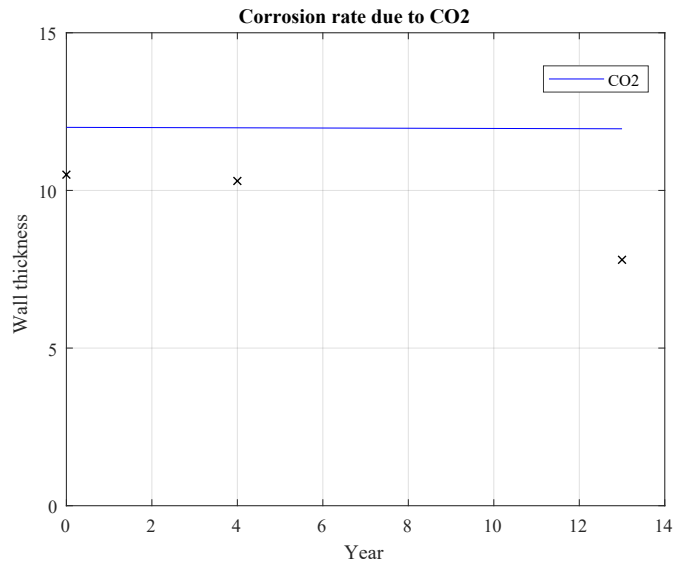
Figure 4.5: Shows the corrosion rate calculated by the model for vessel 2

Figure 4.5 describes the same as figure 4.4 that the corrosion rate over the years of operation calculated by the model, where the marks in the figure represent the measured corrosion depth given in table 4.2. The corrosion rate due to CO_2 for vessel 2 is $0.0035 \frac{mm}{year}$

Vessel 3

Table 4.3: Shows the detected corrosion inside vessel 3 during inspection

year	2005	2009	2017
Corrosion detected	1.2[mm]	1.6 [mm]	1.2 [mm]

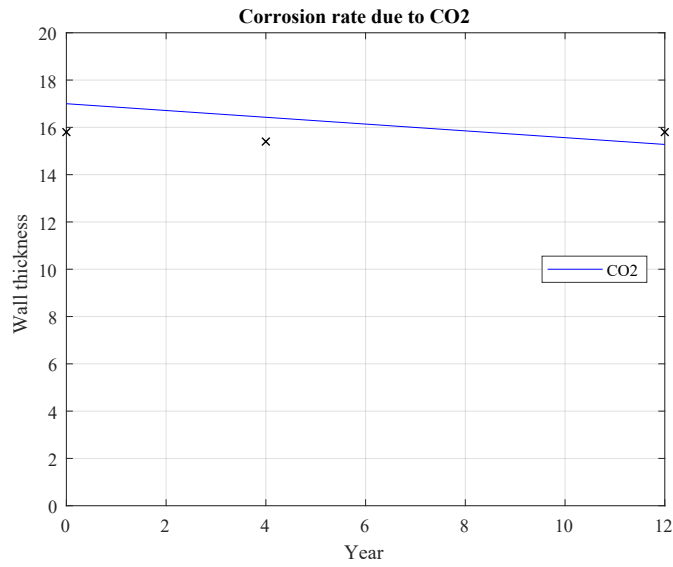Figure 4.6: Shows the corrosion rate calculated by the model for vessel 3

Figure 4.6 is the corrosion rate over years calculated by the model, where the marks in the figure represent the measured corrosion depth given in table 4.3. Since the temperature for this vessel is ambient, the scale factor is neglected in the model. The corrosion rate due to CO_2 for vessel 3 is 0.1435 $\frac{mm}{year}$

Chapter 5

Discussion

The idea of creating a digital twin for pressure vessels was proposed in the start of this project since a digital twin could be used for predicting the inside state of the wall in a pressure vessel, which presently is not available. The reason for making it is that the state of the inner wall in large pressure vessels are not known since no measuring devices are fitted inside the vessel, and it is unknown if they can handle the content of the vessel without failing, and when inspecting the vessel. The state of the wall can either be worse than expected or that the inspection shows no mediate danger for failure. To solve this problem, a digital twin should be used to determine when the inspection is needed.

The project is, however, set to be a part of the investigation into creating this digital twin, in cooperation with Rambøll. The scope of this project was to investigate the possibility of creating a model using the software Matlab, that describes the corrosion rate on a wall, that is coursed by CO_2, on three pressure vessels, with inspection data provided by Rambøll.

The state-of-the-art for corrosion rate is mainly the de Waard-Milliams model reworked in 1995, which is the model most of the industrial software, created by other companies, are based on. The model which de Waard-Milliams proposed, is for free access for the public, and for this reason, this is the model in which is used as the base for the model created in Matlab. The other model which are mentioned are all software specially made by the companies, from there own data and their own experiences in the field. For this reason, these models are pay to use models, where the basic functions behind the models, are not shown since companies rarely want competing companies to know how they do things. All the models which are in the state-of-the-art, are all used for either pipeline corrosion or wellhead corrosion, meaning that they are not used in the same complete context as wanted for this project(pressure vessel). Since no model is found for corrosion rate on the inner wall of a pressure vessel, the de Waard-Millaims model is seen as sufficient, and probably the best fit, for the use of determining the corrosion rate for pressure vessels.

Most pressure vessels are long cylindrical containers with oval ends, and for most pressure vessels there are several inputs and outputs, in this project for simplification, the pressure vessels were set to only have one inlet, and one outlet. By only having one inlet and one outlet, the flow through the vessel is easier to define, since the volume flow is consistent through the vessel. If there were different points of inlet in the vessel, then the flow would not be the same throughout the vessel, and the flow would have to put into regimes, with no knowledge of how the flow looks like. Furthermore, the oval ends are neglected, and the pressure vessel is seen as a cylinder. Doing this it made it possible to implement the model which elsewhere are used for pipeline flow. The cylindrical vessel can in some form be seen as a small part of a pipe, and for this reason, it made sense using the model.

The model in itself is not that complex since it only uses known variables and values from existing pressure vessel inspections to predict. One of the major assumptions made in the model is that the CO_2 mole fraction has a linear trajectory from the first inspection, to the last inspection. This is, however, not true since the inspection years are random, and not done with a fixed spread in years. As an example of this is vessel 2, where the gap between the third inspection and fourth inspection is six years. When looking at the mole fraction of CO_2 in the third inspection, the mole fraction in the model after seven years does not fit. This is especially seen for vessel 3, where the two in between inspections of Co_2 mole fraction are well above the linear line.

In determining the corrosion rate for each vessel it is essential only to use the factor in which applies for the content, and the specifications of each vessel. Vessel 1 was a pressure vessel for NGL gas, which is a sour gas, meaning that the factor of crude oil, are not present in the vessel, so the factor should not be taken into account. The results by the model for vessel 1, show that the corrosion rate due to CO_2 is $0.1065e^{-5} \frac{mm}{year}$ this is not that and does not really describe the corrosion detected under inspection that good. It should, however, be noted that there is H_2O present in the mixture, and since this vessel operates a 1 Barg pressure and ambient temperature, it is likely that some of the water condense which can help in the oxidization of metal, should the water contain any part of salt. It should also be noted that the corrosion rate calculated by the model starts from the first inspection year, and not from the year the vessel started production, and since vessel 1 started in 1995, and first was inspected in 2010. That is 15 years of production, the corrosion rate from the model still not fit the inspected corrosion, meaning that other factors still play

a role in the corrosion rate.

Vessel 2 is a pressure vessel in which the content was oily water, and for this reason, the factor of oil was used in the model. The model showed that the corrosion rate due to CO_2 for vessel 2 is 0.0035 $\frac{mm}{year}$, which again does not entirely describe the overall corrosion that has happened over the years of service for this vessel. A reason for this is that it is the primary content of vessel 2 is water, and that the CO_2 amounts to a small percentage of the overall content inside the vessel. The data collected is again for the first inspection and not from the start of the production for the pressure vessel, however, this time only two years has gone from the start of the first inspection, meaning that the corrosion rate calculated by the model, does not explain all the corrosion that has been observed.

Vessel 3 is a pressure vessel where oil, gas, and water all are present, meaning that both liquid and gas are known to be present. The model showed that the corrosion rate due to CO_2 for vessel 3 is 0.1435 $\frac{mm}{year}$. The graph does not look that bad, should however be remembered that the vessel started in 2002, so the starting point should be a bit different. The thing about vessel 3 is that the third inspection shows a smaller corrosion debt than from the second inspection. This is hard to explain why, since this should not occur, however, an explanation for this could be that the corrosion measurements is done with ultrasound, and this is normally done by hand, given the chance of human error, or the fact that the same spot has not been measured.

A reason for the model not to give corrosion rates which fits the measured data could be that the assumptions made in the model, not being how the model should look like if it gets worked on for a more extended period of time. The assumption of one inlet and one outlet does not show how it looks for the vessels in real life. The fact that CO_2 mole fraction is seen as linear between the first inspection and last inspection is also a thing that should be investigated if the trajectory could be described better.

The coating is one of the factors in which should be investigated, for better understanding of how the corrosion has gotten as it is in all of the pressure vessels. It has not been found to what extend coating of surfaces reduces the corrosion rate of CO_2.

As mentioned a great deal of time in this project was used on trying to get a flash calculation of the vapor-liquid equilibrium by means of a PTFlash function in Mat-

lab. The idea of doing this proved to be more difficult than anticipated, and for this reason, this part is left out of the model in the end. The PTFlash also calculates the fugacity of all the different species of the content within the pressure vessel, meaning that the fugacity of CO_2 would be better explained in mixtures than the current model does.

Another part which needs to be incorporated into the model is a time step, for the model to be a predictor of the corrosion rate, and not just defining the corrosion rate from existing inspection data. The current time step is set to be in years if the model should predict a more exact time of needed inspection. Depending on how accurate the model can be, every month would be a better time step, this would give a better indication of the corrosion going on inside the vessel, and at the same time by having a shorter time step, it is easier to the state of the wall and determine when and if inspection is needed.

Chapter 6

Conclusion

The idea given by Rambøll by creating a digital twin to determine when it is necessary to inspect pressure vessels was scaled down to investigating how the corrosion of pressure vessels due to CO_2 corrosion, and in that extend creating a model using Matlab as the software for a model, that describes the corrosion rate of CO_2.

The model in which was produced in the software of Matlab, describes the corrosion rate due to CO_2 to some extent, but it does not describe the corrosion that have been inspected in either of the three vessels to a complete extent. Furthermore, the model only describes the corrosion rate from collected inspection data, and does not yet describe the predicted corrosion for the future. Therefore, it can be concluded, that for predicting the corrosion rate due to CO_2 inside of pressure vessels, the model is sufficient, and does what is asked. However the conclusion should also state that the model is far from finished, if it should do the job as predicting the entire rate of corrosion inside a pressure vessel.

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Appendix A

Appendix

Table A.1: Information as it is given by Rambøll for three different pressure vessels

Basics	Vessel 1	Vessel 2	Vessel 3
Medium	NGL (sour gas)	Oily water	Oil - Water - Gas
Operation Pressure	1 Barg	Atmosphere	10 Barg
Operation Temperature	Ambient	80 degrees Celsius	Ambient
Design Pressure	3.5 Barg	7 Barg	10 Barg
Design Temperature	38 degrees Celcius	-40-116 degrees Celsius	-10-93 degrees Celsius
Corrosion Allowance	3 mm	3 mm	3 mm
Shell Diameter	1500 mm	1400 mm	1800 mm
Shell Thickness	12.5 mm	12 mm	17 mm
Volume Flow	11 $\frac{m^3}{hr}$	40 $\frac{m^3}{hr}$	52 $\frac{m^3}{hr}$
Total Volume	6.2 m^3	5.5 m^3	27.2 m^3
Start up	1995	1995	2002

Inspections for Vessel 1

Table A.2: Table is showing the mole fraction of the component in vessel 1

Component	2010	2011	2016
Methane	0.202	0.195	0.246
Ethane	0.120	0.134	0.175
Propane	0.193	0.183	0.183
n-Butane	0.289	0.300	0.148
n-C20	0	0	0
n-C30	0	0	0
n-Octane	0	0	0
n-Nonane	0	0	0
n-Decane	0	0	0
n-Heptane	4.92E-02	5.00E-02	4.00E-02
n-Pentane	1.78E-02	1.77E-02	3.77E-02
H2O	5.32E-02	5.33E-02	6.75E-02
CO2	5.40E-02	5.38E-02	6.79E-02
H2S	2.33E-02	2.39E-02	3.48E-02
sum	1	1	1

First inspection - 2010

- Scale formation - 4.5 mm

- corrosion depth - 0.3 mm

- Scale removed and rust coated

Second inspection - 2011

- Scale - 3.6 mm

- Corrosion depth - 0.37 mm

Third inspection - 2016

- Scale - 4.1 mm

- Corrosion depth - 0.79 mm

Inspections for Vessel 2

Table A.3: Table is showing the mole fraction of the component in vessel 2

Component	1997	2001	2004	2010
Methane	1.09E-02	1.08E-02	1.07E-02	1.06E-02
Ethane	9.95E-03	9.88E-03	9.79E-03	9.74E-03
Propane	9.95E-03	9.88E-03	9.79E-03	9.74E-03
n-Butane	1.34E-03	1.33E-03	1.32E-03	1.31E-03
n-C20	9.04E-02	8.98E-02	8.90E-02	8.85E-02
n-C30	4.52E-03	4.49E-03	4.45E-03	4.43E-03
n-Octane	9.04E-02	8.98E-02	8.90E-02	8.85E-02
n-Nonane	9.04E-03	8.98E-03	8.90E-03	8.85E-03
n-Decane	1.63E-02	1.62E-02	1.60E-02	1.59E-02
n-Heptane	4.96E-02	4.92E-02	4.88E-02	4.85E-02
n-Pentane	4.88E-03	4.85E-03	4.81E-03	4.71E-03
H2O	0.642	0.638	0.632	0.629
CO2	2.93E-02	3.21E-02	3.81E-02	4.03E-02
H2S	3.15E-02	3.53E-02	3.71E-02	4.01E-02
sum	1.00E+00	1.00E+00	1.00E+00	1.00E+00

First inspection - 1997

- Scale - not given

- Corrosion depth - 1-1.5 mm

Third inspection - 2004

- Scale - not given

- Corrosion depth - 1.2-1.7 mm

Fourth inspection - 2010

- Scale - not given

- Corrosion depth - 4.2 mm

Inspections for Vessel 3

Table A.4: Table is showing the mole fraction of the component in vessel 3

Component	2005	2009	2017
Methane	0.147	0.134	0.132
Ethane	0.101	9.21E-02	9.09E.02
Propane	7.35E-02	6.70E-02	6.61E-02
n-Butane	3.68E-02	3.35E-02	3.31E-02
n-C20	9.19E-03	8.37E-03	8.26E-03
n-C30	9.19E-03	8.37E-03	8.26E-03
n-Octane	2.76E-02	2.51E-02	2.48E-02
n-Nonane	2.76E-02	2.51E-02	2.48E-02
n-Decane	2.76E-03	2.51E-03	2.48E-03
n-Heptane	1.65E-02	1.51E-02	1.49E-02
n-Pentane	1.56E-02	1.42E-02	1.41E-02
H2O	0.441	0.402	0.397
CO2	8.41E-02	8.69E-02	9.07E-02
H2S	8.04E-02	8.69E-02	9.28E-02
sum	1	1	1

First inspection - 2005

- Scale - not defined because of sludge present
- Corrosion depth - 1.2 mm - measured with ultra sound

Second inspection - 2009

- Scale - not defined because of sludge present
- Corrosion depth - 1.6 mm - measured with ultra sound

Third inspection - 2017

- Scale - not defined 6-7 m^3 oil/slugde in the vessel
- Corrosion depth - 1.2 mm - measured with ultra sound