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Pitting corrosion on stainless steel with and without passivation

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Abstract

The stainless steel metal includes a large group of alloys and which one should choose for a process can be difficult to determine. Despite much research on corrosion, there is still disagreement on the impact of the corrosion resistance from passivation. This master thesis was assembled together with Tetra Pak to see the influence of passivation on stainless steels used in their processes.

The goal of this master thesis was to understand whether the passivation of the two stainless steels gave a better protection against corrosion. This was supposed to be investigated at different temperatures and concentrations of chloride ions. A large part of the project however, became finding out the right method to measure with. Because of this, the master thesis has given large insight of how a project proceeds from start to finish and has brought knowledge in problem solving and planning.

In this project, stainless steel types 304 and 316 were studied using polarization and OCP measurements. The stainless steels in half of the measurements had been passivated with citric acid. From the initial measurements it was clear that the OCP measurements required more time than the project could offer - after 12 hours it had still not reached a stable value and thus could not be used to draw any conclusions. One could nevertheless see tendencies for an increased protection by passivation in the beginning of the measurements, but after some time the values tended to reach stagnation.

The polarisation measurements gave more varying results and appeared to be more sensitive against small differences in the system. From the polarisation measurements one could see that the pitting potential (E_{pit}) ranged from 2.37E-6 mm/year to 1.44E-4 mm/year. The corrosion rate (C_{rate}) with the estimated compositions of the steel varied between 149mV and 1235mV. The reliability of the measurements was questioned early in the process since the results differed from what was expected. The accuracy was later seen more clearly by comparing results from the same tests with each other. Since the temperature in this project differed greatly from the temperatures that are used in Tetra Pak's processes, one cannot advise on whether to passivate or not. However, the report can lead to knowledge of methods to measure corrosion and knowledge of how materials are affected at lower temperatures. The report also contains advice on how the research should continue.

Sammanfattning

Rostfritt stål inkluderar en stor grupp av legeringar och vilken sort man bör välja i en process kan vara svårt att avgöra. Trots mycket forskning kring korrosion finns det fortfarande delade meningar angående påverkan genom passivering. Detta projekt var framtaget tillsammans med Tetra Pak för att utifrån deras situation se påverkan av passivering på två olika rostfria stål som används inom deras processer.

Projektets huvudsakliga mål var att förstå huruvida passivering av de två rostfria stålen gav ett bättre skydd mot korrosion. Detta skulle kontrolleras vid olika temperaturer och koncentrationer av kloridjon. En stor del i projektet blev dock istället att ta reda på vilka metoder detta bör undersökas med. Tack vare det har detta arbetet gett en stor insikt om hur ett projekt går till från start till slut och medfört kunskap om problemlösning och planering.

I detta projekt har rostfritt stål av typerna 304 och 316 undersökts med hjälp av polarisations- och OCP-mätningar. De rostfria stålen har i hälften av mätningarna varit passiverade med citronsyra. Från de initiala mätningarna framkom det att OCP-mätningarna krävde mer tid än vad projektet kunde erbjuda då de efter 12 timmar fortfarande inte nått ett stabilt värde och därmed skulle inte kunna användas till att dra några slutsatser. Man kunde trots det se tendenser till att passivering ger ett ökat skydd i början av mätningarna, men efter en viss tid tenderar de att stagnera i värden som inte skiljer sig märkbart mycket.

Polarisationsmätningarna gav mer varierade resultat och verkar vara känsligare för små skillnader i systemet. Från polarisationsmätningarna kunde man se att gropfrätningspotentialen (E_{pit}) varierade från 2.37E-6mm/år till 1.44E-4mm/år. Korrosionshastigheten (C_{rate}) med de uppskattade sammansättningarna på stålet varierade mellan 149mV och 1235mV. Mätningarnas tillförlitlighet började ifrågasättas tidigt under arbetet då resultaten skilde sig från vad som förväntats och kunde senare observeras tydligare genom att jämföra resultat från likadana prov med varandra. Då temperaturen i det här projektet skilde sig väldigt mycket från de temperaturer som används i Tetra Paks processer kan inga råd om eventuell passivering ges. Däremot kan rapporten medföra kunskap om metoderna för att mäta korrosion och kunskap om hur materialen påverkas vid lägre temperaturer. Rapporten innehåller även råd om hur undersökandet bör fortsätta.

Innehåll

1	Introduction	1
2	Theory	2
2.1	Stainless steel	2
2.2	Corrosion	3
2.3	Types of corrosion.....	3
2.3.1	<i>Pitting corrosion.....</i>	4
2.4	Thermodynamics of corrosion.....	5
2.5	Kinetics of corrosion	6
2.6	Prevent corrosion	6
2.7	Passivation	7
2.8	Measuring corrosion.....	8
2.8.1	<i>Faradays law</i>	9
2.8.2	<i>Open circuit potential measurements (OCP)</i>	10
2.8.3	<i>Polarization curves.....</i>	10
3	Method.....	12
3.1	Sample preparation	12
3.2	Solution preparation	13
3.3	Experimental setup.....	13
3.4	Measurements.....	15
3.5	Calculations	16
4	Results and discussion.....	17
4.1	Part one of the project.....	17
4.2	Part two of the project	19
4.3	Measurement accuracy	26
5	Conclusions.....	27
6	Future work.....	28
7	References.....	29
8	Appendix	30
8.1	Appendix 1.....	30
8.2	Appendix 2.....	31

1 Introduction

Corrosion is an important aspect in all types of metallurgy due to its vast impact on materials. This has led to a large amount of information about the subject and many methods of measuring corrosion have been developed. Which method to choose could be complicated to find out because the different methods give different knowledge of the subject. This project was performed in collaboration with Tetra Pak and was meant to provide a better understanding of corrosion, passivation and the methods of measuring corrosion.

The aim of this project was to measure the impact of passivation of two types of stainless steels at different temperatures and with different chloride concentrations in the media. The goal was to be able to draw conclusions of whether it is worth passivating the steel before using it in the process or not.

This project included;

- A literature study
- Finding a suitable method and tracking down needed equipment
- Preparing and passivation of samples
- Corrosion measurements
- Compilation of results
- Drawing conclusions
- Thoughts about future investigation

2 Theory

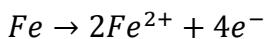
This chapter includes the relevant theory behind this project. The chapter starts with basic knowledge and ends with the theory behind the performed measurements.

2.1 Stainless steel

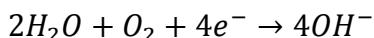
Stainless steel is a collective word for a wide range of iron alloys and the material is often used in corrosive environments due to its protective features. The alloy classified as stainless steel contains at least 10.5% chromium which is added due to that chromium has a better resistance against corrosion than iron. With around 15% of chromium in the stainless steel, the corrosion resistance of pure chrome is reached instead of the resistance for iron. [1]

The corrosion procedure of iron in presence of oxygen and water is shown in figure 1 and starts with dissolution of iron into the water in the form of Fe^{2+} which leaves two electrons that can wander through the metal. These electrons react with oxygen and water and forms 2OH^- . Now, these hydroxide ions react with the dissolved iron and forms solid Fe(OH)_2 which oxidizes to $(\text{Fe}_2\text{O}_3 * \text{XH}_2\text{O})$ and gives rise to what we call rust. [2]

The corrosion procedure is divided into two half cells where one of them is anodic and the other cathodic. The anodic corrosion site has the following formula:



The cathodic corrosion site has the following formula:



This gives the overall reaction:

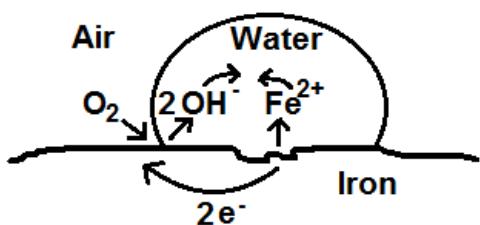
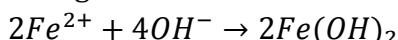


Figure 1. Simplified picture of the corrosion of Iron in the presence of water and air.

In the presence of chromium however, the steel can self-passivate and form a protective layer of chromium oxide on the surface. This layer makes it harder for the iron to meet the solution which will give the metal a better protection against corrosion. For the alloy to be able to self-passivate, oxygen needs to be present. The chromium reaches the surface, oxidizes spontaneously in the air and forms chromium(III)oxide (Cr_2O_3) which is the protective layer. If the layer is destroyed in presence of oxygen, it can be rebuilt. This is what makes the stainless steels more resistant against corrosion compared to some alloys. Passivation in general will be explained more thoroughly later in this chapter.

Despite this protective layer, the stainless steel is not immune against corrosion. Some environments, for example where chloride ions are present, will make the steel corrode anyway. Regarding of stainless steel, this corrosion process is a form called pitting and will also be explained later.

There are five main groups of stainless steels which are based on their microstructure and compositions. These groups are austenitic, martensitic, ferritic, ferritic-austenitic (duplex) and martensitic-austenitic. The type of stainless steel studied in this project is the *austenitic* stainless steel. The austenitic stainless steel alloy has a face centred cubic structure [1]. This group includes both of the commonly used 316 and 304. The similarities between these two materials are their microstructure which is, well, austenitic. Their similarities are also that the alloy for both materials contains nickel. The difference between 304 and 316 is that the 316 contains molybdenum (Mo). Molybdenum is said to further increase the resistance towards pitting corrosion by increasing the lattice strain of the alloy structure. The increased strain makes it harder for the iron atoms to detach from the surface. This difference makes the stainless steel 316 more suitable for environments with presence of chloride ions where there is an increased risk for pitting. However, since there is a large price difference between these two types of stainless steels, it is common to use the 304 in these environments as well. When choosing a material, this higher cost needs to be considered against the eventual costs of repairing and replacing of material more frequently.

2.2 Corrosion

When corrosion is discussed, most people think about the corrosion appearing on a material that is not soluble in the environment. This corrosion appears as rust on the surface of the material. However, if the material is soluble in the environment, the metal can be dissolved in the solution as ions. [3] The latter mentioned corrosion is an electrochemical process where the metal is dissolved to form a more stable formation. The corrosion process includes both an anodic and a cathodic reaction which is occurring on the surface of the metal. These reactions are two half-cell reactions, one oxidation and one reduction. During a corrosion process, both a charge- and a mass-transfer occur on the metal surfaces. For corrosion to occur there has to be metallic contact between the anodic and cathodic sites and there has to be an electrolyte present as well. [2]

The cathodic reaction is a reduction, where the oxidation number of the oxygen is decreased and electrons are consumed. The anodic reaction is the oxidation. Here is where there is a loss of metal due to that the metal oxidizes and dissolves into the solution as ions. Since the two reactions are coupled, if one of them is changed, so is the other. [2] In this project, the anodic reaction will mainly be studied.

2.3 Types of corrosion

There are eight types of corrosion; general, crevice, pitting, stress-corrosion cracking, galvanic, intergranular, dealloying and erosion. From this eight types, three of them; crevice, pitting and stress-corrosion cracking form a group called localised corrosion. In

all the localised corrosion types the metal is attacked in certain positions, where some of the other types forms a uniform corrosion that spreads over the entire metal surface. [2] In this project, the localised corrosion type pitting will be studied.

2.3.1 Pitting corrosion

Pitting is a corrosion which occurs where there is for example a local breakdown of the passive film on the metal surface. This breakdown could happen because of ions in the electrolyte. For stainless steel, those anions are often chloride ions. [2] [4] The breakdown also has a dependence of the inhomogeneities in the atomic structure of the metal. Pitting usually does not occur on surfaces without a strong protecting layer, in these cases, the uniform corrosion is more common. For pitting to begin, a critical pitting potential must be reached since that is the potential when the electrochemical process breaks through the protective layer. [1] Pitting can also be initiated if the protective layer is scratched or if there is inhomogeneities in composition of the atoms. Pitting is a corrosion type that is very dangerous for materials. Although it does not spread over the entire surface, pitting can cause deep damage to the material that one cannot easily see [2] [4] [5]. A stainless steel surface attacked by pitting corrosion can be seen in figure 2.

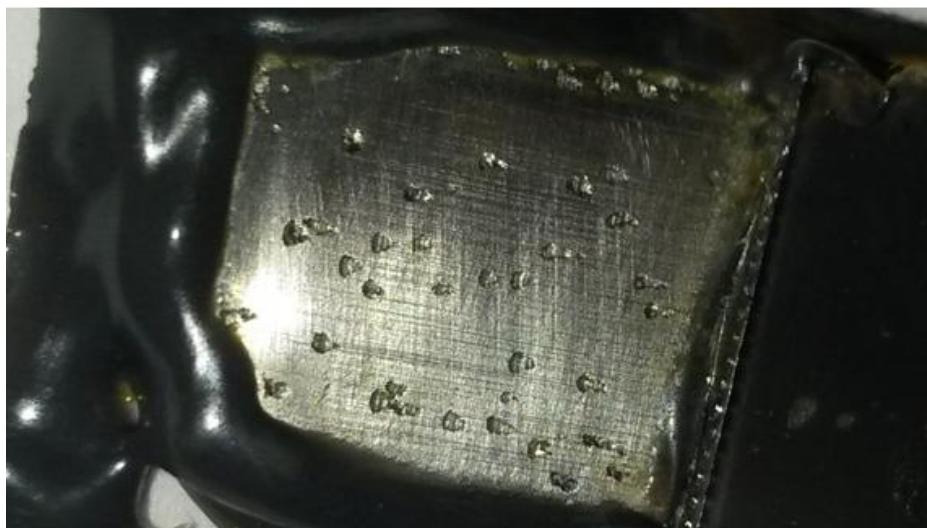


Figure 2. The surface of stainless steel showing clear signs of pitting corrosion. The area in the picture corresponds to 1cm².

The initiation of pitting includes three theories; penetration, adsorption and film breaking. The penetration mechanism is when the ions are penetrating the passive film, causing dislocations between the metal and the oxide film. The adsorption mechanism of the passive layer starts with chloride ions that adsorb onto the layer and forms complexes with the oxide film, this leading to dissolution of the film. The dissolving of the passive film further makes the passive film thinner at local areas until the metal is reached and the pitting can begin. The film breaking mechanism evolves from the principle that chloride ions enter through already existing cracks in the film [4] [2] [6]. Figure 3 shows the three different pitting initiations explained by E.McCafferty.

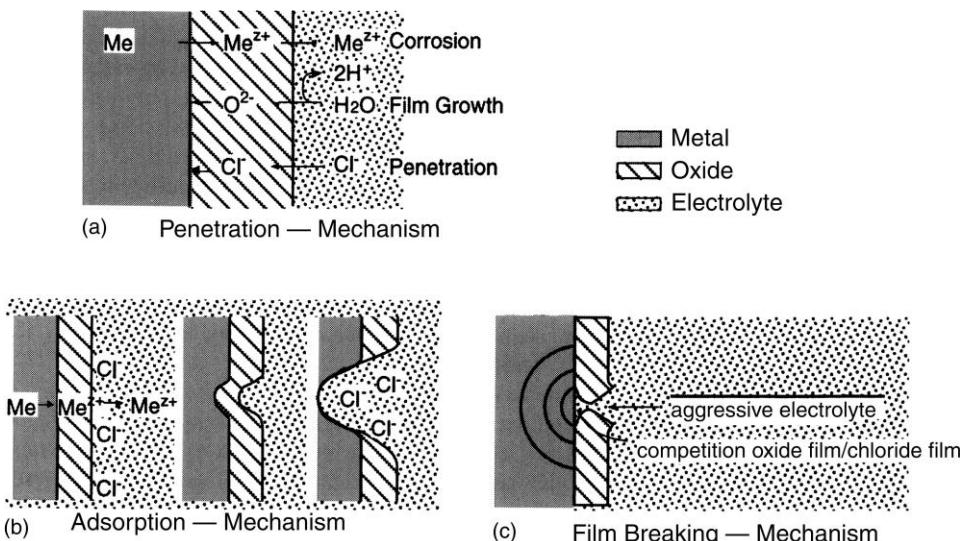


Figure 3. Visualization of the three types of pitting initiation [2].

There are also different stages of the pitting corrosion that can be seen while performing polarization curves (see section 2.8.3). At low potentials, there is a stage called metastable pitting, in this stage the forming pits will be repassivated rapidly. At higher potentials called the stable pitting stage, the pits do not repassivate. This curve will have a different appearance depending on the media and material. More information about these curves can be seen in section 2.8.3. [4] [5]

When pitting has started in a liquid (where there is not enough oxygen to rebuild the protective layer,) the pitting will continue due to that the environment in the already formed pit is preferable for corrosion. There will be even less oxygen inside the pit which will hinder the repassivation. In the pit, there will also be a higher concentration of chloride ions present. [1]

Critical pitting potential

Pitting potential is a measurement of how resistant the material is against pitting corrosion. A high value means a high resistance against pitting. The critical pitting potential (E_{pit}) is the potential value where the stable pitting stage is reached. This value depends on a number of factors like for example the concentration of chloride ions in the environment, the surface of the material, temperature. Therefore; one cannot compare the E_{pit} of two materials if their situations differ. [7] [2] [4] The pitting potential is sometimes compared with the redox potential of the medium. If the pitting potential is higher than the redox potential, pitting will not occur spontaneously. [8] [9]

2.4 Thermodynamics of corrosion

A summary of the thermodynamics of corrosion can be read out from a Pourbaix diagram (equilibrium diagram) which is a type of diagram that gives a relation between the electrode potential and the pH of the system. This makes it possible to predict the corrosion feature of the metal in a certain environment and at a certain temperature. Pourbaix diagrams are available in databases for several metals. The electrode potential

of different forms of the metal that can occur in the system is calculated using Nernst equation. In that way, one can create a diagram that can be used for predicting if the corrosion will be favorable or not simply by measuring the pH and the electrode potential. These diagrams do not give corrosion rates but one can use them to compare and confirm the predicted behavior with kinetic data. The Pourbaix diagrams do however not consider pitting corrosion with chloride ions present and does not apply on alloys. The potential-pH diagram can be useful in the beginning of experiments to get an approximated picture. [2]

2.5 Kinetics of corrosion

How fast a corrosion reaction takes place (corrosion rate, C_{rate}) cannot be determined by the thermodynamic approach of corrosion. Even if a reaction is spontaneous, it does not mean that the environment will be a problem of the material for a long time. There are several ways to calculate corrosion rates for example by measuring weight loss/gain, making a chemical analysis of the solution. The corrosion rate has many units depending on which measurement you use. In this project, electrochemical measurements will be used. In electrochemical measurements, one can measure the corrosion by controlling the potential of the electrode [2]. This will be explained later in section 2.8. To calculate the corrosion rate from an electrochemical measurement, Faradays law can be used. More explanation of Faradays law can be seen in section 2.8.1.

2.6 Preventing corrosion

There are several ways to prevent corrosion on metals. This section will explain some of them. However, it is important to think of the possibility to carry out these prevention techniques depending on the situation of where the metal should be used.

Coating

It is possible to create a corrosion resisting surface on the metal using different types of coating. Coating with polymers is commonly used and is a very effective way to protect the metal, although some problems are still related to the method. If the coating would crack and corrosion should start in the crack, there might be an environment with very little oxygen in the crack. This will be preferable for corrosion to continue. The coating inside a process can also cause other problems, such as migration into the product and there could be a problem with these coatings at high temperatures such as melting or break down. [1]

Changes in the media in contact with the metal

In some situations it might be possible to change the media that causes corrosion. The changes can be either an addition of corrosion inhibition substances or a removal of the amount of corroding substances. These changes can be very difficult in many processes since one might not want to change the product in any way [1]. For example, in food processes, one does not want to add the corrosion inhabitation chromate to the media for obvious reasons.

Changes of the metal composition

As for the adding of molybdenum into the stainless steel 316 to improve the corrosive protecting features against pitting, one can add several other substances to get similar effects. This is a very difficult method that requires a lot of research since one change in the alloy composition can alter a lot of the material properties. Some properties that might change are the conducting properties, mechanical properties, the alloys strength or diffusivity. This method is therefore more expensive.

Designing to prevent corrosion

When one speaks of corrosion in both buildings and processes there is a major difference of the corrosion resistance depending on the design of the parts in the process. With smart designing of the process, one can avoid a lot of the corrosion. The interesting part of this type of corrosion protection is that it does not necessarily have to be an increased cost if this is taken into consideration before designing the process. [4]

Passivation

Passivation is another method that can make the metal more resistant against corrosion. Since passivation is a major topic in this master thesis, it will be explained more thoroughly in the next section.

2.7 Passivation

A metal that reacts with its environment and forms a solid protective layer on its surface has been passivated. This reaction is an electrochemical reaction between the metal and the environment that forms a very thin layer of metal oxide that usually is as thin as 10-100Å. [1] The protective layer makes the chemical and electrochemical reactions less possible on the surface. However, the thick passive oxide film does not necessarily mean a better protection, since a thicker film has more atomic defects than a thin film. [3]

One of the studies within the subject even state that passivation is just an extra cost with no improvement at all if the stainless steel has been pickled in the right way. One article states that the optimal corrosion resistance in the specific environment are reached within two days anyway. [8]

Effect of atomic defects in oxide layer

M. Tordova states that knowledge of the present defects might make it possible to predict the breakdown of the oxide layer. The environment will contribute to the amount and type of defects that will be present. The studied types of defects in an oxide layer are mainly point defects, both vacancies and interstitial defects. [10]

Passivity methods

One can use many different methods to perform passivation. Stainless steel self-passivates when the chromium in the metal reacts with the oxygen in the air but one can use different acids to passivate as well. The most common acid to use is nitric acid. However, lately the citric acid has become a popular acid to use as well and is therefore chosen in this master thesis. However, both methods give acidic waste which can have a

negative effect on the environment. The method used in this project will be explained in section 3.2.

2.8 Measuring corrosion

Since corrosion is a major subject within metallurgy there are as previously mentioned plenty of methods for measuring corrosion. In this experiment, two electrochemical techniques are used to be able to compare the results and these methods will be explained in this chapter. In both methods, a potentiostat is used. More information about the practices behind measuring using these methods will be explained in next chapter, chapter 3.

One of the two different methods is open circuit potential (OCP) measurements, where one measures the change in voltage as a function of time. The other method used is polarization measurements where one polarizes the electrode and measures the voltage as a function of the current. Both of these measurements are done using a three electrode system.

Three electrode system

A two electrode system consists of one working electrode and one reference electrode where the reference electrode also is used as a counter electrode. In a three electrode system, there is one working electrode, one counter electrode and one reference electrode. [11] The reference electrode is positioned close to the working electrode. The three electrode system is more favourable than the two electrode system when one only is interested of measuring half of the cell. In OCP measurements for example, the working electrode will be studied and with a three electrode system, the measurements do not include any potential changes at the counter electrode [11]. In figure 4, one can see a simplified sketch of the measurements using a three electrode system, where WE stands for working electrode, RE is the reference electrode and CE is the counter electrode. The current source in the measurements of this project is a potentiostat.

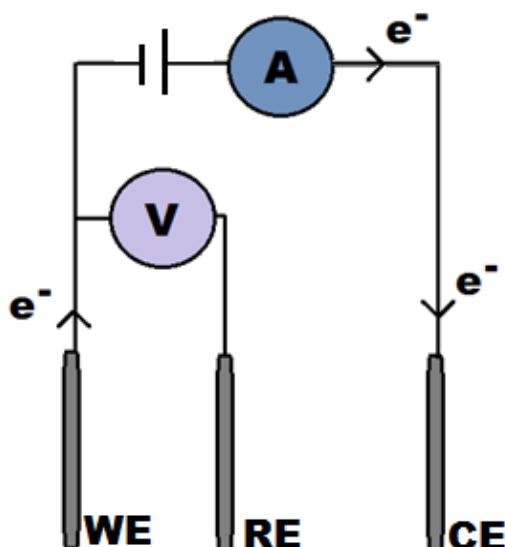


Figure 4. An illustration of a three electrode system used in OCP measurement.

2.8.1 Faradays law

To be able to compare different materials in different environments, one can use Faradays law to calculate the corrosion rate:

$$C_{rate} = \frac{M * I_{corr}}{n * F * \rho}$$

C_{rate} = Corrosion rate (cm/s)

n = Number of electrons taking place in the reaction

M = Molar mass (g/mol)

I_{corr} = Corrosion current (A/cm²)

F = Faradays constant (96485 A * s/mol)

ρ = Density of the sample

For alloys however, one needs to take the composition into consideration and weigh the molar mass, density and the number of electrons. To take the composition into consideration, one uses the following equation:

$$\frac{M}{n * \rho} = \frac{M_{alloy}}{n_{alloy} * \rho_{alloy}} = \sum_i \frac{M_i}{n_i * \rho_i} * x_i$$

M_i = Molar mass for the substance

n_i = Number of electrons for the substance

x_i = Fraction of substance in the sample

ρ_i = Density of the substance

2.8.2 Open circuit potential measurements (OCP)

Open circuit:

An open circuit refers to a circuit without any load, in other words, a circuit where there is nothing that consumes the energy [12]. In corrosion measurements, the OCP method measures the difference in electric potential between the working electrode (the metal sample) and a reference electrode as a function of time [12] [13]. A typical OCP-curve for stainless steel with oxygen present can be seen in figure 5. One can see that the OCP changes during the measurement and it could take long time for the value to stabilize, when the curve is stabilised, the OCP value is the same value as the corrosion potential, E_{corr} . From these curves, one can compare two different samples corrosive protection as long as the environment during measurements has been the same for both samples. A higher E_{corr} value means that the corrosive protection is better than for the lower value.

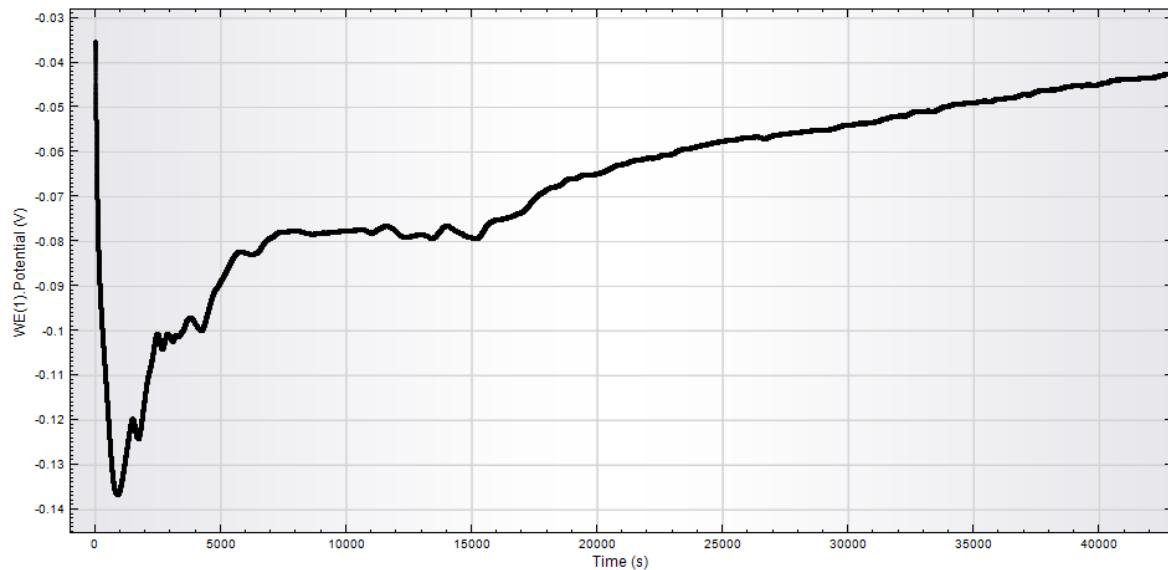


Figure 5. A typical OCP curve for stainless steel in the presence of oxygen.

2.8.3 Polarization measurements

Polarization curves can be used to find out the kinetics of the corrosion process. From these curves one can for instance obtain parameters to calculate the corrosion rate. This rate can be used to compare different steels in different environments. A typical polarization curve for stainless steel (in the presence of oxygen) can be seen in figure 6. The large drop in current arises when the anodic and cathodic processes are in equilibrium, and the net current is zero [2] [14] [5]. This value is called the corrosion potential and should be the same as measured in the open circuit potential measurements. Sometimes these differ, and that could be explained from the fact that in polarization curves, the equipment starts by polarizing the sample to a cathodic value (the part of the curve to the left of the large drop). The cathodic reactions taking place at those values might remove some of the oxide layer on the sample [5].

One can also find the corrosion current, I_{corr} (see figure 6) and this value is required to

calculate the corrosion rate by using Faradays law mentioned in section 2.8.1. As mentioned in section 2.3.1, there are different stages for pitting corrosion. The earlier the stable pitting stage is reached (E_{pit}), the less energy is required to make the metal corrode [4].

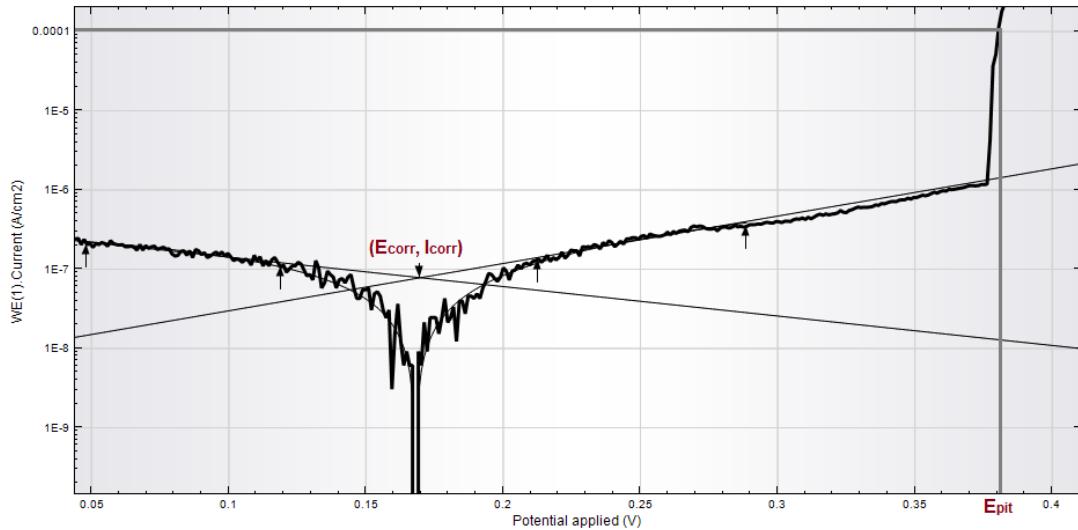


Figure 6. Polarization curve for stainless steel in presence of oxygen. Important parameters are marked in the figure.

3 Method

This part will explain the experimental setup and sample preparation in more detail. The two different methods used in this experiment are as mentioned open circuit potential (OCP) measurements, where one measures the change in voltage during time and the other method used is linear polarization where one measures the voltage as a function of the current. These two methods were chosen due to the experimental setup that was available and due to its simplicity of usage and evaluation.

3.1 Sample preparation

The samples were made of stainless steel 304 and 316 that has been cut into pieces of 1x8 cm at the Tetra Pak facility in Lund, Sweden.

The sample was first ground with a metal file to remove the sharp edges. Then, the surface of the sample was ground with very fine grounding paper to remove any impurities. The surface was then cleaned with ethanol. The samples that were not passivated were stored in air for at least 24 hours to have time to build up their natural passive layer.

The samples to be passivated were directly immersed in the acid solution after washing. The passivation method can be seen in table 1. After passivation, the samples were washed in distilled water and then stored in air for at least 24 hours.

Table 1. Experimental parameters used for the passivation.

Acid	Concentration (g/L)	Temperature (°C)	Time (min)
Citric acid	5	20	30

Coating of the sample

The goal was to perform the measurements on an area of 1cm² and therefore, the rest of the sample needed to be coated. This was performed after the pre-treatment of the sample due to the increased difficulty with the coating on the sample.

The coating included epoxy glue and pieces of plexi-glass. The plexi-glass was there to simplify the coating and also to be able to easier observe any air bubbles in the coating. Only the part of the metal piece immersed in water was coated. The sample was coated on top of the surface (on the edges) as well to avoid crevice corrosion that could form on edges. The coating procedure of the samples can be seen in figure 7.



Figure 7. Coating procedure of the samples.

3.2 Solution preparation

The experiments were performed in a solution of tap water with 0M NaCl and 0.5M NaCl. The solution was based on tap water to increase the reality of the process where these materials are used. To maintain a solution with 0.5M NaCl, 29.22g 99.9% NaCl salt were dissolved in 1 L of water. The solutions were made 1L each time to decrease the errors while weighing the salt and pouring up the water.

3.3 Experimental setup

The experiments were as mentioned performed using a three electrode system, where the working electrode was the sample, the reference electrode was an Ag/AgCl-electrode maintained from Metrohm AUTOLAB and the counter electrode was a 5x8 cm piece of bent stainless steel. A potentiostat PGSTAT101 from AUTOLAB was used as a current source with the software NOVA 1.9. In NOVA 1.9, the polarization procedure was used with some changes in the program. The polarization was performed with a sweep rate of 0.1mV/s. For the experiments done with a higher temperature than room temperature, a heating plate with temperature probe was used. The temperature probe was protected by covering it in a thin layer of parafilm. This cover was there to protect the probe from corroding. Some pictures of the experimental setup can be seen in following figures (figure 8 and 9).

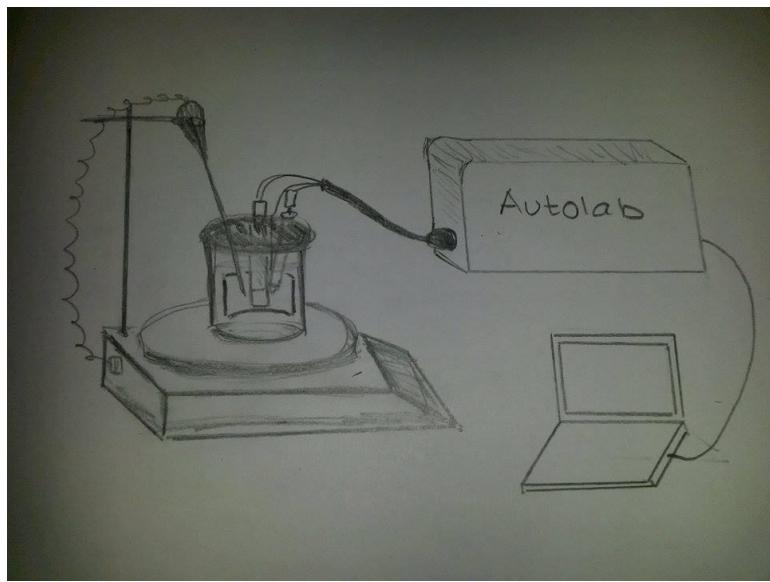


Figure 8. A sketch of the complete setup for the measurements.



Figure 9. Pictures of the experimental setup, including the corrosion cell, the electrodes and the potentiostat.

3.4 Measurements

The first part of the project included measurements that started with an OCP-measurement during 12 hours and continued with a polarization measurement directly after. These measurements were done at room temperature and their test matrix can be seen in figure 10. In these first measurements, the Ir-drop was not corrected.

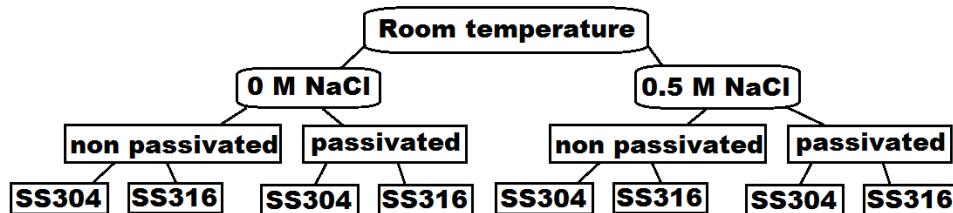


Figure 10. The test matrix for the first part of the experiment.

In the second part, after evaluating the results, the OCP measurements were excluded from the measurements and only polarization was performed. In this part, redox potential and pH- measurements were performed at the beginning of the polarization measurement using two electrodes and a computer showing the obtained value. The test matrix for these measurements can be seen in figure 11. In these measurements, the Ir-drop was compensated for by making changes in the software. This compensation was made by changing the method in the NOVA-software. The measurements at room temperature needed to be redone since there could be a change in the polarization curve depending on how long the sample has been in the medium. In the measurements from part one in the project, the samples had been subjected to the media for 12 hours before the polarization was performed. One other difference is that the first part did not compensate for the Ir-drop.

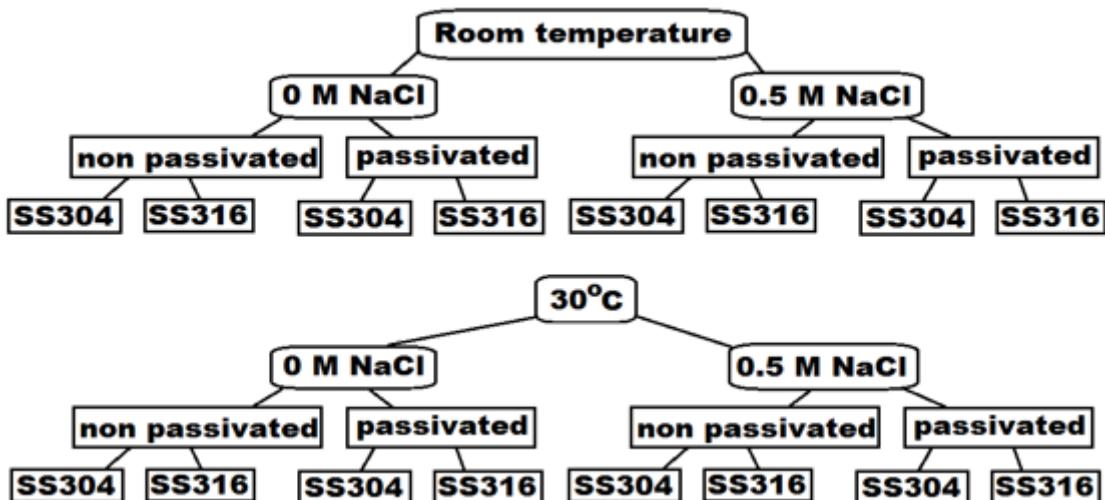


Figure 11. Test matrix for the second part of the project.

3.5 Calculations

As mentioned in section 2.8.1, Faradays law is used to calculate C_{rate} from the measured I_{corr} . For alloys, the molar mass and the number of electrons needed to be weighted depending on the composition of the material.

Faradays law:

$$C_{rate} = \frac{M * I_{corr}}{n * F * \rho}$$

C_{rate} = Corrosion rate (cm/s)

n = Number of electrons taking place in the reaction

M = Molar mass (g/mol)

I_{corr} = Corrosion current (A/cm²)

F = Faradays constant (96485 A * s/mol)

ρ = Density of the sample

Samples of the stainless steel used in this project were sent to Degerfors laboratory to obtain the composition. Their approximated composition can be seen in table 2 and these compositions is the one used in the calculations of C_{rate} . Their complete compositions can be seen in appendix 1.

Table 2. The approximated composition of the two stainless steels investigated in this project.

	Fe (%)	Cr (%)	Ni (%)	Mo (%)	Mn (%)
304	71.0	18.0	8.0	0.0	2.0
316	69.0	17.0	10.0	2.0	1.0

The calculated values for the molar mass, density and the number of electrons can be seen in table 3.

Table 3. Calculated parameters based on the approximated compositions of stainless steel 304 and 316.

	n_{alloy}	M_{alloy} (g/mol)	ρ_{alloy} (g/cm ³)
304	1.80	54.72	7.741
316	1.79	55.63	7.818

The corrosion rate will maintain the unit cm/s. To make it easier to relate to, this unit will be converted to mm/year by dividing the value with

$$10 \left(\frac{\text{mm}}{\text{cm}} \right) * 3.171 * 10^{-8} \left(\frac{\text{year}}{\text{s}} \right) = 3.171 * 10^{-7} \left(\frac{\text{mm*year}}{\text{cm*s}} \right).$$

The critical pitting potential was determined by using a fixed value of 100 mA/cm². When that value is reached the system is said to have reached its stable pitting stage and the critical pitting potential will be maintained.

4 Results and discussion

This chapter has been divided into two parts, just like the performed measurements. The most important findings of this project will be presented and discussed in this chapter.

4.1 Part one of the project

Following curves are a compilation of the OCP-polarization measurements performed at room temperature. The first two curves (figure 12 and 13) are passivated and non-passivated stainless steel 304 and 316 performed in 0M NaCl solutions. From these curves, one can see that the OCP measurements (figure 12) gives unclear results since the curve has not yet reached a stable value and can therefore not give any reliable results. These curves, as mentioned, should be evaluated with an approach that a less negative value means a better resistance against corrosion.

The polarization curve (figure 13) shows that the stainless steel 316 is more resistant against corrosion than the 304 in both the passivated and the non-passivated cases. A passivation gives the impression of a slightly higher resistance according to these curves. Since the Ir-drop was not compensated for, these curves will not give results good enough to calculate any corrosion rates or determine the critical pitting potential.

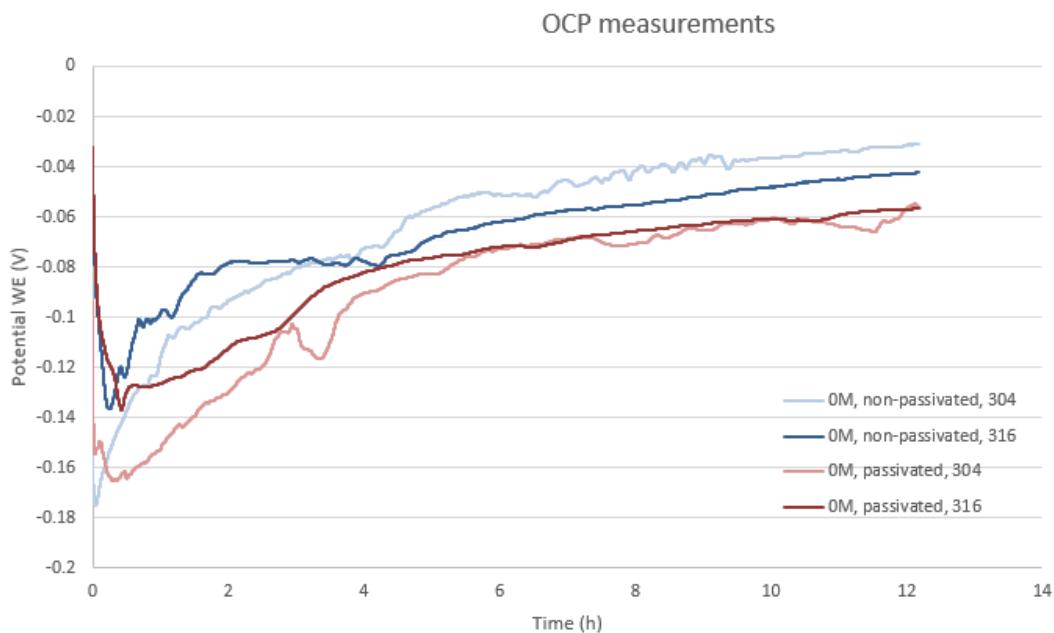


Figure 12 . OCP measurements in 0M NaCl solution.

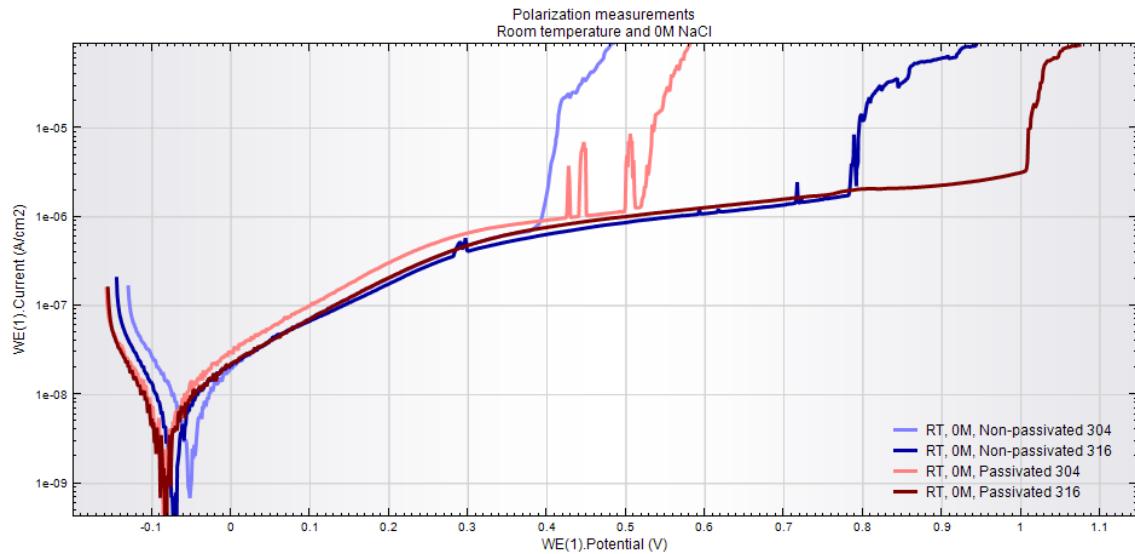


Figure 13 Polarization measurements in 0M NaCl solution.

The next two curves (figure 14 and 15) are passivated and non-passivated stainless steel of 304 and 316 performed in 0.5 molar NaCl solutions. As for the other OCP measurements, this measurement gave unreliable results as well, and cannot be used for any conclusions.

As for the 0M NaCl solutions, these polarization curves show that the stainless steel 316 is more resistant against corrosion than the 304 in both passivated and the non-passivated cases. Also, these curves show that passivation gives a slightly better resistance against corrosion as well.

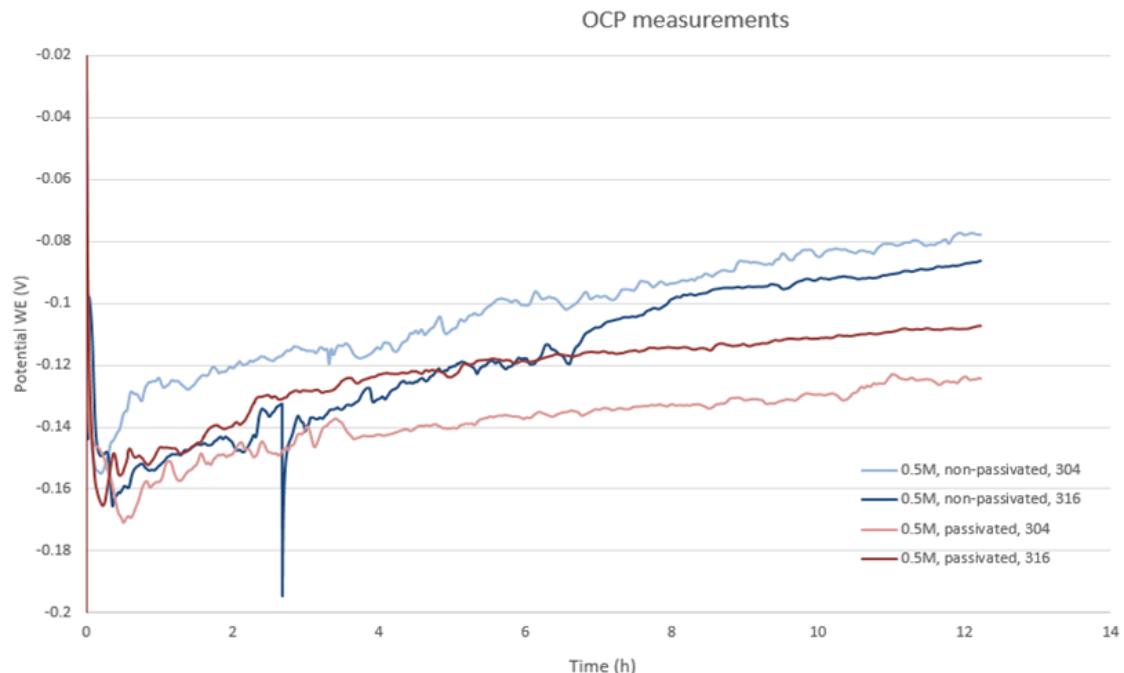


Figure 14. OCP measurements in 0.5M NaCl solution.

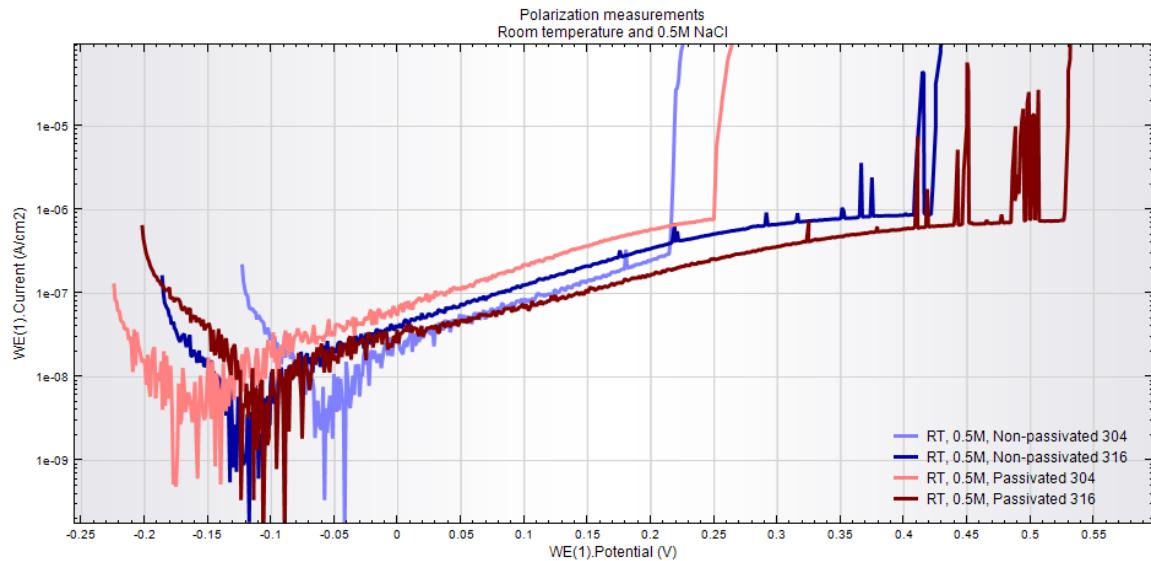


Figure 15. Polarization measurements in 0.5M NaCl solution.

As one can see from the OCP measurements in both media, these curves do not seem to have been stabilized during the time when they were measured (12h) and since there was not enough time to perform longer measurements, this method was not used in later experiments. This is the reason why the experiments were divided into two parts. One can however see that the resulting curves from the OCP measurements shows that the curves tend to reach for values that do not differ very much depending on the different situations. The polarization curves do however tend to give a clear picture of the effect of passivation and the dependency of the concentration of chloride ions.

When the measurements where changed, the results from the first part where not able to be used in comparison with later results. Since the polarization curves for this first part were performed after 12h of OCP measurements, they have had more time to stabilize the system than the ones without. That stabilization of the system may affect the polarization curves and therefore, the measurements in room temperature needed to be repeated with these new conditions in the second part of the experiment.

4.2 Part two of the project

In the second part of the experiment, similar curves will be presented. This part does not include the OCP measurements. However, this part includes one more temperature which will be discussed. In the following measurements, more parameters were added as well; pH and redox potential. The addition of these parameters was done to have more data to compare the results with. Since all of the different samples needed to be repeated, the addition of those new parameters could become handy during the evaluation of the results. The measurements in the first part of this project do not include the parameters due to a too late acquirement of the equipment.

The presentation of these results will start with a comparison between the stainless steel 304 and 316, passivated and non-passivated, immersed in the same solution at the

same temperature. After that, the important data will be shown in two tables. Later, the temperature effect will be shown for each stainless steel in the different environments.

Following four figures show the polarization curves for stainless steel 304 and 316 in different media and at different temperatures. The light color is 304 and the dark is 316. Blue stands for non-passivated and red is the passivated sample.

This first figure show the polarization curves for stainless steel 304 and 316 in 0M solution at room temperature.

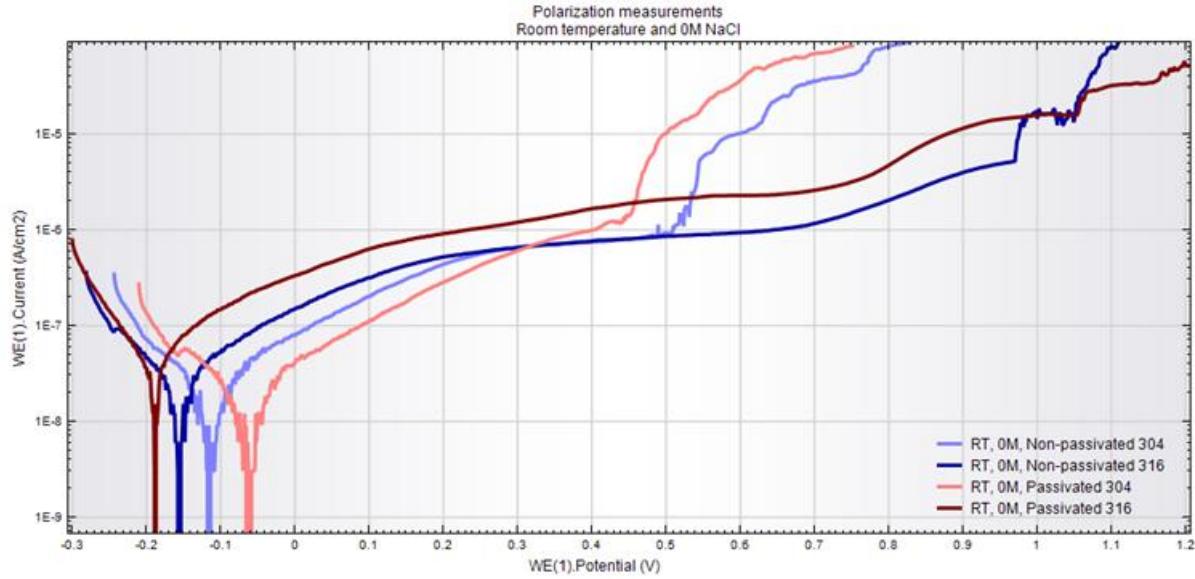


Figure 16. Polarization curve for stainless steel 304 and 316 in 0M NaCl at room temperature.

This figure shows the polarization curves for stainless steel 304 and 316 in 0.5M solution at room temperature.

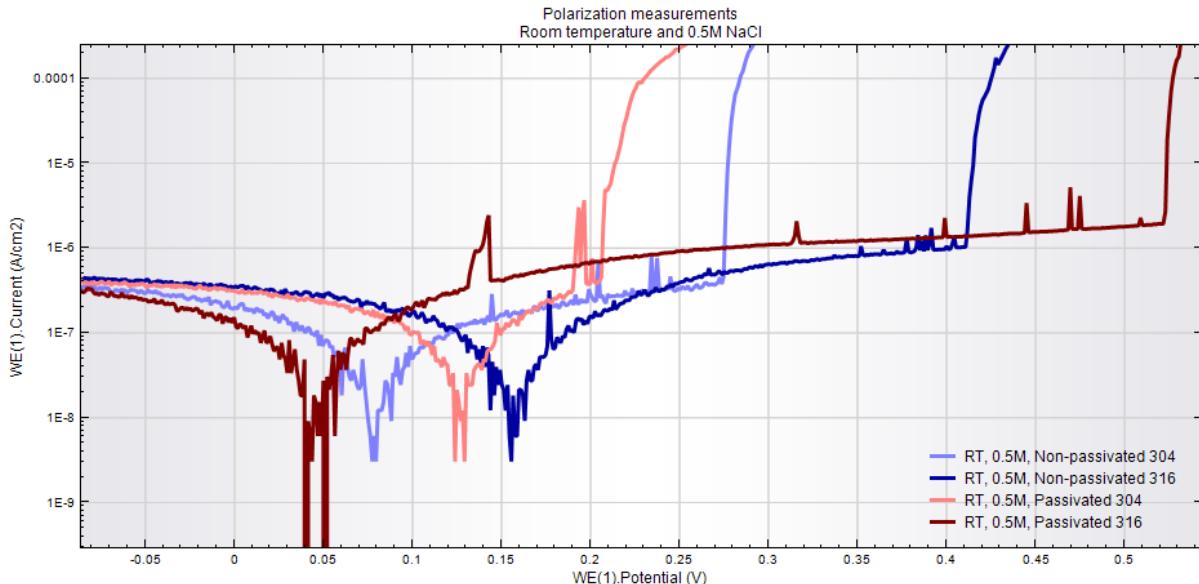


Figure 17. Polarization curve for stainless steel 304 and 316 in 0.5M NaCl at room temperature.

Figure 18 show the polarization curves for stainless steel 304 and 316 in 0M solution at 30°C.

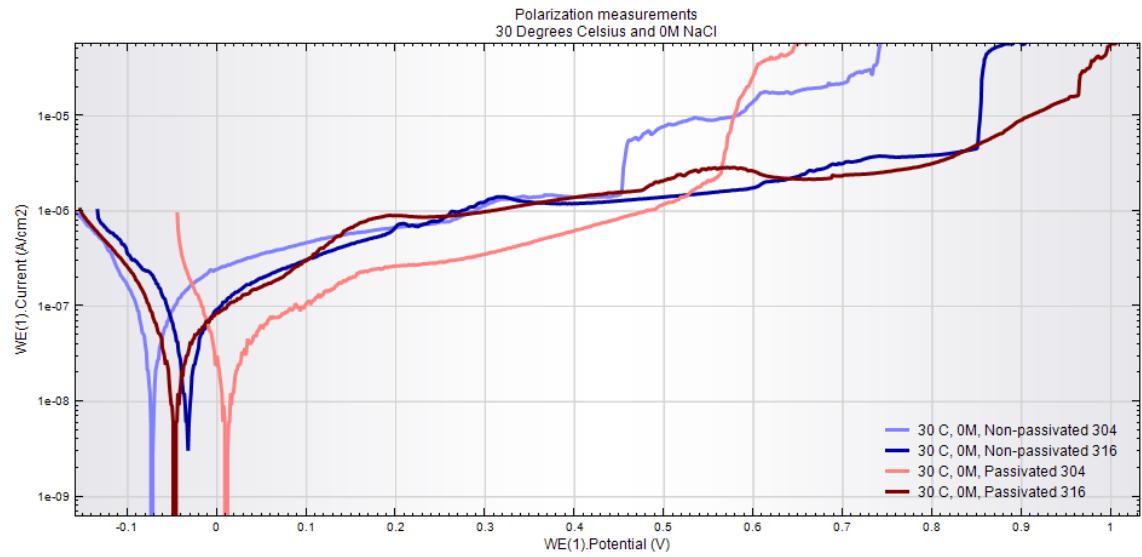


Figure 18. Polarization curve for stainless steel 304 and 316 in 0M NaCl at 30°C.

This figure shows the polarization curves for stainless steel 304 and 316 in 0.5M solution at 30°C.

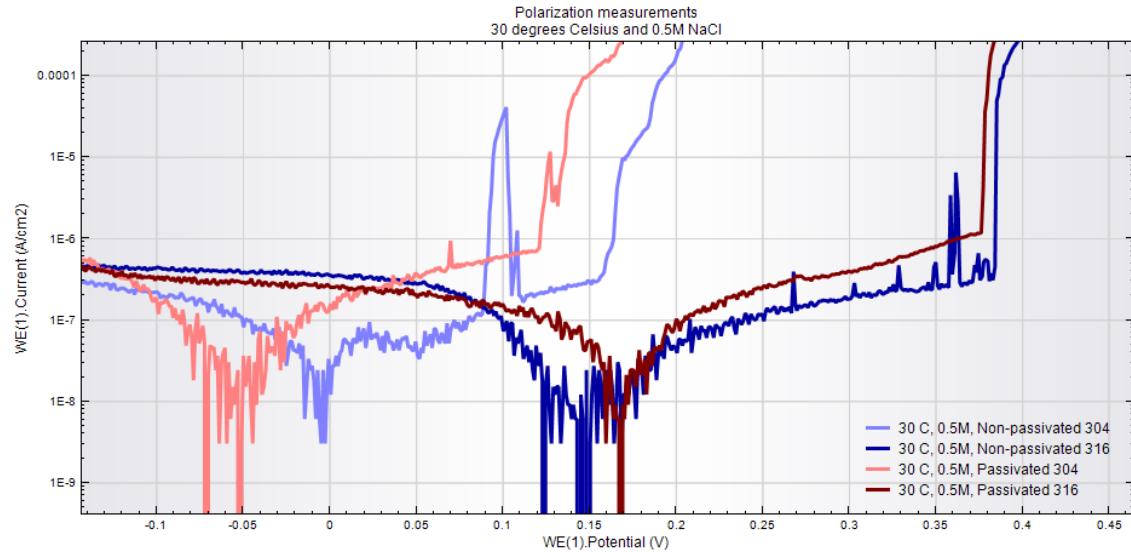


Figure 19. Polarization curve for stainless steel 304 and 316 in 0.5M NaCl at 30°C.

As one can see from all four curves, there is a significant difference between the E_{pit} for 304 and 316. However, the passivation effect does not show a clear sign of having a positive effect on the corrosion resistance. The difference of the 304 and the 316 is most significant in the media with 0.5M NaCl solution and shows the most difference at 30°C. This could mean that the increased temperature increases the difference in corrosion resistance between the materials.

Following table (table 4) is a compilation of the parameters obtained and calculated in the measurements at room temperature.

Table 4. Compilation of important parameters for the room temperature polarization experiments.

Room temperature								
Salt content (M)	Passivated	Material	pH	Redox potential (mV)	E_{corr} (mV)	I_{corr} (nA/cm ²)	C_{rate} (mm/year)	E_{pit} (mV)
0	Yes	304	8.799	371.1	-75.19	153.57	1.971E-5	785
0	Yes	316	8.520	355.6	-219.19	113.52	1.475E-5	1235
0	No	304	8.526	359.1	-119.95	164.25	2.108E-5	855
0	No	316	8.436	376.6	-171.77	78.34	1.018E-5	1150
0.5	Yes	304	8.164	176.0	141.09	834.52	1.071E-4	230
0.5	Yes	316	7.996	202.1	40.131	537.37	6.982E-5	527
0.5	No	304	8.180	142.1	97.85	1125.1	1.444E-4	284
0.5	No	316	8.128	187.7	158.71	1035.5	1.345E-4	425

Following table is a compilation of the parameters obtained and calculated in the measurements at 30°C.

Table 5. Important parameters for the 30°C polarization measurements.

30°C								
Salt content (M)	Passivated	Material	pH	Redox potential (mV)	E_{corr} (mV)	I_{corr} (nA/cm ²)	C_{rate} (mm/year)	E_{pit} (mV)
0	Yes	304	8.381	342.2	2.164	61.183	7.854E-6	695
0	Yes	316	8.252	332.1	-44.709	69.063	8.975E-6	1030
0	No	304	8.562	317.5	-77.58	44.093	5.659E-6	770
0	No	316	8.358	334.1	-42.364	127.13	1.652E-5	945
0.5	Yes	304	7.886	152.1	-55.676	18.456	2.369E-6	149
0.5	Yes	316	8.142	121.7	160.31	798.36	1.037E-4	381
0.5	No	304	8.101	164.1	36.88	50.40	6.469E-6	192
0.5	No	316	8.013	144.0	193.48	619.03	8.043E-5	385

For all of the corrosion rates it should be taken into consideration that the rates are based on the approximated compositions (see chapter 3.4). As one can see from looking at the pH, the situation does differ even when it is meant to be the same. The lowest corrosion rate (i.e the system with the slowest corrosion) according to the measurements is passivated 304 in 0.5M NaCl solution at 30°C where the C_{rate} is 2.369E-6mm/year. This seems very unlikely which could mean that this measurement probably is an outlier. The system with highest corrosion is the non passivated 304 in

0.5M NaCl at room temperature where the C_{rate} is 1.444E-4 mm/year. The corrosion rates do differ a lot but one can see a trend of a higher corrosion rate in 0.5M NaCl solution compared to the 0M solution. The temperature does not seem to have as much influence as the concentration of chloride ions as one can see that the C_{rate} is quite close within the same system at different temperatures. However it seems to be a higher corrosion rate in room temperature than in 30°C in almost all cases which is greatly unexpected.

One other important parameter to take into consideration is the procedure of finding out the I_{corr} used to calculate the C_{rate} . This is performed by fitting the curve in the NOVA 1.9 software and the obtained values differed between every fit.

The pitting potential (E_{pit}) ranged from 149 mV to 1235 mV and one can see a more predicted trend from these measurements. The highest E_{pit} corresponded to the passivated stainless steel 316 in room temperature and 0M NaCl and the lowest corresponded to passivated 304 in 30°C and 0.5 M NaCl. The higher the value of the pitting potential, the more resistant is the steel against pitting corrosion. Within all temperatures, the solution with 0.5M NaCl gave significant lower values on the pitting potential which was expected. One can also see that the pitting potential in the different solutions are always better (higher) for the ones with the stainless steel compared to the 304 measurements. The comparison between the passivated and the non-passivated steels does not seem to have a clear effect on the pitting potential since it sometimes is positive (gives a higher E_{pit}) and sometimes negative (gives a lower E_{pit}) in the passivated cases.

Since the measurements did not have any replicates, the accuracy is unknown, but due to some highly unexpected results, the accuracy seems small. The accuracy of the measurements will be discussed in section 4.3.

One can see from the tables that the redox potential decreases with an increasing concentration of NaCl. An increasing of NaCl-concentration will decrease the amount of dissolved oxygen in the water which will have a reducing effect on the redox potential. This comes from the fact that the salt ions will be surrounded by the water molecules to be able to be solved in the solution. This makes the environment more polar which makes the non-polar oxygen molecules less solvable in the solution. The temperature also has an effect of the solubility of air in the water. One can see a trend that the higher temperatures have a slightly lower redox potential as well, this seems reasonable since the increased temperature increases the kinetic energy of the oxygen molecules which will increase the possibility for them to leave the solution.

These next four figures (20-23) will present the results from a temperature dependent view. The light blue curve is the non passivated sample at room temperature, the dark blue curve is the passivated sample at room temperature, the gray curve is the non passivated sample at 30°C and the black curve is the passivated sample at 30°C.

This figure shows the curves obtained from measuring on stainless steel 304 (passivated and non-passivated) in 0M solution at the two different temperatures.

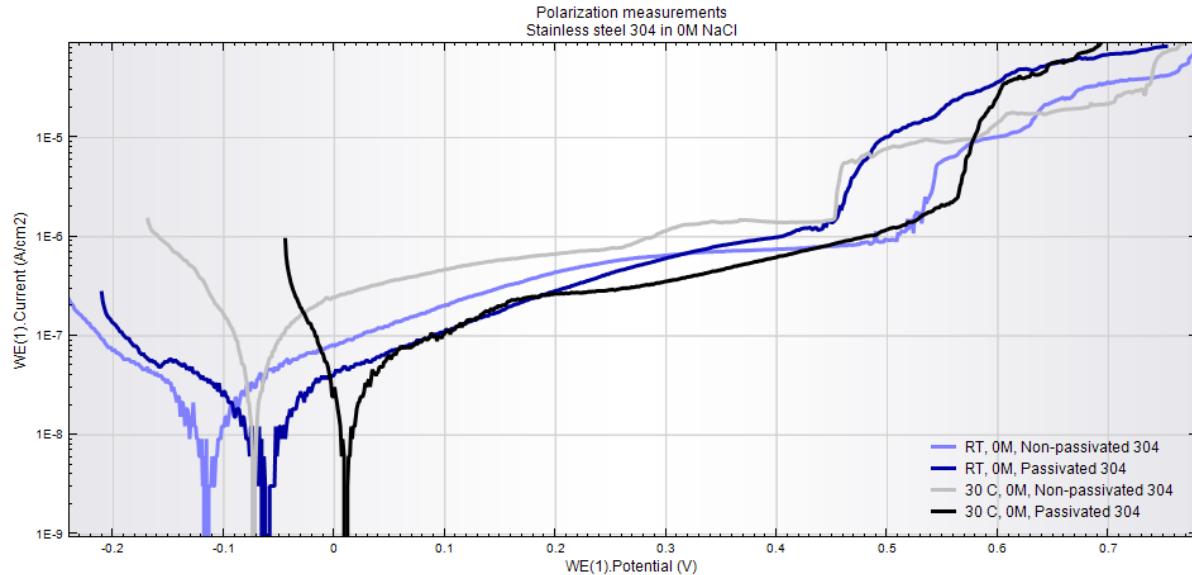


Figure 20. Polarization curve for stainless steel 304 in 0M NaCl.

This figure shows the curves obtained from measuring on stainless steel 316 (passivated and non-passivated) in 0M solution at the two different temperatures.

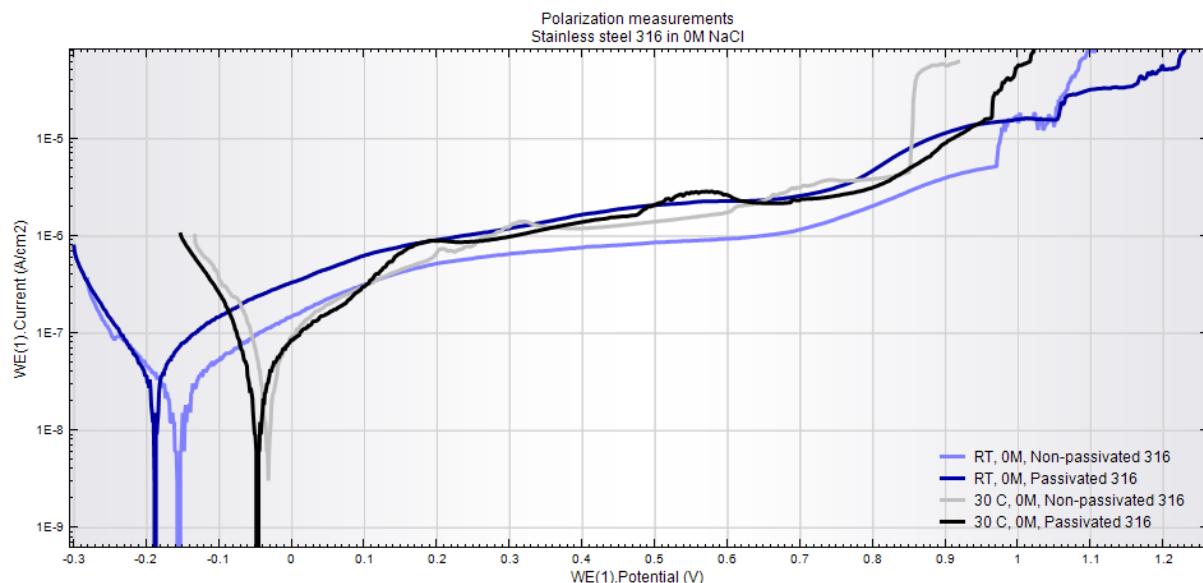


Figure 21. Polarization curve for stainless steel 316 in 0M NaCl.

This figure shows the curves obtained from measuring on stainless steel 304 (passivated and non-passivated) in 0.5M solution at the two different temperatures.

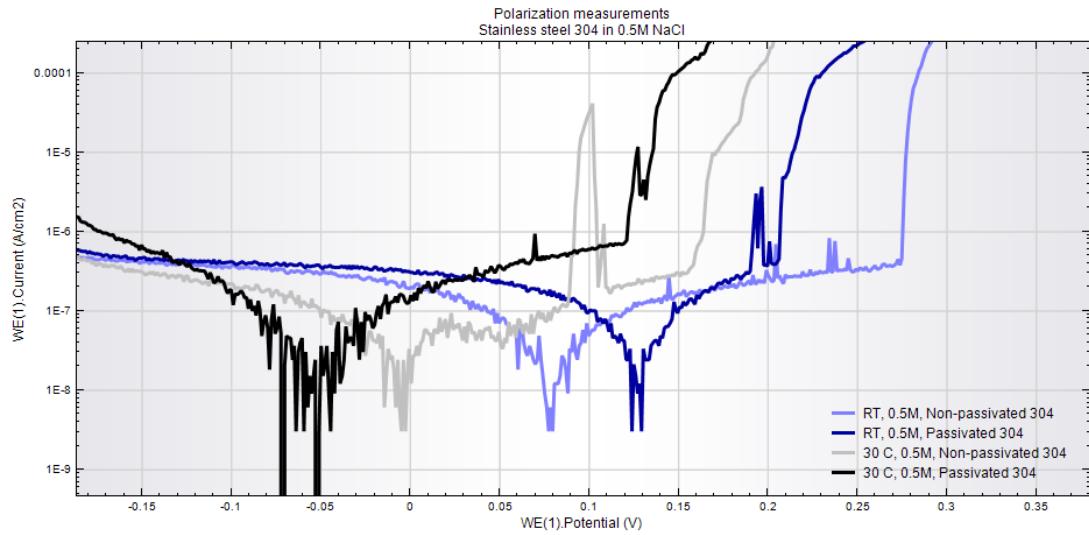


Figure 22. Polarization curve for stainless steel 304 in 0.5M NaCl.

This figure shows the curves obtained from measuring on stainless steel 316 (passivated and non-passivated) in 0.5M solution at the two different temperatures.

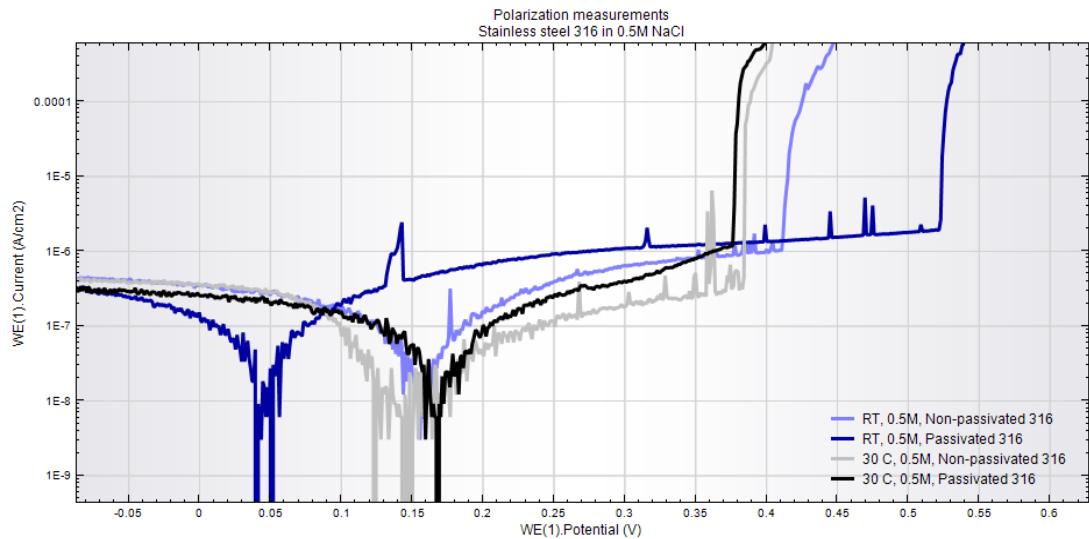


Figure 23. Polarization curve for stainless steel 316 in 0.5M NaCl.

As one can read out from these four curves, the higher temperature gave higher corrosive behavior (lower E_{pit}) in almost all cases. However, in some of the cases, this difference is very small and it is possible that the difference is just instrumental errors. The difference between a passivated and non passivated material does not give any conclusions due to that the passivation has a positive effect in some cases and negative in other. One error that might be present in the second part of the project is that the polarization measurements took place long before the system was stabilized since the measurements started instantly. And as one can see from part one, the system are not stabilized even after 12 hours.

4.3 Measurement accuracy

During the measurements, the equipment was sometimes started with incorrect instrumental setups so that the measurement needed to be redone. When performing the new measurements, new samples were prepared in the same way as the first time. These measurements with the incorrect setups helped to understand the accuracy of the measurements. Since there was no time to do replicates of the measurements, these curves were the only way to compare two measurements that should be exactly the same (i.e. same solution, same preparation and same temperature). From these curves, one can see that the accuracy was not very good in many cases. The difference within the same systems was sometimes larger than the difference obtained between two different systems.

One of the comparisons of the polarization measurements can be seen in figure 24. More curves can be seen in appendix 2. Within the figures, the same colour stands for the same system and therefore, if the measurements were accurate, these curves should not differ. Since there was a mistake made in the setup, only parts of the curve were obtained.

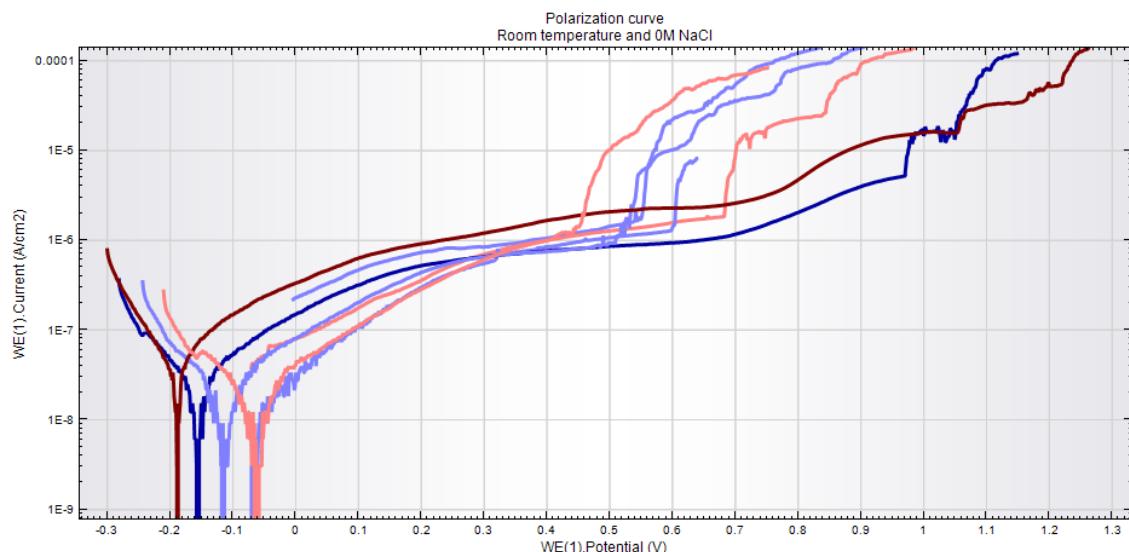


Figure 24. Polarization curve meant to illustrate the accuracy of the measurements.

5 Conclusions

Since the experiments in this project are performed at quite low temperatures it does not mean that the metals will have the same behaviour temperatures present in real processes. None of the measurements have replicates which are a major drawback in the project. The time frame limited this because of the long time every measurement required. Other factors that could have caused errors are coating of the sample. The goal was to have one cm^2 of the surface exposed to the solution but since the coating was done by hand, this might differ a bit.

An error in the second part of the project might be that the systems were not stable when performing the polarization curves. A concentration of 0.5M NaCl was a fair concentration of salt, if comparing with real food processes. Nevertheless, this amount can also sometimes be much higher. For example, when one processes soy sauce, the concentration of salt could be around 90g/L, which corresponds to almost 1.5M.

The most significant difference between the polarization measurements in the first and the second part of the project seems to be the stabilization of the system. It seems that the polarization measurement in the second part was performed way too early after immersing the sample into the solution. Also, the Ir-drop was not compensated for in the polarization measurements in the first part.

The only clear conclusion able to be drawn is that there is a significant difference in corrosion resistance between the stainless steel 304 and 316 when subjected to higher concentrations of chloride ions. This is also in correspondence with previous studies found in literature.

6 Future work

To continue with this project one should make longer OCP measurements to be able to require a stable value followed by a polarization sweep performed once the system is stabilized. One other alternative is to perform the polarization with a faster sweep on the system a few times before performing the real measurement.

Higher temperatures and different concentrations of chloride ions need to be measured to obtain results closer to the real system. Replicates were not within the time limit, and needs to be done a lot of times to be able to get a more accurate value. It would be interesting to try the same approach with a food media though it is possible that there is something else in that media that has an effect on corrosion more than just the chloride ions. There are also several other passivation techniques that can be studied.

7 References

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8 Appendix

8.1 Appendix 1

Complete composition of the stainless steel 304 and 316 investigated in this project.

Resultat/Results	Måtosäkerhet/Uncertainty of measurement	Standard metod/method	Dlab metod/method
C	0.021 %	0.002 %	ASTM E 1019-11
Si	0.38 %	0.007 %	ASTM E 572-13
Mn	1.51 %	0.007 %	ASTM E 572-13
P	0.031 %	0.004 %	ASTM E 1086-14
S	0.002 %	0.0010 %	ASTM E 1019-11
Cr	17.98 %	0.09 %	ASTM E 572-13
Ni	8.00 %	0.03 %	ASTM E 572-13
Mo	0.27 %	0.001 %	ASTM E 572-13
Ti	0.004 %	0.0007 %	ASTM E 572-13
Nb	0.010 %	0.0007 %	ASTM E 572-13
Cu	0.48 %	0.004 %	ASTM E 572-13
Co	0.14 %	0.005 %	ASTM E 572-13
N	0.049 %	0.003 %	ASTM E 1019-11
Sn	0.016 %	0.0006 %	ASTM E 572-13
W	0.03 %	0.005 %	ASTM E 572-13
V	0.060 %	0.0006 %	ASTM E 572-13
Al	0.004 %	*	ASTM E 1086-14
Ta	0.008 %	*	ASTM E 1086-14
Ca	0.0006 %	*	ASTM E 1086-14
B	0.0022 %	0.0003 %	ASTM E 1086-14
As	0.006 %	0.0007 %	ASTM E 1086-14
Fe	71.00 %	*	5.4-057M

Figure 25. Composition of stainless steel 304

Resultat/Results	Måtosäkerhet/Uncertainty of measurement	Standard metod/method	Dlab metod/method
C	0.018 %	0.002 %	ASTM E 1019-11
Si	0.53 %	0.009 %	ASTM E 572-13
Mn	0.94 %	0.005 %	ASTM E 572-13
P	0.031 %	0.004 %	ASTM E 1086-14
S	0.001 %	0.0009 %	ASTM E 1019-11
Cr	16.72 %	0.08 %	ASTM E 572-13
Ni	10.00 %	0.04 %	ASTM E 572-13
Mo	2.06 %	0.009 %	ASTM E 572-13
Ti	0.008 %	0.001 %	ASTM E 572-13
Nb	0.017 %	0.0007 %	ASTM E 572-13
Cu	0.42 %	0.003 %	ASTM E 572-13
Co	0.20 %	0.005 %	ASTM E 572-13
N	0.042 %	0.003 %	ASTM E 1019-11
Sn	0.010 %	0.0005 %	ASTM E 572-13
W	0.05 %	0.006 %	ASTM E 572-13
V	0.058 %	0.0006 %	ASTM E 572-13
Al	0.003 %	*	ASTM E 1086-14
Ta	0.008 %	*	ASTM E 1086-14
Ca	0.0004 %	*	ASTM E 1086-14
B	0.0021 %	0.0003 %	ASTM E 1086-14
As	0.010 %	0.001 %	ASTM E 1086-14
Fe	68.87 %	*	5.4-057M

Figure 26. Composition of stainless steel 316.

8.2 Appendix 2

This appendix complements the section 8.3 with polarization curves to show the accuracy of the measurements.

