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Norwegian University of
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# Influence of test parameters on high temperature cathodic disbonding testing of fusion bonded epoxy coatings

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# Preface

This master's thesis was carried out at the Department of Materials Science and Engineering in the Norwegian University of Science and Technology (NTNU) as the completion of a five year integrated master's degree program in Chemical Engineering and Biotechnology, with specialization in Materials Chemistry and Energy Technology. The work was done in collaboration with Jotun AS and builds on the specialization project "High temperature cathodic disbonding testing of fusion bonded epoxy coatings - parameter study" conducted during the fall of 2019 [1]. This project was supervised by Ole Øystein Knudsen (Department of Mechanical and Industrial Engineering), Andreas Erbe (Department of Materials Science and Engineering), Maxim Mitrokhin (Jotun) and Stefanie Römhild (Jotun). The thesis has been written during the spring of 2020. Some parts of the introduction, theory, experimental procedure and results are reused from or formulated in the same manner as in the preceding project as this was a continuation of the preliminary work and mostly consisted of the same activities.

The work has been performed by the author. The experimental work was performed at the Department of Mechanical and Industrial Engineering at NTNU.

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# Abstract

Fusion bonded epoxy (FBE) coating in combination with cathodic protection is often used as a corrosion protection system on steel pipelines submerged in seawater. However, coatings in combination with cathodic protection can lead to cathodic disbondment (CD) if the coating is damaged. Testing coating for resistance to cathodic disbondment is therefore a crucial part of coating development and qualification testing. Jotun does CD tests both in oven and on hotplate. However, both test set-ups do not result in the same disbonded area. In general, it is noted, that the cathodic disbondment when testing FBE coatings in the oven set-up is larger compared to when tested in the sand bath set-up. The reasons for the difference in performance and whether there are unknown differences in the testing conditions giving different disbondment rates are not understood today.

In this project CD tests in oven and on hotplate were done. A series of four experiments of CD tests were completed. There were three to six parallels in the oven and three to six parallels on the hotplate in each test. The duration of the tests were two, three and four weeks. Temperature in the damage and potential were manually measured throughout the experiments. The current going through the cells, the potential in the damage, the temperature in the steel, the interface between the steel and the coating, and in the solution were logged. Two panels were put in a beaker containing 1 M NaOH for nine days, at 70 °C. Electrochemical impedance spectroscopy was carried out five times, the adhesion and the hardness of the coating were tested.

The results of the CD tests in this project correlated with the tests done at Jotun and the tests done in the preceding specialization project [1].

In both the first and second test a ring with adhesion was discovered followed by a new area where the adhesion was lost. If the measured disbondment front of the panels tested on the hotplate was compared to the measured disbondment of the panels tested in the oven, they showed similar results of disbondment. A hypothesis is that the area with adhesion is caused by the difference in temperature gradients and the difference in the temperature in the steel as that were the only systematic differences that were detected between the cells tested on the hotplate and in the oven. Further, the ring with adhesion was affected when the temperature in the steel was changed.

The regaining of adhesion of the coating happened for cells tested for longer than 2 weeks. The regaining of adhesion was most dominant after three weeks compared to tests carried out for four weeks.

A hypothesis was that the regained adhesion was caused by degradation of the coating by hot NaOH or by intermediates as radicals in the oxygen reduction. The results of electrochemical impedance spectroscopy, adhesion tests and hardness tests indicated that there was no degradation of the coating due to exposure of hot NaOH. The lifetime of a radical was estimated to be too short for the radical to reach and react with the coating.

There is a strong indication that the temperature in the steel affects the area with adhesion and the difference in the disbondment, but no good theory has been found on how this happens.

# Sammendrag

Fusjonsbundet epoksybelegg brukes sammen med katodisk beskyttelse for å beskytte stålrør i sjøvann mot korrosjon. Belegg i kombinasjon med katodisk beskyttelse kan føre til katodisk avbinding hvis belegget er ødelagt. Derfor er testing av belegg for deres motstand mot katodisk avbinding en viktig del av utvikling av belegg og kvalifiseringstesting. Jotun gjør CD tester både i ovn og på varmeplate. Begge test-oppsettene gir ikke samme resultat i avbinding. Generelt gir testing av belegg i ovn større avbinding enn tester gjort på varmeplate. Grunnen for forskjellen i resultater og om det er ukjente forskjeller i testforholdene som gir forskjellige avbindingshastigheter er ikke forstått.

I dette prosjektet ble det gjort CD tester i ovn og på varmeplate. En serie av fire eksperimenter ble gjennomført. Det var tre til seks paralleller i ovn og tre til seks paralleller på varmeplate for hver test. Testene varte i to, tre og fire uker. Temperatur i skaden og potensialet ble målt manuelt gjennom forsøkene. Strømmen som gikk gjennom cellene, potensialet i skaden, temperaturen i stålet, grensesnittet mellom stålet og belegget, og løsningen ble logget. To paneler ble satt i et begerglass med 1 M NaOH i ni dager, ved 70 °C. Elektrokjemisk impedansspektroskopi ble gjennomført fem ganger, heften og hardheten til belegget ble testet.

Resultatene i dette prosjektet korrelerte med testene som ble gjennomført hos Jotun og testene som ble gjennomført i det foregående fordypningsprosjektet.

Både i den første og den andre testen ble det funnet en ring med heft etterfulgt av et nytt område hvor heften var mistet. Hvis den målte avbindingsfronten på panelene som var testet på varmeplaten ble sammenlignet med den målte avbindingen på panelene som var testet i ovnen hadde de lignende avbinding. En hypotese er at området med heft er forårsaket av forskjellen i temperaturgradientene og forskjellen i temperaturen i stålet, siden dette var de eneste systematiske forskjellene som ble oppdaget mellom cellene som var testet på varmeplaten og i ovnen. Videre ble ringen med heft påvirket da temperaturen i stålet ble endret.

Gjenvinningen av heften skjedde for celler som ble testet lenger enn to uker. Gjenvinningen av heft var mest dominant etter tre uker, sammenlignet med testene som varte i fire uker.

En hypotese var at gjennvinningen av heft var forårsaket av degradering av belegget av varm NaOH eller av mellomprodukter som radikaler i oksygen reduksjonen. Resultatene av den elektrokjemiske impedansspektroskopien, avtrekkstestene og hardhetstestene indikerte at det ikke var noe degradering av belegget på grunn av eksponering for varm NaOH. Levetiden til et radikal ble estimert til å være for kort til at radikalet når og reagerer med belegget.

Det er en sterk indikasjon på at temperaturen i stålet påvirker området med heft og forskjellen i avbinding, men det er ikke funnet noen god teori på hvordan det skjer.

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# 1 Introduction

This thesis is a continuation of the specialization project "High temperature cathodic disbonding testing of fusion bonded epoxy coatings - parameter study" [1]. Thus, the background and motivation for this thesis coincides with the preceding project and has been reused with some changes.

## 1.1 Background and motivation

Steel pipelines submerged in seawater need corrosion protection to have a sufficient lifetime. A corrosion protection system subsea is normally a combination of cathodic protection and a coating system [2]. Fusion bonded epoxy (FBE) coatings are frequently used. A FBE coating is a single-component, thermosetting-epoxy resin powder which utilizes heat to melt and adhere to the metal surface [3]. However, coatings in combination with cathodic protection can lead to cathodic disbondment (CD) if the coating is damaged. Cathodic disbondment is a process where the coating loses its adhesion to the substrate due to oxygen reduction that take place under the coating if there are defects in the coating [4]. Testing coating for resistance to cathodic disbondment is therefore a crucial part of coating development and qualification testing. However, even though CD is a well-studied topic there are a lot of questions that remain.

Today, CD testing of fusion bonded epoxy coatings is for instance described in CSA-Z245.20, which allows testing at elevated temperature (65 °C) either in a set-up where cells are placed on a e.g. sand bath or heating source heating the cells from beneath, or by placing the CD cells in an oven. However, both test set-ups do not result in the same disbonded area. In general, it is noted, that the cathodic disbondment when testing FBE coatings in the oven set-up is larger compared to when tested in the sand bath set-up. The reasons for the difference in performance and whether there are unknown differences in the testing conditions giving different disbondment rates are not understood today. Understanding the mechanism of cathodic disbondment of FBE in a better way could allow for improved test set-up for development purposes as well as improved optimization of FBE coating formulations.

The FBE coating that was used for this project is one of Jotun's formulations which is still under developement and testing and is named OCR-400. It was chosen because of having shown large difference in hotplate and oven testing and moderate performance. Jotun have done three separate CD tests with this formulation and the results are shown in Figure 1.1. The duration of all the tests were four weeks. The third test is the same batch of coating that was used for one of the tests done in this project. The third test was started by the author at Jotun Powder Coatings' lab in august and ended by Jotun in september 2019. Measured disbondment for all the panels from the third test is given in Table A.1 in Appendix A. The average disbondment of the panels where the test was done on a hotplate was 5.5 mm with a standard deviation of ±0.7 and the average disbondment of the panels where the test was done in an oven was 13.4 mm with a standard deviation of ±1.0 [1]. In the preceding project to this project, there were done CD tests with the same formulation that lasted for two, three and four weeks. The results are shown in Figure 1.2. Measured disbondment for all the panels from the tests in the preceding project is given in Table B.1 in Appendix B. The average disbondment of the coating for the cells tested on a hotplate for two, three and four weeks were 6.3 mm, 8.2 mm and 11.8 mm with a standard deviation of ±0.7, ±3.4 and ±2.1, respectively. The average disbondment of the coating for the cells tested in an oven for two, three and four weeks were 3.7 mm, 13.8 mm and 14.2 mm with a standard deviation of ±0.4, ±1.1 and ±1.3, respectively. The average disbondment of the coating for all the tests are shown in Figure 1.3. In 'High temperature cathodic disbonding testing of fusion bonded epoxy coatings - parameter study' it was concluded that the results from Jotun were reproduced to a certain degree in the experiment and further tests can be done with a duration of three weeks, with six panels in parallel [1].

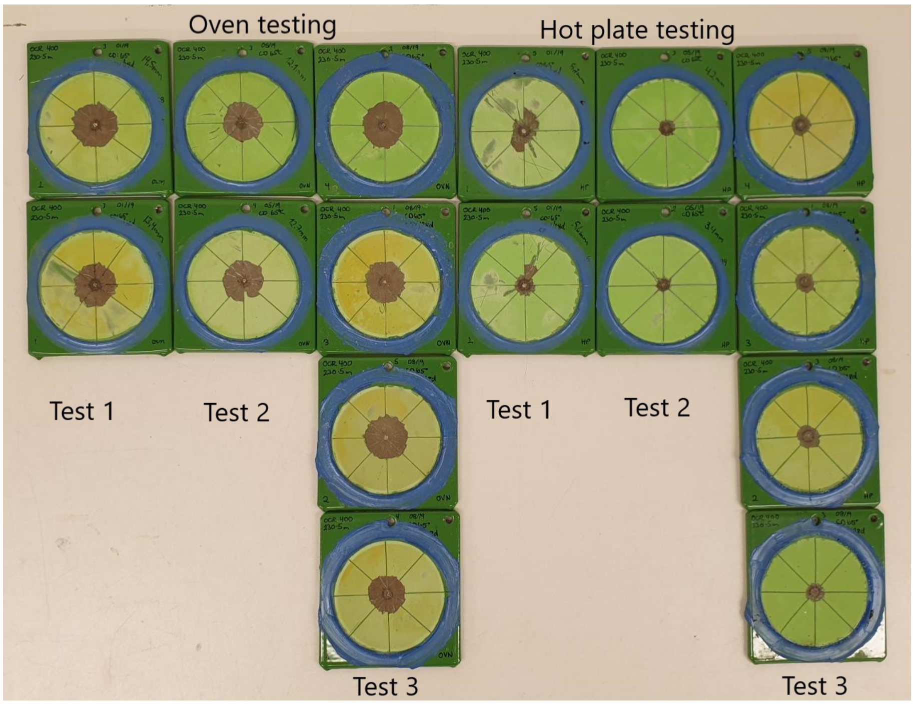
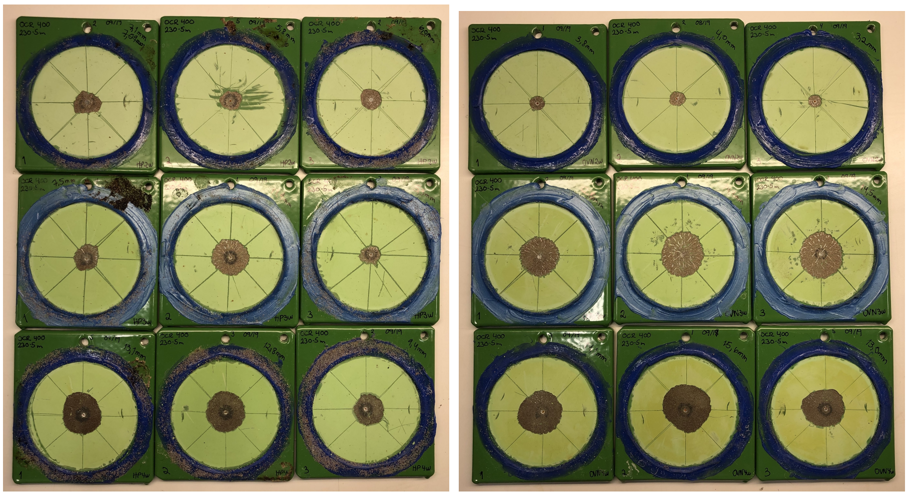


Figure 1.1: Results of CD tests for OCR-400 done at Jotun [1].



(a) Hotplate

(b) Oven

Figure 1.2: Results of CD tests for OCR-400 done in the preceding project [1]. From top to bottom, the tests lasted for two, three and four weeks.

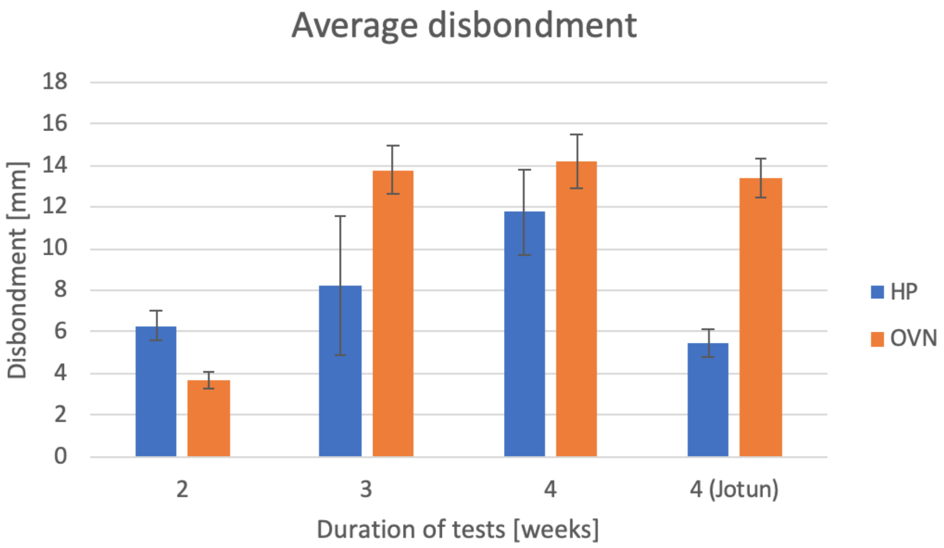


Figure 1.3: Results of CD tests for OCR-400 done at Jotun and in the preceding specialization project [1].

## 1.2 Aim and scope of the work

The aim for this project was to further investigate the difference between hotplate and oven testing of cathodic disbondment. In order to achieve this, available literature on cathodic disbondment, effect of test parameters and degradation of Fusion Bonded Epoxy coating in alkaline environment were investigated. Experimental work was performed to study the effect of the test parameters. The effect of temperature, potential, oxygen concentration, pH and current in the cells were investigated in the preliminary work. The effect of temperature and potential was further examined in this project, and additionally, the effect hot NaOH solution has on the coating was examined.

# 2 Theory

Major parts of the activities conducted in this project are the same as the ones in its preceding specialization project. Therefore, it is covered by much of the same theory and large parts are reused from the preliminary work with some changes.

## 2.1 Cathodic disbondment

The mechanism of cathodic disbondment is, despite a lot of research, not fully understood. There have been suggested several mechanisms for cathodic disbonding. These have been put into three groups by Watts, depending on their loci of failure; dissolution of the iron oxide layer on the steel surface, chemical degradation of the coating near the interface or failure at the interface caused by the high pH [5]. Generally it is agreed upon that the disbonding is caused by the alkaline environment generated by the cathodic reaction at the steel surface under the coating [6, 7]. There are two possible cathodic reactions at the surface that will lead to an increase in pH. The two reactions are oxygen reduction as in Equation 1 and hydrogen evolution as in Equation 2.

$$O_2 + 2H_2O + 4e^- = 4OH^- \tag{1}$$

$$2H_2O + 2e^- = H_2 + 2OH^- \tag{2}$$

Structures submerged in seawater protected by anodes made of aluminium or zink are cathodically polarized. Depending on the material of the anode and the distance to it, the applied potential is between -0.800 and -1.150 V Ag/AgCl. Both oxygen reduction and hydrogen evolution can be the cathodic reaction at these potentials. When bare steel submerged in seawater is polarized to approximately -1.000 V SCE, these reactions have the same rate according to Leidheiser [7]. Oxygen reduction is the dominant reaction when the potential is higher than this value and hydrogen evolution is the dominant reaction when the potential is lower than this value. The potential will be higher under the coating, nevertheless the oxygen reduction will be the only cathodic reaction. This is because the resistance in the electrolyte is so high in the narrow crevice between the surface of the steel and the coating that the potential is too high for hydrogen evolution [4, 6, 7, 8]. It is shown by Haji-Ghassemi et al. that to get a significant hydrogen evolution, potentials lower than -1.200 V SCE is needed [9]. This means that for both free corrosion potential and polarization with anodes, the dominating cathodic reaction will be oxygen reduction.

The oxygen reduction reaction consists of multiple reaction steps involving a number of unstable intermediates, including hydrogen peroxide and free radicals [10]. Some of the possible reaction steps with their reduction potentials are shown in Table 2.1. Primarily, oxygen is electrochemically reduced directly to hydroxyl ions. However, under cathodic polarization, the formation of peroxides and free radicals is also thermodynamically favored, and as much as 50 % of the oxygen can be reduced to reactive intermediates [11, 12, 13]. The disbonding of the coating may be caused by the reactive intermediates attacking the coating binder. Analysis of the coating after cathodic disbonding has revealed chemical changes in the binder. This agree with the suggestion of chemical degradation of the coating [4, 14]. In a study by Sørensen et al. it was shown that modifying epoxy coatings with free radical scavengers could reduce the rate of cathodic delamination by up to 50 %. A coating modified with 3 wt% radical scavengers (DBTHQ) on stainless steel showed a cathodic delamination of 18.6 mm ±1.6 compared to a reference coating without free radical scavengers that showed a cathodic delamination of 40.4 mm ±1.3 [15]. This agree with chemical degradation of the coating as a mechanism. However, the scavengers also will prevent formation of hydroxide and is expected to have the same effect on interfacial failure and dissolution of the iron oxide [4].

Table 2.1: Reduction potentials of oxygen and related species at pH 14.

| *Reaction* | $E^0$ *(V SHE)* |
|---|---|
| $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ | 0.401 [16] |
| $O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-$ | -0.076 [17]<br>-0.0649 [18]<br>-0.068 [19] |
| $HO_2^- + H_2O + 2e^- \rightarrow 3OH^-$ | 0.88 [17]<br>0.867 [18] |
| $O_2 + e^- \rightarrow {}^{\bullet}O_2^-$ | -0.3 [12]<br>-0.137 [19] |
| ${}^{\bullet}O_2^- + 2H_2O + 3e^- \rightarrow 4OH^-$ | 0.7 [17] |
| $\frac{1}{2}O_2 + H_2O + e^- \rightarrow {}^{\bullet}OH + OH^-$ | -0.61 [17] |
| ${}^{\bullet}OH + e^- \rightarrow OH^-$ | 1.4 [17] |
| ${}^{\bullet}O_2^- + H_2O + e^- \rightarrow HO_2^- + OH^-$ | 0.007 [19]<br>0.17 [12] |

Other analysis of the metal surface after cathodic disbonding has shown the locus of failure to be at the oxide-polymer junction, which suggest that the failure was mainly adhesive. Additionally, aluminium pigments in the first layer of coat has been proven to reduce cathodic disbonding. It is indicated that the aluminium reacts with the hydroxide, removing it and acting as a buffer. This indicates that the disbonding is caused by the high pH induced by the hydroxide [20, 21]. The third suggested mechanism is the loss of adhesion by dissolution of the iron oxide. This is because steel surfaces are covered with oxides where the stability and composition depend on the potential and pH [7, 22].

For systems that are cathodically protected, the cathodic disbonding initiates where the steel surface is exposed to the electrolyte, for example at mechanical damages, coating edges or blisters. The cathodic reaction happens on the steel surface under the coating while the anodic reaction happens at the sacrificial anodes. To maintain charge neutrality, electrons are transported from the anode and through the steel, while sodium ions are transported in the electrolyte under the coating. The sodium ions form sodium hydroxide with the hydroxide from the cathodic reaction. The coating starts to lose adhesion because of the high pH. pH values as high as 12 to 14 has been observed. There has been disagreement regarding the transport of cations to the disbonding front. In theory, the cations can be transported under the coating or through the coating. Leidheiser et al., Stratmann et al., and Knudsen and Skar have based on experimental results concluded that the cations are transported under the disbonded coating. Oxygen and water have relatively high solubility in coatings. Therefore, it is generally assumed that they are transported through the coating. This is also verified by Leidheiser et al. and Knudsen and Skar [4, 5, 6, 7, 23, 24]. Figure 2.1 shows a schematic illustration of cathodic disbondment on a subsea steel surface [4].

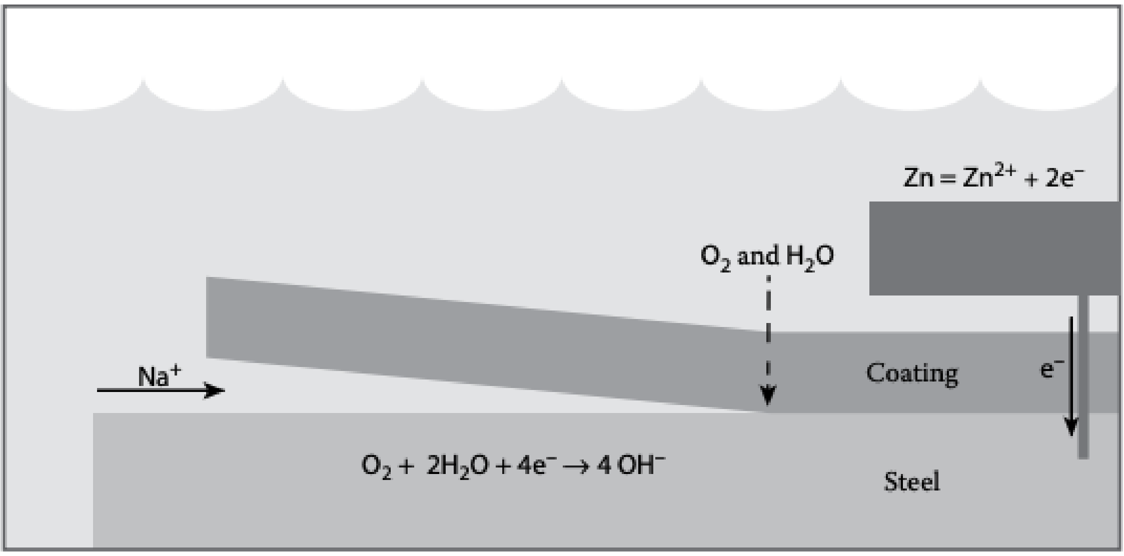


Figure 2.1: Schematic illustration of cathodic disbondment on a subsea steel surface [4].

## 2.2 Disbondment rate - film thickness and time

Increased coating film thickness decreases the cathodic disbonding. Leidheiser et al. and Jin et al. came to the conclusion that the disbondment rate decreased linearly with dry-film thickness based on their investigations. Their studies were conducted on coatings with less than 100 µm film thickness. In a more recent study, Knudsen and Skar found that the effect of film thickness depends on the properties of the coating. One epoxy showed a linear decrease in cathodic disbondment with increase of film thickness, while for the other the film thickness did not affect the disbondment rate. The other epoxy contained aluminium flakes, which is affecting the cathodic disbondment. Zhou et al. showed in their study that the disbonding decreased with increasing film thickness, but for higher film thicknesses the decrease in disbonding was not as big as for thinner coatings. Holub et al. did tests with coating thickness above 400 µm that showed decrease in disbonding with increase in film thickness [6, 7, 25, 26, 27]. Tests conducted in the preceding specialization project showed no clear relationship between the thickness of the coating and the disbondment of the coating. This may be due to the thickness or the properties of the coating. The coating was rather thick and the variation in thickness of coating was not that big, therefore, the effect may have been to small to be distinguished from the experimental variation [1].

The disbonded distance increases linearly with the square root of time. This means that disbonded distance plottet against the square root of time will give a straight line. The same apply for disbonded area against time. At the start of an experiment there is an initiation period where there is no disbonding, called delay time by Leidheiser. The delay time is attributed to the ingress of reactants into the coating [7, 26, 28].

## 2.3 Effect of test parameters

To accelerate the disbondment rate, several CD testing methods are done at elevated temperatures. Holub et al. stated that the rate of disbondment is directly proportional to temperature after doing tests at 23 °C and 65 °C. Results of other studies have also shown that high temperatures increase the rate of disbonding. A study by Cameron et al. showed that the disbondment increased up to temperatures at about 65-80 °C and started to decrease at temperatures higher than this. This may be related to the lower solubility of oxygen at higher temperatures. Knudsen et al. did a study where they calculated the temperature profile for a sample with a 500 µm thick coating. If the test panel is heated from below and the temperature of the electrolyte is lower than the temperature on the steel panel, there will be a slight temperature gradient in the steel and a bigger gradient in the coating, depending on temperature of the electrolyte. Payer et al. did a study where they found that thermal gradients have a major effect on performance. If the coating is cooler than the steel, there will be less disbondment compared to when the coating and steel have the same temperature. If the coating is hotter than the steel, there will be more disbondment compared to when the coating and steel have the same temperature [27, 29, 30, 31, 32, 33, 34]. In the preceding specialization project the differences in the temperatures measured in the damages were not big enough to assume that they were causing the difference in the disbondment between hotplate and oven testing [1].

The oxygen concentration in the electrolyte affects the disbondment rate. Studies done by both Leidheiser and Wang, and Knudsen and Skar have found that when the oxygen is removed from the electrolyte, little cathodic disbondment occurs. In a later study by Leidheiser et al, it was found that the disbondment rate increased when the oxygen concentration increased. The study by Knudsen and Skar showed that when the electrolyte was oxygen saturated the coatings had significantly more cathodic disbonding than when the electrolyte was air saturated. They used synthetic seawater as electrolyte. The air saturated electrolyte had an oxygen concentration of about 6 ppm and the oxygen saturated electrolyte had an oxygen concentration above 20 ppm. Similar tests done by Sørensen et al showed the same tendency. Increasing the oxygen concentration in the electrolyte may shorten the delay time or increase the slope of the disbonded area/time curve [6, 7, 35, 36]. In the preceding specialization project the differences in the measured oxygen content were not big enough to assume that they were causing the difference in the disbondment between hotplate and oven testing [1].

The results of a study by Jin et al. showed a linear relationship between disbondment rate and applied potential. In later studies by Knudsen and Skar, and Sørensen et al. there were also found a linear relationship between disbondment rate and applied potential. A linear relationship between disbondment rate and applied potential indicates that the process is controlled by an Ohmic resistance. Knudsen and Skar found an increase in disbondment rate with decreasing potential from -0.700 V to -1.4 V SCE, the same did Sørensen et al. Results from Rodriguez et al. indicated the same tendency for applied potential from -1.00 V SCE to -1.50 V SCE. Kendig et al. had earlier found that the disbonded distance increased with decreasing potential down to about -1,000 V Ag/AgCl, but the results showed that the effect of potential was smaller below -1.000 V Ag/AgCl [6, 26, 35, 37, 38]. In the preceding specialization project the differences in the measured potential were not big enough to assume that they were causing the difference in the disbondment between hotplate and oven testing [1].

The potential on the exposed metal is approximately the same as the applied potential. The potential is increasing with distance from the initial coating defect due to the resistance in the electrolyte under the coating that has disbonded. The potential at the disbonding front is therefore higher than the applied potential. Stratmann et al. did measurements with a Scanning Kelvin Probe under the disbonded coating. They found that the potential increased from -0.750 V SCE in the holiday to -0.350 V SCE at the disbonding front when the disbonded distance was about 6 mm. Steinsmo has found that the charge transport through continuous coatings increases with decreasing potential [6, 35, 39, 40].

Results of a study by Rodriguez et al. showed that an increase in pH in the solution lead to an increase in disbondment. The tests were carried out in 0.01 M $Na_2SO_4$, 0.01 M NaOH and 1.0 M NaOH at pH 5.5, 12 and 14 [37]. In the preceding specialization project the differences in the measured pH were not big enough to assume that they were causing the difference in the disbondment between hotplate and oven testing [1].

## 2.4 Degradation of Fusion Bonded Epoxy coating in alkaline environment

The degradation of polymer materials can be categorized into chemical degradation (as oxidation and hydrolysis) and physical degradation (as swelling). The mechanical strength and the barrier property of a coating can be affected by chemical degradation [41]. In a study by Al-Borno et al. FBE coated carbon steel samples were exposed to 5 % NaOH at elevated temperature for 30 days to examine the effect hot NaOH solution has on the performance of a FBE coating system [42]. In this study, the substrate temperature was kept at 140 °C and the solution temperature recorded was 93 °C. Changes in the coatings microstructure, surface morphology, glass transition temperature, barrier properties, type of deposit layer formed, adhesion strength and extent of deterioration within the coating were investigated. This was done by attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR), scanning electron microscopy (SEM), differential scanning calorimetry (DSC), electrochemical impedance spectroscopy (EIS), energy-dispersive X-ray (EDAX) spectroscopy and pull-off adhesion strength method (ASTM D4541-09e1). The FBE coating system showed formation of a dense, adherent deposit layer with a discolored zone underneath and remaining un-affected bulk of the coating. The deposit layer was formed by low molecular weight hydrolyzed fragments leaching from the coating. Chemical deterioration of the coating in the discolored zone was indicated by the obtained results. The barrier property and bulk adhesion strength were not affected. The polymer matrix in the affected zone had irreversible changes in the surface microstructure, mainly chemical structure, and significant decrease in the glass transition temperature. This can cause serious deterioration of the coating functional properties.

In a study by Al-Sagour and Al-Mansour the effect of the discoloration on the samples from the study by Al-Borno et al. was further analyzed [43]. The discolored layers of the coating were examined by microscopic examination, dry film thickness (DFT) measurements, pull-off adhesion, EIS, X-ray diffraction analysis (XRD), energy dispersive X-ray spectroscopy (EDX), DSC and ATR-FTIR. The cross-section microscopic examination revealed there was a light beige deposit material on the surface, a discolored top layer and the original color underneath. Increase in thickness or swelling was an indication that the electrolyte managed to permeate into the coating layers. The coating only lost cohesion in the top layer and retained adhesion to the substrate underneath. This argue that the electrolyte did not penetrate all the way through the thickness of the coating.

The coating had a slight drop in impedance, but the coating still maintained a very strong barrier behavior. XRD showed that the deposit layer was composed of crystalline compounds, while XRD in combination with EDX showed that the top layer was composed of crystalline and non-crystalline compounds. Combining the findings of XRD and EDX with the findings of DSC, the authors deduced that the deposit layer was composed of fillers leaching from the coating. The top layer had a drop in Tg due to immersion. The drop was not caused by hydrolysis. The ATR-FTIR graphs were agreeing with the findings from XRD, EDX and DSC. Both studies showed that FBE coatings have a good resistance to high pH and withstands exposure to NaOH well.

# 3 Experimental

As the topic of both the preceding project and this thesis was the same, CD testing, a lot of the experimental work was the same and most of this chapter was reused from the preceding project with some rewriting.

## 3.1 Preparation of test panels

The preparation of the test panels were done at Jotun Powder Coatings lab by the author and two of Jotun's technicians. The test panels were 100x100x6 mm and were made of hot rolled steel. The panels were pre-cleaned. This was done by soaking the panels in a methyl ethyl ketone (MEK) solvent overnight and then wiping them dry. They were then wiped with rinse until the tissue or cloth remained fairly white. Next, the panels were blast cleaned. The blast cleaning was carried out using a pressure fed grit blasting unit with grade GL-25 steel grit used. Specified surface profile was Rz between 40-100 µm. After the pre-treatment, the panels were coated. Before spraying, the panels were pre-heated in an oven at 230 °C for 40 minutes. Then they were sprayed with a spray gun with a fluidised bed feeder. Immediately after spraying, the panels were put in an oven at 230 °C for 5 minutes to post cure. Finally, the panels were quenched in running tap water.

The coating used was Jotun's formulation OCR-400 which is a type 4 epoxy cured with dicyandiamide (DICY). The powder contains filler to reach a pigment volume concentration (PVC) of 14 %, flow additive, degassing additive and pigment. The average film thickness of the coatings with standard deviation is shown in Figure 3.1. Film thickness of the coating of all the panels used is shown in Appendix C. The panels were named HP if they were tested on a hotplate and OVN if they were tested in an oven. The numbers are the order of when the tests were started. Test number 2.1 and 2.2 were started at the same time, but had different duration.

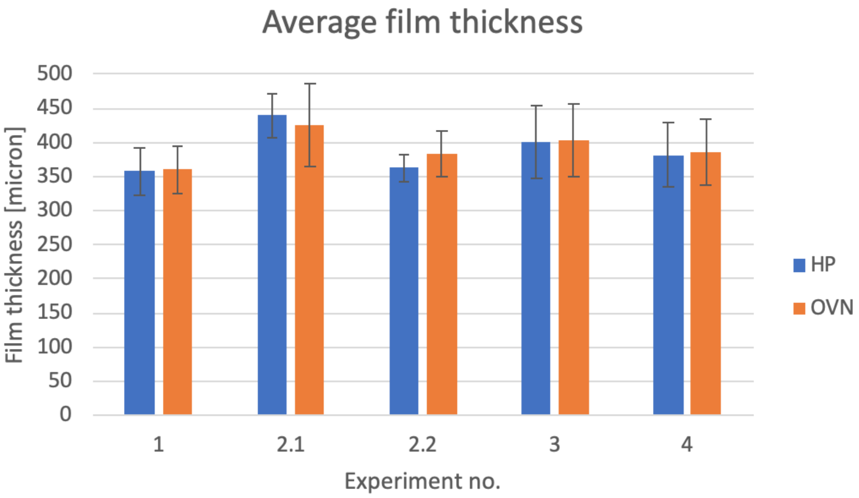


Figure 3.1: Average film thickness of the coatings in micron with standard deviation for the panels used in the CD tests.

## 3.2 Set-up

The set-up of the CD test is shown in Figure 3.2. An Oltronix Power Supply C15-2D was connected to a Galvanostat current distribution box with 16 outlets. The current from each outlet could be adjusted, and switched on or off, individually. Each positive pole of the connection box that were used were connected to a resistor board with a resistance of 1 Ω and then to a platinum counter electrode in each cell. Cables used for logging the current were connected to the resistor board. Each negative pole of the connection box that were used were connected to each of the panels. A cell is a panel coated with OCR-400 where a damage, also called a holiday, was made by drilling a 3 mm hole in the coating. The panel had a hole in one corner for a 6 mm screw for connection of a cable to make electric contact with the steel. A glass tube with an inner diameter of 70 mm was attached to the panel with blue silicone, with the holiday in the center. The cell had a plastic lid with a platinum wire going through it and into the glass tube. In the lid there was a hole that was used when doing measurements, which was covered with a rubber stopper between measurements. The cells were filled with 300 ml 3 % NaCl and refilled with distilled water when the solution evaporated.

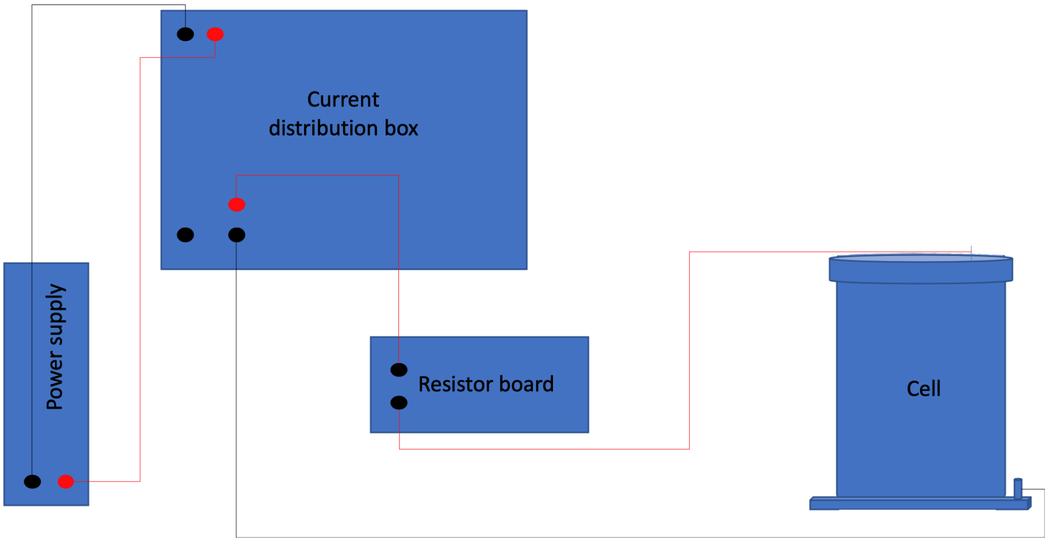


Figure 3.2: Illustration of the test set-up [1].

## 3.3 Procedure

The hotplate was turned on and the amount of sand and effect was adjusted to give approximately the desired temperature in the damage of the panels. The oven was turned on and heated to the desired temperature. Half of the cells were put on the hotplate and the other half in the oven, and the cells were connected as described in Section 3.2. The power was turned on and all the cells were filled with 300 ml of 3 % NaCl solution. The potential was measured using a calomel reference electrode as described in Section 3.4.2, and adjusted to -1,545 V. Logging of current, temperature and potential were started.

The day after the tests were started and every following weekday two different measurements were done. First the temperature in the holidays were measured as described in

Section 3.4.1. Then the potential of the solutions in the cells were measured as described in Section 3.4.2 and the potential was adjusted to -1.545 V SCE. After these measurements the temperatures in the cells on the hotplate were adjusted by moving the cells up or down in the sand. Each cell were refilled with distilled water up to the 300 ml mark on the tube if some of the solution had evaporated, to make sure the concentration of the solution stayed the same. The values logged in the laboratory logging system were checked to make sure everything was working right.

Every seventh day the electrolyte in the cells were replaced with a new 3 % NaCl solution. Before replacing the solution in the cells the regular measurements were done as described in the previous paragraph. The old solution was removed from the cells using a silicon tube and a laboratory water jet pump and new solution added. The new 3 % NaCl solution was preheated in the oven. One hour after the solution was replaced, the potential was measured and adjusted to -1,545 V SCE.

The tests were ended by disconnecting the cells one cell at a time. The solution was discarded and the glass tubes removed by cutting through the silicone with a scalpel or a Stanley knife. Four cuts in the coating down to the steel were made with a scalpel or a Stanley knife as shown in Figure 3.3. The samples were let to cool down to room temperature. The samples were evaluated within an hour. The evaluation was done by placing the tip of the scalpel or the Stanley knife between the coating and the steel and use a levering action to lift the coating that had lost adhesion. The disbonded coating was removed relatively easy without applying extra force. The tip of the scalpel or Stanley knife was inserted under the coating and lifted until the coating started to show a clear resistance to the levering action. The disbonded distance was measured in four diagonals as shown in Figure 3.4. The average radial disbondment was calculated as shown in Equation 3.

$$Average\ radial\ disbondment = \frac{d_1 + d_2 + d_3 + d_4 - 12mm}{8} \tag{3}$$

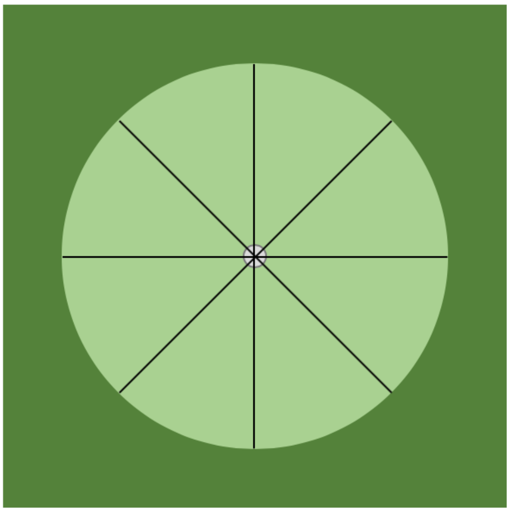


Figure 3.3: Illustration of how the coating was cut prior to peeling off disbonded coating [1].

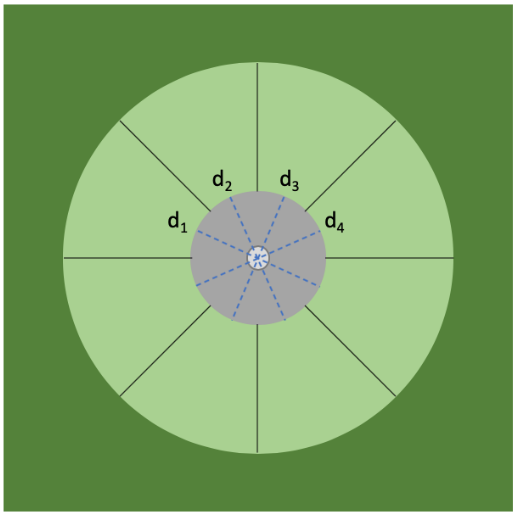


Figure 3.4: Illustration of how the disbondment was measured after peeling of the disbonded coating [1].

## 3.4 Parameter measurements

During the tests, temperature and potential were manually measured, and temperature, potential and current were logged.

### 3.4.1 Temperature measurements

The temperature was measured in the holiday as shown in Figure 3.5. A voltmeter connected to a thermocouple type K sensor was used for the measurements.

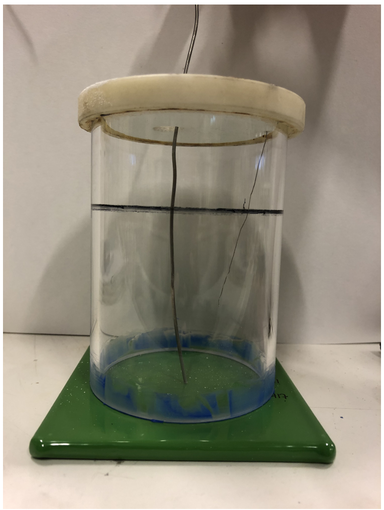


Figure 3.5: Illustration of how temperature was measured [1].

On some cells, thermoelements were connected to measure temperature at different locations. The temperature was measured in the steel, at the interface between the steel and the coating, and in the middle of the solution. Figure 3.6 shows where the thermoelements were attached. Thermocouple type K sensors were used for the measurements.

One sensor was attached in the middle at the underside of the panel as shown at point A in Figure 3.6. A 1 mm wide and 2 mm deep hole was made by drilling and blue silicone was used to attach the sensor. Another sensor was attached on the panel, halfway between the holiday and the glass tube as shown at point B in Figure 3.6. A 1 mm wide hole was made by drilling and epoxy structural adhesive was used to attach the sensor. The last sensor measured the temperature in the middle of the solution as shown at point C in Figure 3.6. The sensor was put in a glass tube that was put through a hole in the lids and attached at a height where the tip of the sensor would be in the middle of the solution. Cables for logging was connected to the thermocouple sensors. A computer with a custom made laboratory logging system for potential measurements made by Sintef was used for the logging.

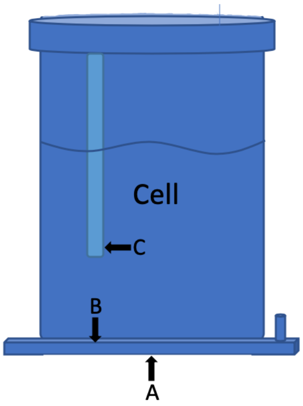


Figure 3.6: Illustration of where the thermoelements were attached.

All the thermocouple sensors used for measuring the temperature were compared to a calibrated thermometer. This was done by heating tap water to about 65 °C in a beaker using a hotplate and measure the temperature of the water with both a thermocouple sensor and the calibrated thermometer simultaneously. The measurements were adjusted accordingly.

Table 3.1 shows an overview of logging of temperature for the experiments. It is stated for how many cells the temperature is measured in each experiment, where the temperature was measured and how often it was logged.

Table 3.1: Overview of logging of temperature.

| | *Temperature* | | | | | | |
|---|---|---|---|---|---|---|---|
| | *Steel* | | *Interface* | | *Solution* | | |
| *Experiment* | HP | OVN | HP | OVN | HP | OVN | Measuring frequency |
| *1* | 3 cells | 1 cell | 3 cells | 1 cell | 3 cells | 1 cell | Every 5 minutes |
| *2* | 3 cells | 1 cell | 3 cells | 1 cell | 3 cells | 1 cell | Every 5 minutes |
| *3* | 1 cell | 1 cell | - | - | - | - | Every 5 minutes |
| *4* | 2 cells | 2 cells | - | - | - | - | Every 5 minutes |

### 3.4.2 Potential measurements

The cell potential was measured by placing a saturated calomel (SCE) reference electrode about 2 cm above the coating as shown in Figure 3.7.

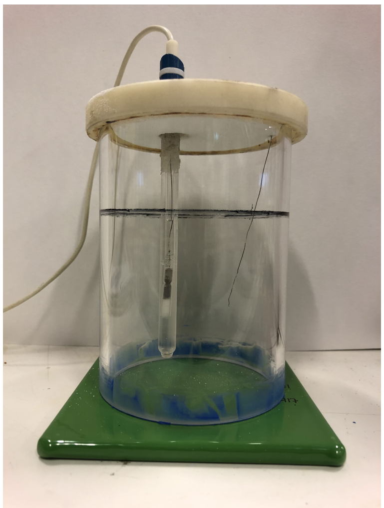


Figure 3.7: Illustration of how potential was measured [1].

The potential in the holiday was measured for some cells. There was made a hole in the lids for a luggin capillary probe connected to a calomel reference electrode using a salt bridge. The capillary was placed in the holiday. Cables for logging were connected to the reference electrodes. The same laboratory logging system as for the thermocouple sensors was used for the logging.

Table 3.2 shows an overview of logging of potential for the experiments. It is stated for how many cells the potential is measured in each experiment and how often it was logged.

Table 3.2: Overview of logging of potential.

| | *Potential* | | |
|---|---|---|---|
| *Experiment* | HP | OVN | Measuring frequency |
| *1* | 2 cells | - | Every 5 minutes (first 24 hours)<br>Every 2 hours |
| *2* | 2 cells | - | Every 5 minutes (first 3 days)<br>Every 2 hours |
| *3* | - | - | - |
| *4* | - | - | - |

### 3.4.3 Current measurements

Table 3.3 shows an overview of logging of current for the experiments. It is stated for how many cells the current is measured in each experiment and how often it was logged.

Table 3.3: Overview of logging of current.

| | *Current* | | |
|---|---|---|---|
| *Experiment* | HP | OVN | Measuring frequency |
| *1* | 5 cells | 4 cells | Every 2 hours |
| *2* | 5 cells | 4 cells | Every 2 hours |
| *3* | 2 cells | 2 cells | Every 2 hours |
| *4* | 6 cells | 6 cells | Every hour |

## 3.5 Test matrix

Test parameters and objectives of all the experiments is given in Table 3.4. It is stated the number of panels tested in each experiment, the duration of the tests and the desired temperature in the holiday on the panels for the hotplate and oven testing. After the first test the hotplate from the old set-up was replaced by a hotplate sent from Jotun's lab.

Table 3.4: Test parameters and objectives of all the experiments.

| *Experiment* | *No. of panels* | *Duration* | *Temperature HP* | *Temperature OVN* | *Objective* |
|---|---|---|---|---|---|
| *1* | 12 | 3 weeks | 65 °C | 65 °C | Examine differences between the old and the new batch of coating, check for fluctuation in the temperature and the potential, investigate the temperature gradient in the cells |
| *2.1* | 6 | 3 weeks | 65 °C | 65 °C | Examine differences between the old and the new set-up of the hotplate, check for fluctuation in the temperature and the potential, investigate the temperature gradient in the cells |
| *2.2* | 6 | 4 weeks | 65 °C | 65 °C | Examine the effect a longer duration of the test has on the disbondment |
| *3* | 6 | 13 days | 65 °C | 65 °C | Examine the effect a shorter duration of the test has on the disbondment |
| *4* | 12 | 3 weeks | 60 °C | 70 °C | Examine the effect a higher or lower temperature of the steel have on the disbondment |

## 3.6 Investigation of coating degradation in sodium hydroxide

Two panels were put in a beaker containing 1 M NaOH for nine days, at 70 °C. Electrochemical impedance spectroscopy was carried out five times. The first time two hours after the panels were put in NaOH, then after 1, 2, 4 and 8 days. After the panels had been in NaOH for nine days, the adhesion of the coating was tested by doing pull of testing according to ISO 4624 using a PAT GM 01/6.3 kN adhesion tester and the hardness of the coating was tested using a FL-2000 H manual hardness tester.

# 4 Results

## 4.1 Disbondment

The average disbondment of the coating for all the tests are shown in Figure 4.1. The average disbondment of the coating for the cells tested on a hotplate for test 1, 2.1, 2.2, 3 and 4 were 5.7 mm, 3.7 mm, 11.1 mm, 4.2 mm and 7.7 with a standard deviation of ±3.3, ±1.6, ±5.6, ±0.7 and ±3.6, respectively. The average disbondment of the coating for the cells tested in an oven for test 1, 2.1, 2.2, 3 and 4 were 11.6 mm, 14.0 mm, 15.2 mm, 5.2 mm and 8.4 mm with a standard deviation of ±4.2, ±0.9, ±0.6, ±4.4 and ±5.1, respectively. The cells that were tested in an oven had the most disbondment. Compared to test 1 and 2.1, test 4 showed a smaller difference between the average disbondment of the coating for the cells tested on a hotplate and in an oven. The average disbondment of the coating increased with the duration of the tests, except for the testing on a hotplate in experiment 2.1.

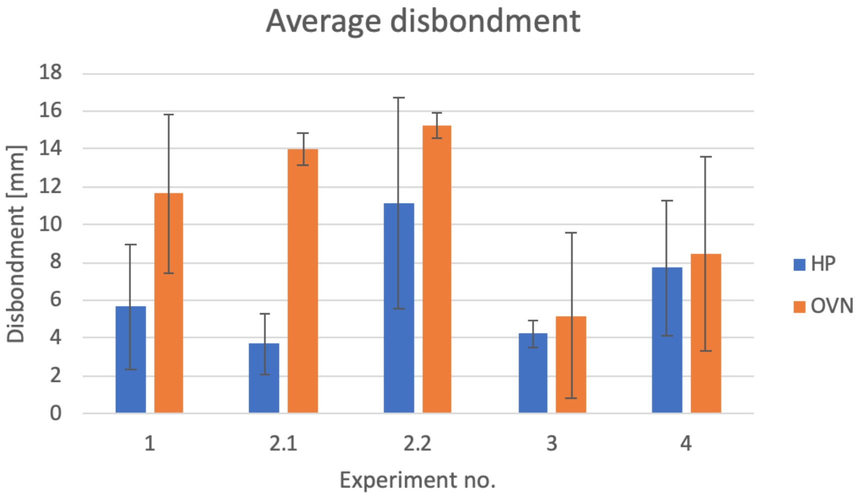
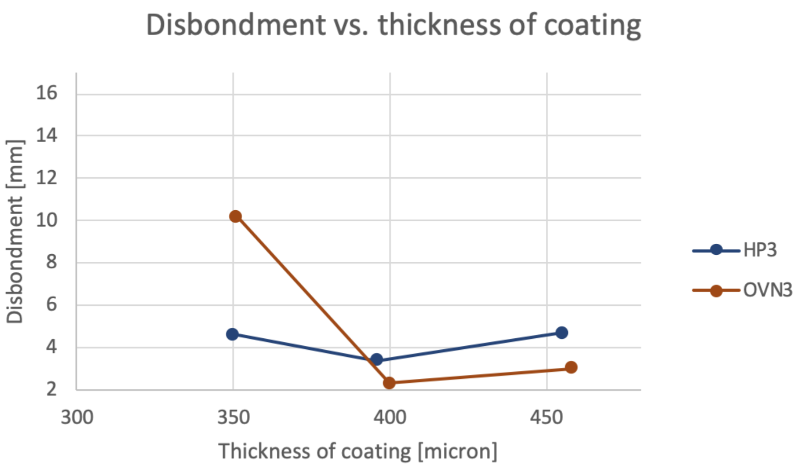
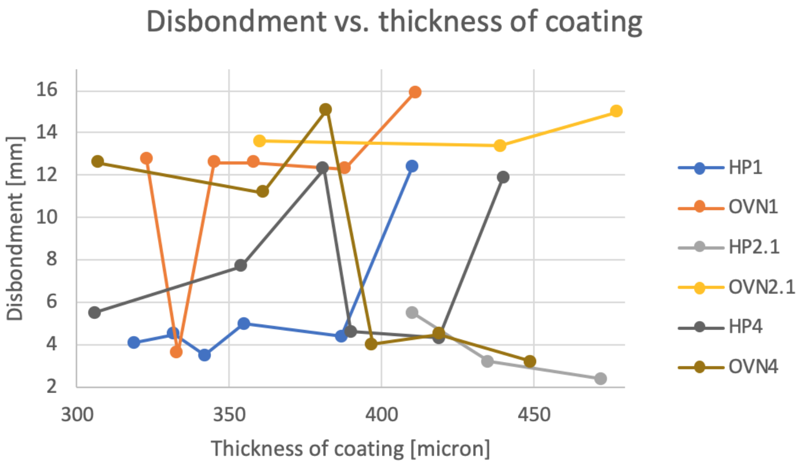


Figure 4.1: Average disbondment of the coating with standard deviation.

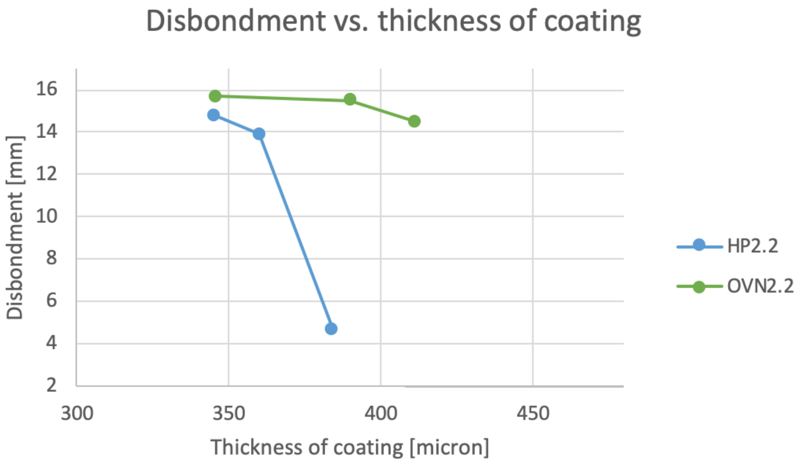
The disbondment plotted against the thickness of the coating is shown in Figure 4.2. The film thickness and the disbondment of coating for all the cells are given in Appendix C and D. There was no clear relationship between the thickness of the coating and the disbondment of the coating, except in experiment 2.2 where the test lasted for four weeks and the results showed a decrease in disbondment when the thickness increased.



(a) Duration of 13 days



(b) Duration of 3 weeks



(c) Duration of 4 weeks

Figure 4.2: Disbondment of the coating plotted against the thickness of the coating.

## 4.2 Disbondment and logged temperature

### 4.2.1 Experiment 1

The results of the first experiment are shown in Figure 4.3. The disbondment of the new batch of coating was similar to the disbondment of the tests conducted with the old batch of coating in the preceding specialization project. During the evaluation of the panels it was discovered a new area with loss of adhesion further away from the holiday compared to the initial disbondment front. Some of the sensors attached in the interface between the steel and the coating came loose before the test was finished. Cathodic disbondment was initiated at these holes in the coatings.

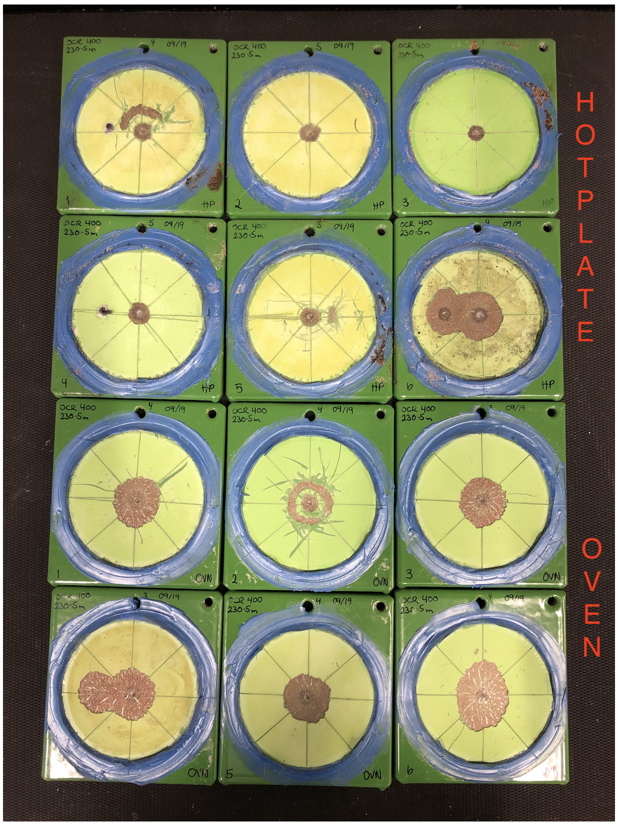


Figure 4.3: Results of CD tests for experiment 1. The upper panels were tested on a hotplate and the lower panels were tested in an oven.

Plots of the average temperature in the steel, the interface between the steel and the coating, and the solution logged for test 1, with average temperature of all measurements are shown in Figure 4.4-4.6. The temperature logged for the cells are given in Appendix E. The average temperature value for the cells tested on a hotplate measured in the steel, the interface between the steel and the coating, and the solution were 70.0 °C, 65,9 °C and 62.9 °C, respectively. The average temperature value for the cells tested in an oven measured in the steel, the interface between the steel and the coating, and the solution were 63.9 °C, 63.4 °C and 63.4 °C, respectively. The thermocouple sensors used for the measurements measured 0-3 °C to high at temperatures around 60 °C. The exact values are given in Appendix F. This is compensated for in the plots. The temperatures at the different locations in the cell were quite similar for the cells tested in an oven, while there was an evident temperature gradient in the cells tested on a hotplate.

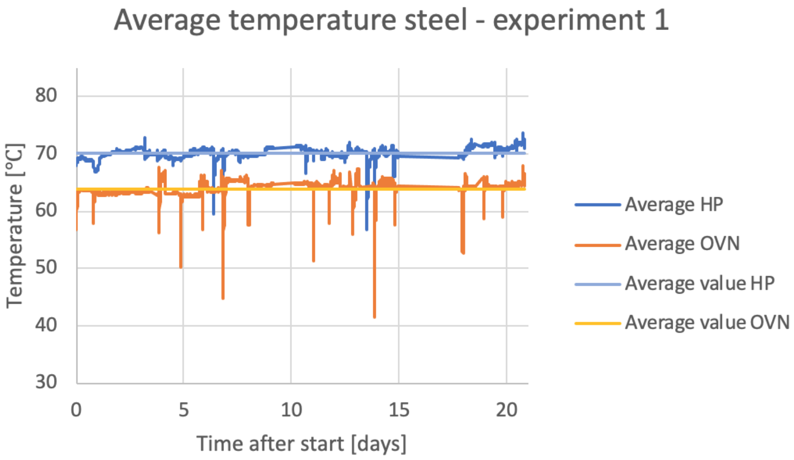


Figure 4.4: Plot of the average temperature in the steel logged for experiment 1, with average temperature of all measurements.

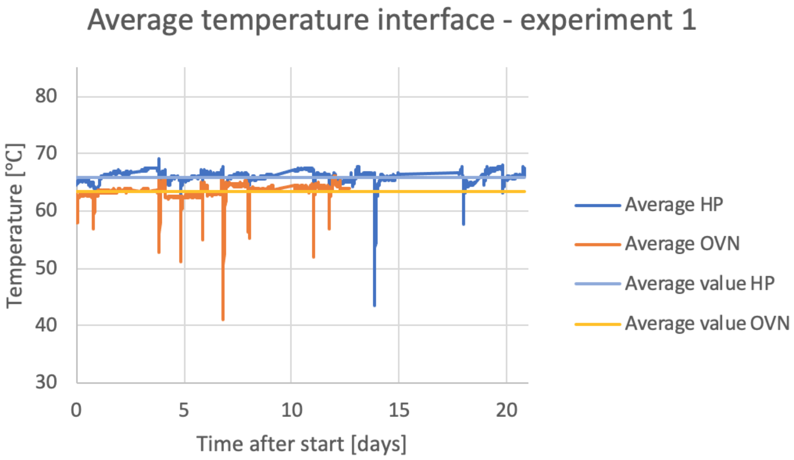


Figure 4.5: Plot of the average temperature in the interface between the steel and the coating logged for experiment 1, with average temperature of all measurements.

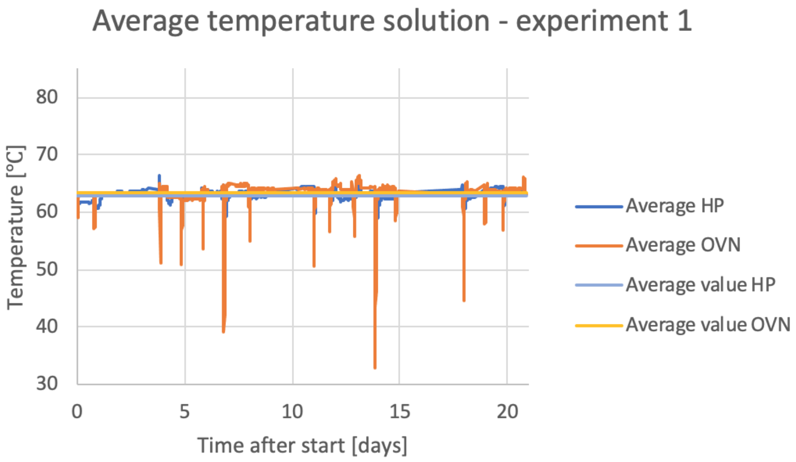


Figure 4.6: Plot of the average temperature in the solution logged for experiment 1, with average temperature of all measurements.

### 4.2.2 Experiment 2

The results of the second experiments are shown in Figure 4.7 and 4.8. The disbondment of coating in experiment 2.1 was similar to the disbondment of the tests conducted with the old hotplate set-up in the first experiment. During the evaluation of experiment 2.1, it was found a new area with loss of adhesion further away from the holiday compared to the initial disbondment front, as in experiment 1. In experiment 2.2, that lasted a week longer than experiment 1 and 2.1, the measured disbondment was larger and the difference in disbondment between the panels tested on a hotplate and in an oven was smaller. Some of the sensors attached in the interface between the steel and the coating came loose before the test was finished. Cathodic disbondment was initiated at these holes in the coatings.

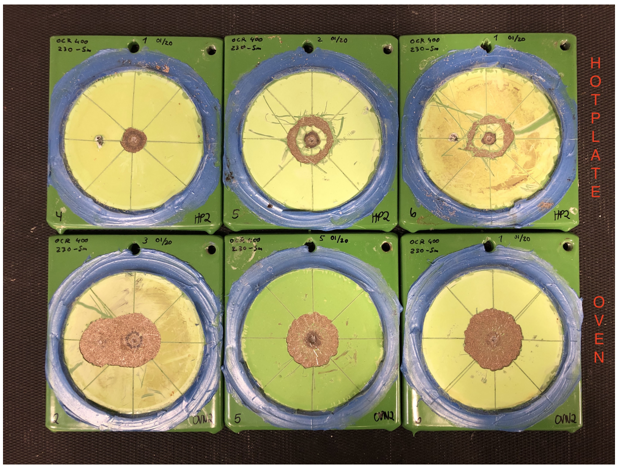


Figure 4.7: Results of CD tests for experiment 2.1. The upper panels were tested on a hotplate and the lower panels were tested in an oven.

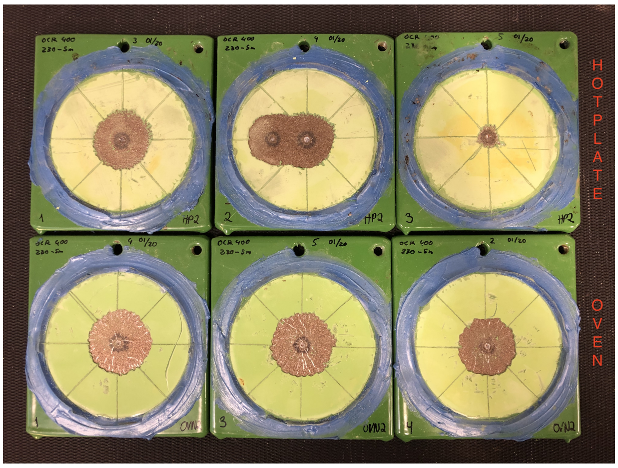


Figure 4.8: Results of CD tests for experiment 2.2. The upper panels were tested on a hotplate and the lower panels were tested in an oven.

Plots of the average temperature in the steel, the interface between the steel and the coating, and the solution logged for test 2, with average temperature of all measurements are shown in Figure 4.9-4.11. The temperature logged for the cells are given in Appendix E. The average temperature value for the cells tested on a hotplate measured in the steel, the interface between the steel and the coating, and the solution were 71.8 °C, 67.8 °C and 63.5 °C, respectively. The average temperature value for the cells tested in an oven measured in the steel and the solution were 65.5 °C and 65.3 °C, respectively. The thermocouple sensor used to measure the temperature in the interface between the steel and the coating broke, therefore there was no data of the temperature in the interface between the steel and the coating for the cells in the oven. The thermocouple sensors used for the measurements measured 0-3 °C to high at temperatures around 60 °C. The exact values are given in Appendix F. This is compensated for in the plots. The temperatures at the different locations in the cell were quite similar for the cells tested in an oven, while there was an evident temperature gradient in the cells tested on a hotplate.

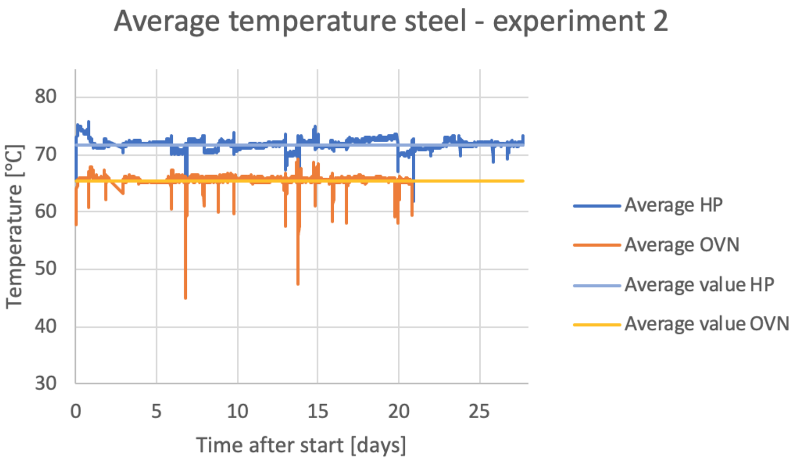


Figure 4.9: Plot of the average temperature in the steel logged for experiment 2, with average temperature of all measurements.

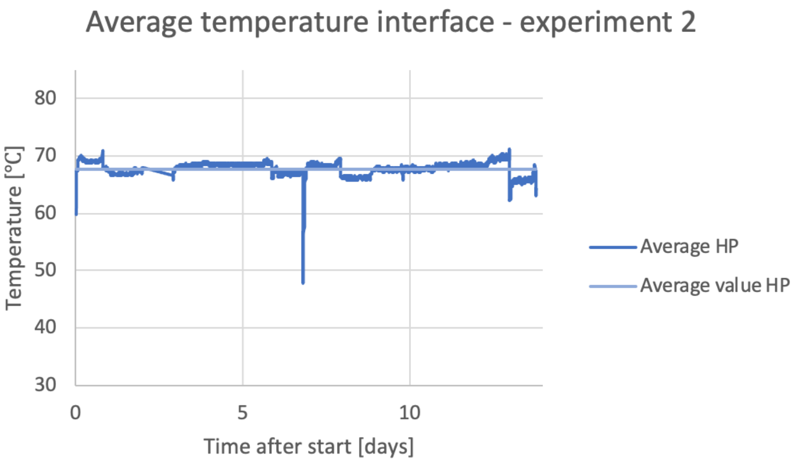


Figure 4.10: Plot of the average temperature in the interface between the steel and the coating logged for experiment 2, with average temperature of all measurements.

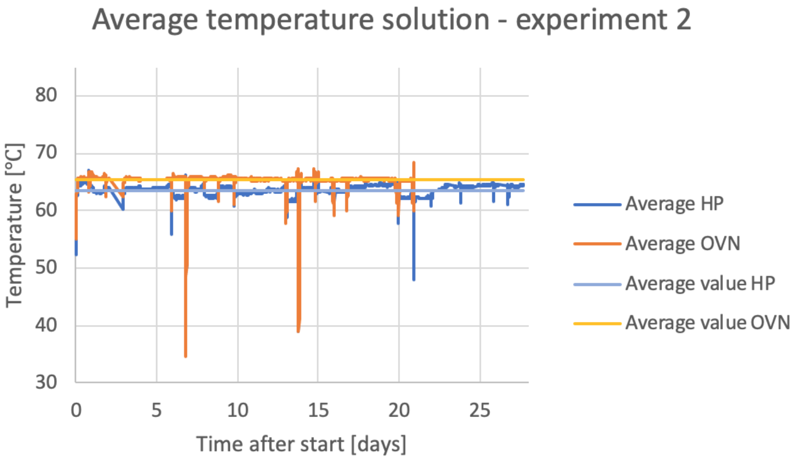


Figure 4.11: Plot of the average temperature in the solution logged for experiment 2, with average temperature of all measurements.

### 4.2.3 Experiment 3

The results of the third experiment are shown in Figure 4.12. In experiment 3, that lasted about a week less than experiment 1 and 2.1, the measured disbondment was lower and the difference in disbondment between the panels tested on a hotplate and in an oven was smaller.

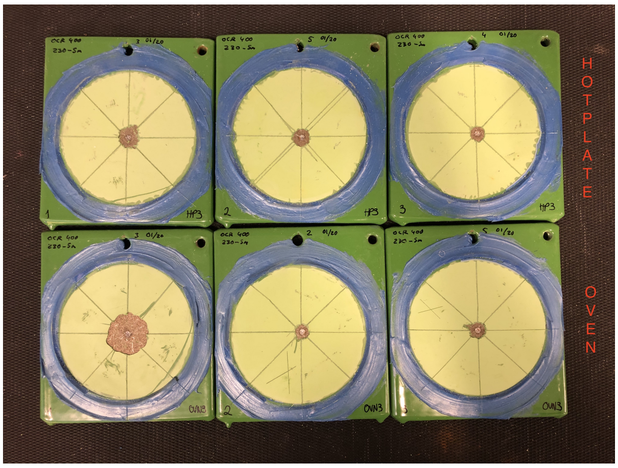


Figure 4.12: Results of CD tests for experiment 3. The upper panels were tested on a hotplate and the lower panels were tested in an oven.

Plot of the average temperature in the steel logged for test 3, with average temperature of all measurements is shown in Figure 4.13. The temperature logged for the cells are given in Appendix E. The average temperature value for the cells tested on a hotplate measured in the steel was 82.3 °C. The average temperature value for the cells tested in an oven measured in the steel was 64.8 °C. The thermocouple sensors used for the measurements measured 0-3 °C to high at temperatures around 60 °C. The exact values are given in Appendix F. This is compensated for in the plots.

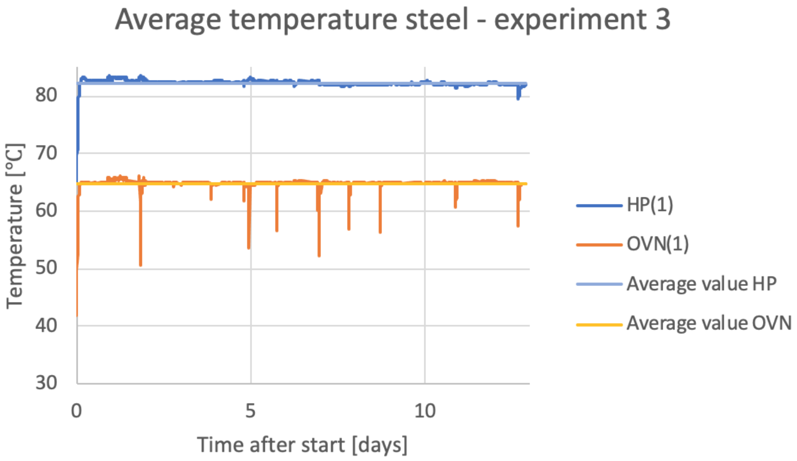


Figure 4.13: Plot of the average temperature in the steel logged for experiment 3, with average temperature of all measurements.

### 4.2.4 Experiment 4

The results of the fourth experiment are shown in Figure 4.14. During the evaluation of experiment 4, it was found a new area with loss of adhesion further away from the holiday compared to the initial disbondment front, as in experiment 1 and 2.1. In experiment 4, that was conducted at other temperatures than experiment 1 and 2.1, there were more similar results of disbondment between the panels tested on a hotplate and in an oven.

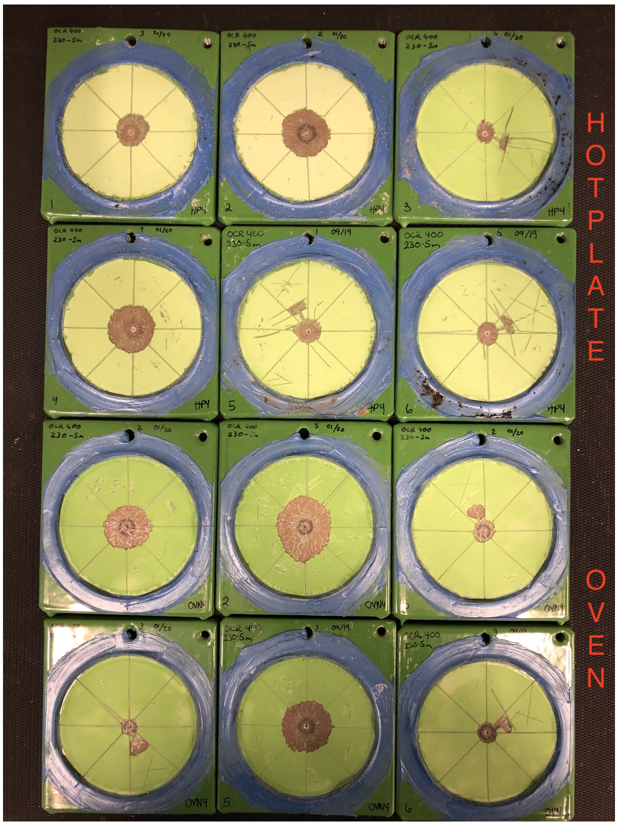


Figure 4.14: Results of CD tests for experiment 4. The upper panels were tested on a hotplate and the lower panels were tested in an oven.

Plot of the average temperature in the steel logged for test 4, with average temperature of all measurements is shown in Figure 4.15. The temperature logged for the cells are given in Appendix E. The average temperature value for the cells tested on a hotplate measured in the steel was 66.5 °C. The average temperature value for the cells tested in an oven measured in the steel was 71.1 °C. The thermocouple sensors used for the measurements measured 0-3 °C to high at temperatures around 60 °C. The exact values are given in Appendix F. This is compensated for in the plots.

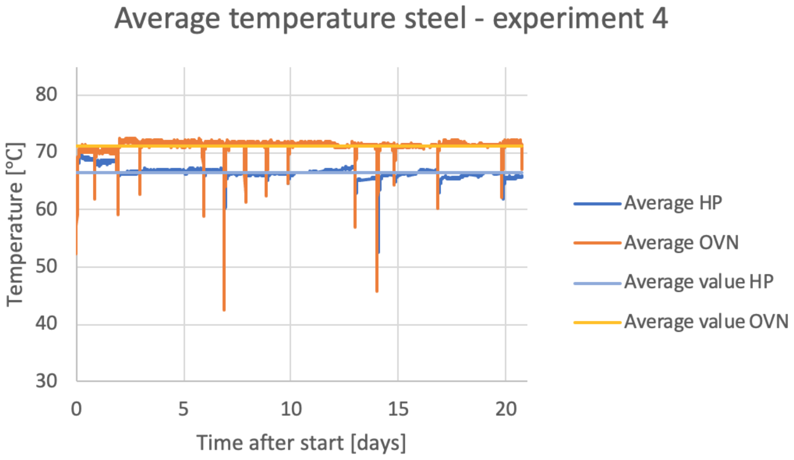


Figure 4.15: Plot of the average temperature in the steel logged for experiment 4, with average temperature of all measurements.

## 4.3 Temperature measurements

Plots of the average temperature measured manually in the holiday for test 1, 2.1, 2.2 and 4, with average temperature of all measurements with standard deviation and limits sat by Jotun are shown in Figure 4.16-4.19. The temperature measured for all the cells are given in Appendix E. The average temperature value for the cells tested on a hotplate for test 1, 2.1, 2.2 and 4 were 63.9 °C, 65.1 °C, 65.5 °C and 59.7 °C with a standard deviation of ±1.8, ±1.0, ±1.5 and ±1.2, respectively. The average temperature value for the cells tested in an oven for test 1, 2.1, 2.2 and 4 were 63.9 °C, 63.4 °C, 63.9 °C and 69.3 °C with a standard deviation of ±1.1, ±1.1, ±1.1 and ±1.0, respectively. The lower limit is 62 °C and the upper limit is 68 °C. The thermocouple sensor used for the measurements measured 1 °C to high at temperatures around 60 °C, this is compensated for in the plots. The average temperature values for the cells tested on a hotplate were higher than the average temperature values for the cells tested in an oven, except for experiment 4 where the temperatures intentionally were different.

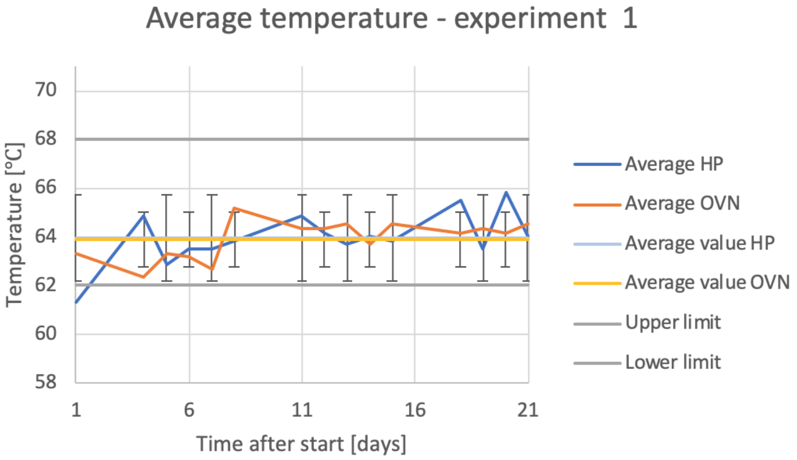


Figure 4.16: Plot of the average temperature measured for experiment 1, with average temperature of all measurements with standard deviation and limits sat by Jotun.

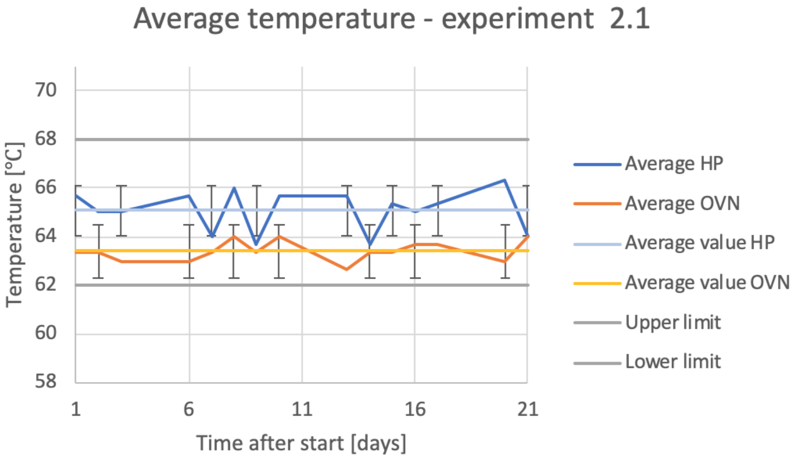


Figure 4.17: Plot of the average temperature measured for experiment 2.1, with average temperature of all measurements with standard deviation and limits sat by Jotun.

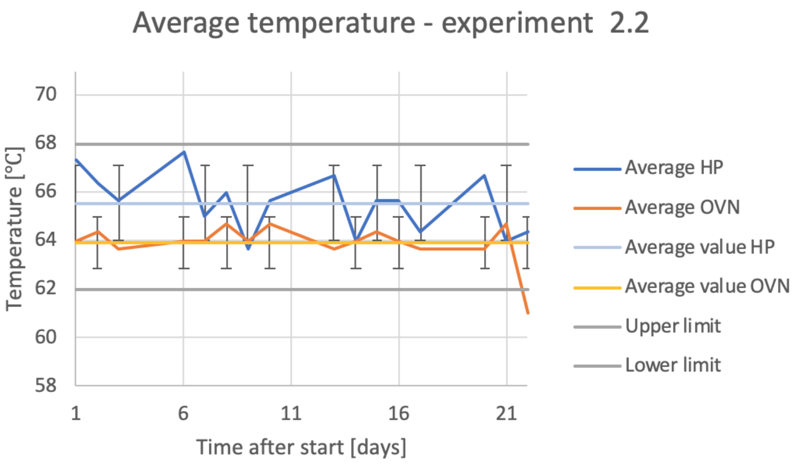


Figure 4.18: Plot of the average temperature measured for experiment 2.2, with average temperature of all measurements with standard deviation and limits sat by Jotun.

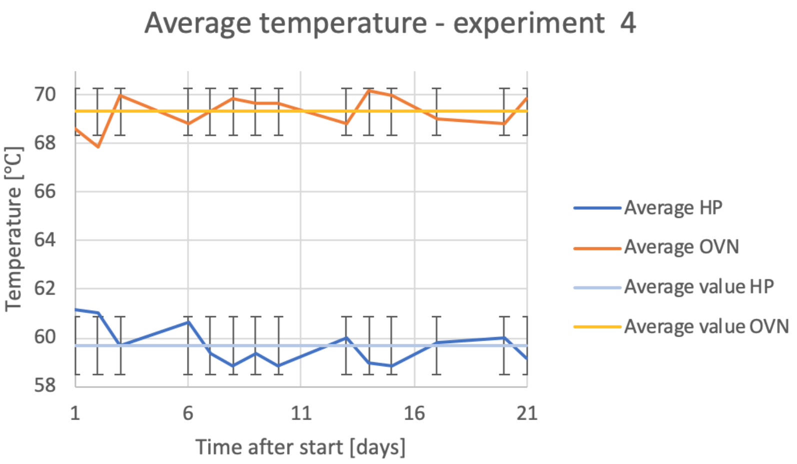


Figure 4.19: Plot of the average temperature measured for experiment 4, with average temperature of all measurements.

## 4.4 Potential measurements

Plots of the average potential measured manually for test 1, 2.1, 2.2 and 4, with average potential of all measurements with standard deviation and limits sat by Jotun are shown in Figure 4.20-4.23. The potential measured for all the cells are given in Appendix G. During the tests a SCE reference cell was used, but in the diagrams all the potentials are given relative to the Ag/AgCl reference cell, since this reference cell is used by Jotun. The average potential value for the cells tested on a hotplate for test 1, 2.1, 2.2 and 4 were -1.496 V, -1.505 V, -1.499 V and -1.489 V with a standard deviation of ±0.059, ±0.038, ±0.079 and ±0.054, respectively. The average potential value for the cells tested in an oven for test 1, 2.1, 2.2 and 4 were -1.494 V, -1.492 V, -1.502 V and -1.480 V with a standard deviation of ±0.025, ±0.057, ±0.032 and ±0.054, respectively. The lower limit is -1.65 V and the upper limit is -1.35 V. The average potential values for the cells were quite similar.

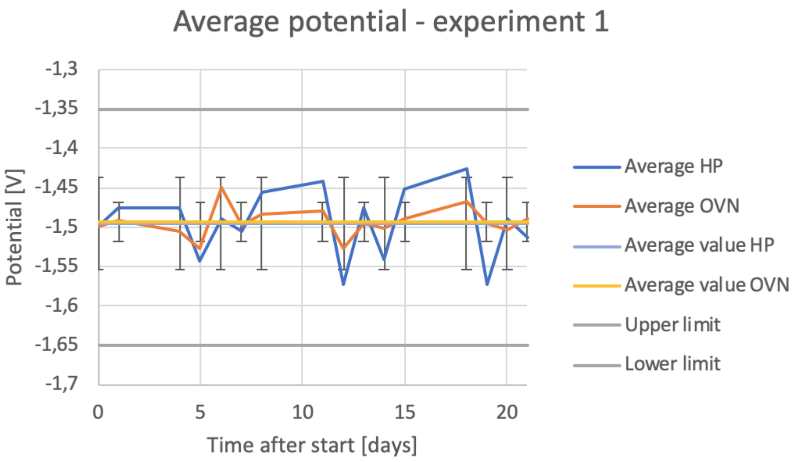


Figure 4.20: Plot of the average potential measured for experiment 1, with average potential of all measurements with standard deviation and limits sat by Jotun.

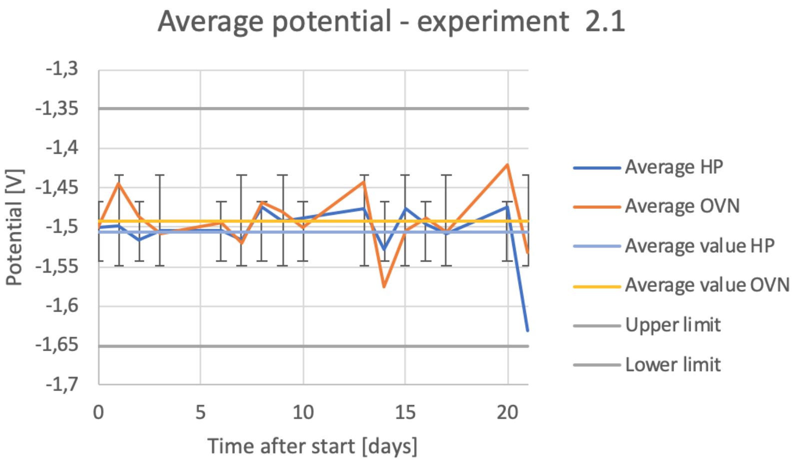


Figure 4.21: Plot of the average potential measured for experiment 2.1, with average potential of all measurements with standard deviation and limits sat by Jotun.

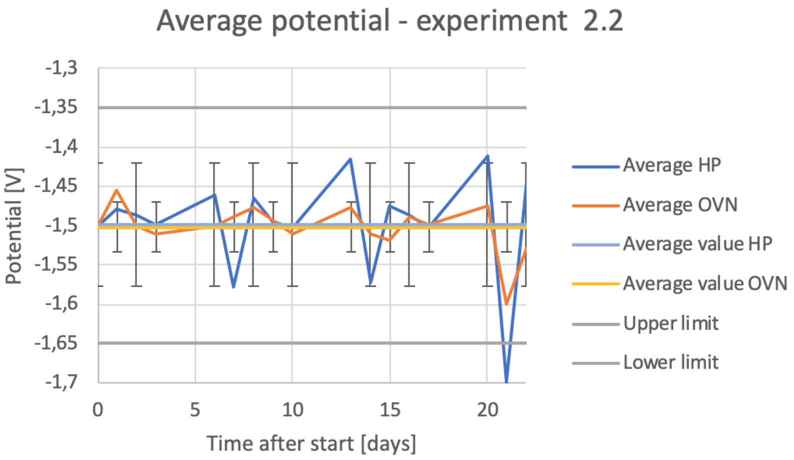


Figure 4.22: Plot of the average potential measured for experiment 2.2, with average potential of all measurements with standard deviation and limits sat by Jotun.

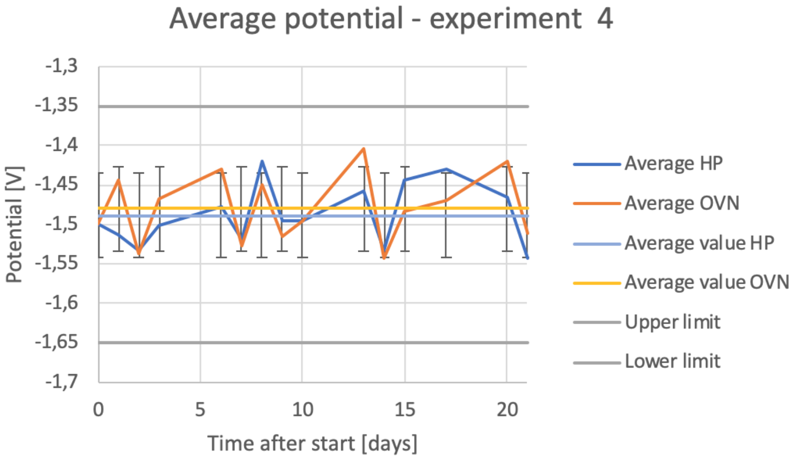


Figure 4.23: Plot of the average potential measured for experiment 4, with average potential of all measurements with standard deviation and limits sat by Jotun.

## 4.5 Potential logged

Plots of the average potential in the holiday logged for test 1 and 2, with average potential of all measurements are shown in Figure 4.24 and 4.25. The potential logged for the cells are given in Appendix G. During the tests a SCE reference cell was used, but in the diagrams all the potentials are given relative to the Ag/AgCl reference cell, since this reference cell is used by Jotun. The average potential value for the cells tested on a hotplate for test 1 and 2 were -1.282 V and -1.310 V, respectively.

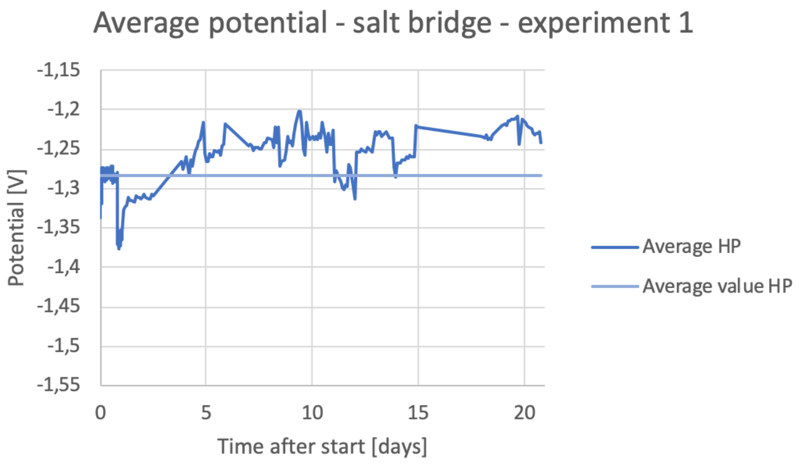


Figure 4.24: Plot of the average potential logged for experiment 1, with average potential of all measurements.

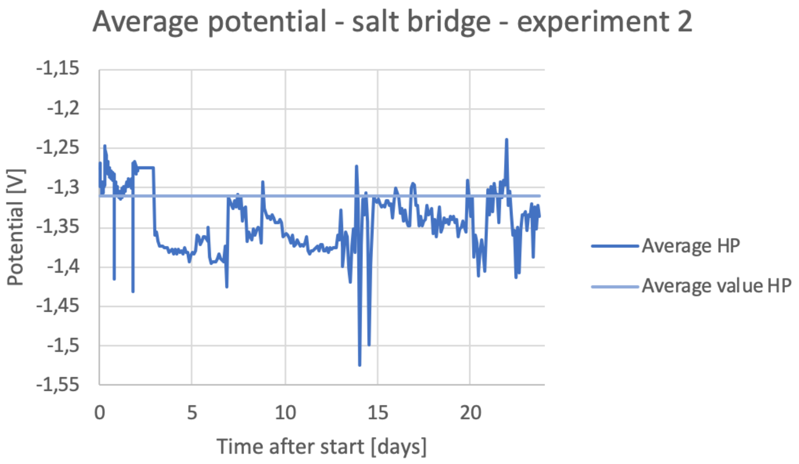


Figure 4.25: Plot of the average potential logged for experiment 2, with average potential of all measurements.

## 4.6 Effect of sodium hydroxide

Electrochemical impedance spectroscopy after 2 hours, 1, 2, 4 and 8 days in NaOH solution for panel 1 and panel 2 are shown in Figure 4.26 and 4.27.

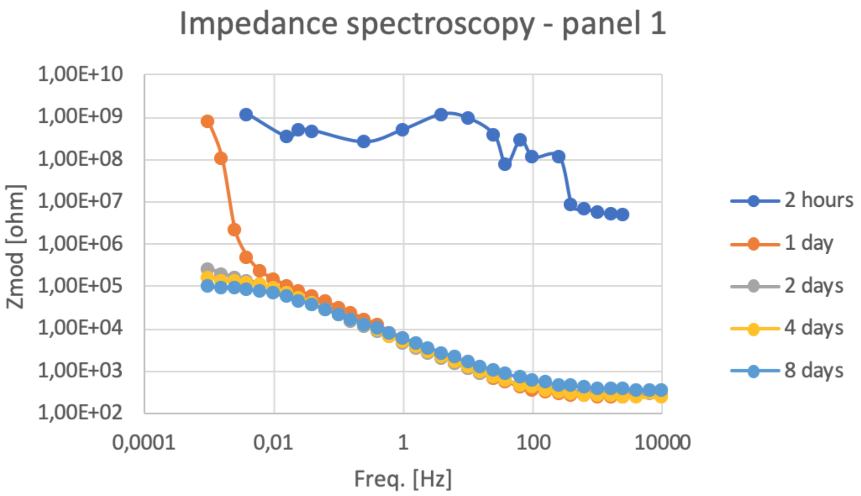


Figure 4.26: Plot of impedance spectroscopy after 2 hours, 1, 2, 4 and 8 days in NaOH solution for panel 1.

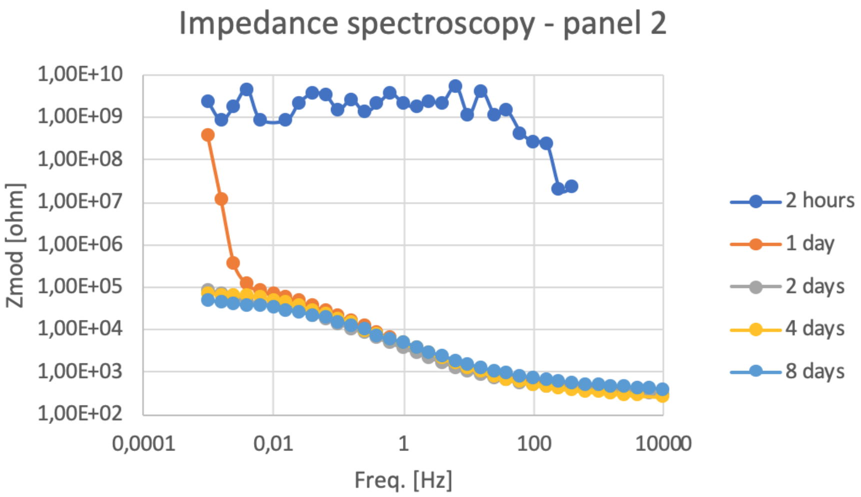


Figure 4.27: Plot of impedance spectroscopy after 2 hours, 1, 2, 4 and 8 days in NaOH solution for panel 2.

The results of the adhesion tests are shown in Figure 4.1. Panel 1 and 2 were in a NaOH solution for 9 days before the tests were conducted. The reference panel was not exposed to NaOH. The adhesion was lost in the epoxy structural adhesive between the coating and the dolly for all the measurements.

Table 4.1: Results of adhesion tests done on two panels exposed to NaOH for nine days and a reference panel not exposed to NaOH.

| Panel | Dolly | Measurement [MPa] |
|---|---|---|
| *Ref* | *1* | 31 |
| | *2* | 31 |
| | *3* | 30 |
| | *4* | 29.6 |
| | *5* | 29 |
| *1* | *1* | 27.6 |
| | *2* | 29.6 |
| | *3* | 32.2 |
| 2 | *1* | 31.6 |
| | *2* | 28.8 |
| | *3* | 30.4 |

The results of the hardness tests are shown in Figure 4.2. Panel 1 and 2 were in a NaOH solution for 9 days before the tests were conducted. The reference panel was not exposed to NaOH. The second and third measurements shows the elasticity of the coating when they are compared to the first measurement. The second and third measurements were done 30 and 60 seconds after the first measurement.

Table 4.2: Results of hardness tests done on two panels exposed to NaOH for nine days and a reference panel not exposed to NaOH.

| Panel | Point | 1. measurement [$\mu$m] | Buchholz | 2. measurement [$\mu$m] | 3. measurement [$\mu$m] |
|---|---|---|---|---|---|
| *Ref* | *1* | -0.007 | 109 | -0.003 | -0.003 |
| | *2* | -0.008 | 102 | -0.003 | -0.003 |
| | *3* | -0.007 | 109 | -0.003 | -0.002 |
| | *4* | -0.008 | 102 | -0.003 | -0.003 |
| | *5* | -0.006 | 118 | -0.001 | -0.001 |
| *1* | *1* | -0.007 | 109 | -0.003 | -0.003 |
| | *2* | -0.006 | 118 | -0.003 | -0.003 |
| | *3* | -0.007 | 109 | -0.003 | -0.003 |
| | *4* | -0.007 | 109 | -0.003 | -0.003 |
| | *5* | -0.008 | 102 | -0.003 | -0.003 |
| | *6* | -0.006 | 118 | -0.002 | -0.002 |
| 2 | 1 | -0.007 | 109 | -0.003 | -0.003 |
| | 2 | -0.007 | 109 | -0.003 | -0.003 |
| | 3 | -0.007 | 109 | -0.003 | -0.003 |
| | 4 | -0.008 | 102 | -0.004 | -0.004 |
| | 5 | -0.007 | 109 | -0.004 | -0.004 |
| | 6 | -0.007 | 109 | -0.003 | -0.003 |

# 5 Discussion

## 5.1 Disbondment

The tests done in the oven gave a higher disbondment distance than the tests done on the hotplate, as shown in Figure 4.1. This correlates with the tests done at Jotun and the tests done in the preceding specialization project [1]. Except for the testing on a hotplate in experiment 2.1, the average disbondment of the coating increased with the duration of the tests. This was expected and according to literature and studies [7, 26, 28]. The results from Jotun and from the preceding project were reproduced to a certain degree in this series of experiments. The tests completed by Jotun on the same coating gave a higher disbondment distance for the cells tested in an oven, compared to the cells tested on a hotplate. The same applied for the tests completed in the preceding project, except for the test that lasted for two weeks. All of Jotun's tests lasted for four weeks, while the tests in the preceding project lasted for two, three and four weeks.

According to theory, increased coating film thickness decreases the cathodic disbonding [6, 7, 25, 26, 27]. As for the preceding project, there was no clear relationship between the the thickness of the coating and the disbondment of the coating for most of the tests [1]. This is shown in Figure 4.2. This may be due to the properties of the coating, as the effect of film thickness can depend on the properties of the coating. Another explanation can be that the decrease of disbonding for higher film thicknesses is not as big as for thinner coatings. The coating was rather thick on all the panels and the variation in thickness of coating was not that big, therefore, the effect may have been to small to be distinguished from the experimental variation.

## 5.2 Effect of test parameters

In both the first and second test a ring with adhesion was discovered followed by a new area where the adhesion was lost, as can be seen in Figure 4.3 and 4.7. This has also been experienced in other CD tests done at Jotun. The measured disbondment front for the panels checked for further loss of adhesion is shown in Table D.2 in Appendix D. If the measured disbondment front of the panels tested on the hotplate is compared to the measured disbondment of the panels tested in the oven, they show similar results of disbondment.

The average potential values measured for the cells were quite similar, as shown in Figure 4.20-4.23. As in the preceding project, the differences in potentials were very small [1]. This confirms that there is no reason to believe that the differences in disbondment and the ring with adhesion were caused by the potential in the electrolyte. The potential was adjusted to the same value every weekday, so it makes sense that they were quite similar.

In experiment 1 and 2, the potential in the holidays was logged every five minutes to check if fluctuation in the potential could be causing the difference in disbondment between the tests done in the oven and on the hotplate. The results, shown in Figure 4.24 and 4.25, showed no systematic fluctuation of potential in the oven or on the hotplate. The variation in the measurements is caused by an ohmic voltage drop. In the preceding project it was found that the measurement vary a lot when the reference electrode is close to the damage [1]. The potential measurements would be more stable if they were measured a bit away from the holiday.

The variation of the current logged can be seen in Figure H.1-4 in Appendix H. In the preceding project it was concluded that the current probably had nothing to say for the results because the measured values are for the current through the holiday, not at the disbonding front [1]. The results in this project confirms the conclusion, as the measurements of the current had no correlation with the disbondment of the coating. The logging of the current was mainly used to control that the tests were running and had electric contact.

The average temperature values measured in the holidays for the cells tested on a hotplate were higher than the average temperature values for the cells tested in an oven, except for experiment 4 where the temperatures intentionally were different, as shown in Figure 4.16-4.19. As in the preceding project the values were quite similar for the tests done at the standard temperature of 65 °C [1]. This confirms that the differences in disbondment between the tests done in the oven and on the hotplate for the tests done at standard temperature probably were not caused by the temperature difference measured in the holiday.

The temperature in the cells was logged every five minutes to check if fluctuation in the temperature could be causing the difference in disbondment between the tests done in the oven and on the hotplate. The results, shown in Figure 4.4, 4.9, 4.13 and 4.15, showed that there was no significant fluctuation of temperature in the oven or on the hotplate for neither the old nor the new set-up for the hotplate. The sudden drop of temperature at some times for the logged temperature in the oven is probably because of temporary cooling during manual measurements.

The results of the logging of temperature at different locations in the cell are shown in Figure 4.4-4.6 and Figure 4.9-4.11. The logging of the temperature in the steel, the interface between the steel and the coating, and in the solution showed that the temperature of the cells in the oven was pretty uniform in both experiment 1 and 2. This is because the whole cells were heated to the same temperature by the circulating heated air. The results showed that there was a temperature gradient in the cells on the hotplate in both experiment 1 and 2. The average temperature in the interface between the steel and the coating was 4.1 °C lower than in the steel in experiment 1 and 4 °C lower in experiment 2. The average temperature in the solution was 3 °C lower than in the interface between the steel and the coating in experiment 1 and 4.3 °C lower in experiment 2. This is because the cells were cooled down by the air at room temperature surrounding them while the cells were heated from below. The temperature gradient may have affected the transport of oxygen through the coating and the disbondment of the coating. The difference in the temperature gradient between the cells tested in the oven and on the hotplate can be a factor influencing the cathodic disbondment. These results indicate that the tests performed at Jotun may also be affected by the temperature gradient, as they have the same set-up for the hotplate as the one used in the second experiment.

In experiment 4 the temperature in the oven was set to 70 °C to try to replicate the disbondment resulting from testing on a hotplate at 65 °C in the holiday, where the temperature in the steel is about 70 °C. The temperature on the hotplate was set to 60 °C to try to replicate the disbondment resulting from testing in an oven at 65 °C in the holiday, where the temperature in the steel is about 65 °C. The logged temperature in the steel is shown in Figure 4.15. The results showed a more similar disbondment of the coating between the cells tested in the oven and the cells tested on the hotplate, as can be seen in Figure 4.14. The regained adhesion on the cells tested on the hotplate where a bit weaker and the regained adhesion on the cells tested in the oven where a bit stronger compared to former tests.

A hypothesis is that the area with adhesion is caused by the difference in the temperature in the steel between the cells tested on the hotplate and in the oven, as this is the only systematic difference that has been detected between hotplate and oven testing. For the disbondment to happen, the transport of ions must be possible all the way to the disbondment front. It is therefore reasonable to think that the coating had first lost adhesion then regained the adhesion later. The regained adhesion may be caused by degradation of the coating by hot NaOH or by intermediates as radicals in the oxygen reduction, which are more reactive than sodium hydroxide.

## 5.3 Effect of duration of the tests

Experiment 2.2 and 3 had different duration than the other tests and lasted for four and two weeks, respectively. The panels in these tests were stored in a freezer for several weeks before they were defrosted and the disbondment was evaluated. This may have affected the results of the tests. The results of these tests are shown in Figure 4.8 and 4.12. As for the CD tests conducted in the preliminary work, the panels that were tested for two weeks gave lower disbondment than the panels that were tested for three weeks and the panels that were tested for four weeks gave higher disbondment [1]. In experiment 3 the disbondment of the coating was quiet similar for all the cells. This indicates that the the difference in disbondment between hotplate testing and oven testing may be initiated after two weeks. It seems like the regaining of adhesion of the coating happen for cells tested for longer than 2 weeks. It also seems like the regaining of adhesion is most dominant after three weeks compared to tests carried out for four weeks.

## 5.4 Effect of hot NaOH

Two panels were immersed in 1 M NaOH solution for nine days to investigate the effect alkaline environment had on the coating. The results of the electrochemical impedance spectroscopy, shown in Figure 4.26 and 4.27, showed that the impedance of the coating went down. It may be caused by degradation of the coating or creepage up to the contact point through liquid on the surface. The results of the hardness tests, shown in Table 4.2, showed that the hardness of the coating had not been affected by the NaOH solution. In the adhesion tests, the adhesion was lost in the epoxy structural adhesive between the coating and the dolly for all the measurements. The coating did not fracture within itself or disbond from the substrate. The coating possessed good adhesion strength and the adhesion strength of the coating did not seem to have been affected by the NaOH solution. The results of the hardness tests and the adhesion tests indicates that the coating was very resistant to hot NaOH, which suggest that the decrease in impedance was due to creepage. The appearance of the coating did not seem to have changed after being immersed in the NaOH solution. All these tests indicates that there was no degradation of the coating due to exposure of hot NaOH. The alkaline environment may have bigger impact on the coating if the coating is exposed to NaOH for a longer period of time as in the studies by Al-Borno et al. and Al-Sagour and Al-Mansour [42, 43]. However, both these studies also showed that FBE coatings have a good resistance to high pH and withstands exposure to NaOH well.

## 5.5 Radicals

A possible explanation of the regained adhesion is that radical intermediates from the oxygen reduction reacts with the coating. Then the radicals have to possess a long enough lifetime to leave the steel and reach the coating. The lifetime is estimated to a magnitude of $10^{-9}$ s [44]. The diffusion coefficient is estimated to a magnitude of $0.5\text{-}5 \cdot 10^{-5}$ cm$^2$/s [45]. The distance between the steel and the coating is estimated to 5 $\mu$m [28]. By using the following equation:

$$D = \frac{L^2}{15.3t} \tag{4}$$

where D is the diffusion coefficient, L is the distance and the t is the breakthrough time, the breakthrough time was calculated to be in the interval $3.3 \cdot 10^{-4}$ s to $3.3 \cdot 10^{-3}$ s. The estimated lifetime of a radical is too short for the radical to reach and react with the coating. Hence, the hypothesis that radicals reacts with the coating must be discarded.

# 6 Conclusion

The results of the CD tests in this project correlated with the tests done at Jotun and the tests done in the preceding specialization project [1].

In both the first and second test a ring with adhesion was discovered followed by a new area where the adhesion was lost. If the measured disbondment front of the panels tested on the hotplate was compared to the measured disbondment of the panels tested in the oven, they showed similar results of disbondment. A hypothesis is that the area with adhesion is caused by the difference in temperature gradients and the difference in the temperature in the steel as that were the only systematic differences that were detected between the cells tested on the hotplate and in the oven. Further, the ring with adhesion was affected when the temperature in the steel was change.

The differences in the temperature measured in the holidays and the measured potential were not big enough to assume that they were causing the ring with adhesion and the difference in the disbondment. The results of the logged temperature and potential showed no systematic fluctuation of temperature and potential in the oven or on the hotplate, which excluded this to be causing the ring with adhesion and the difference in the disbondment. The measurements of the current had no correlation with the disbondment of the coating.

The regaining of adhesion of the coating happened for cells tested for longer than 2 weeks. The regaining of adhesion was most dominant after three weeks compared to tests carried out for four weeks.

A hypothesis was that the regained adhesion was caused by degradation of the coating by hot NaOH or by intermediates as radicals in the oxygen reduction. The results of electrochemical impedance spectroscopy, adhesion tests and hardness tests indicated that there was no degradation of the coating due to exposure of hot NaOH. The lifetime of a radical was estimated to be too short for the radical to reach and react with the coating.

There is a strong indication that the temperature in the steel affects the area with adhesion and the difference in the disbondment, but no good theory has been found on how this happens.

# 7 Further work

- CD tests with longer duration should be completed to investigate how the ring with adhesion develops.
- Cross sections of the coated panels should be examined in a scanning electron microscope (SEM) after CD tests are conducted to obtain more information about the ring with adhesion.
- Measurements with a Scanning Kelvin probe should be completed on coated panels after CD tests are conducted to see if potential differences under the coating will give more information about the ring with adhesion.

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# Appendix A: Results Jotun

Measured disbondment of coating in mm for coating OCR-400 of CD tests done on a hotplate and in an oven at Jotun are shown in Table A.1. The test lasted for four weeks [1].

Table A.1: Measured disbondment of coating in mm for coating OCR-400 of CD tests done on a hotplate and in an oven at Jotun [1].

| *Panel no.* | *Hotplate* | *Oven* |
|---|---|---|
| *1* | 4.8 | 12.0 |
| *2* | 6.4 | 14.1 |
| *3* | 5.3 | 13.6 |
| *4* | 5.4 | 13.9 |

# Appendix B: Results preceding project

Measured disbondment of coating in mm for coating OCR-400 of CD tests done on a hotplate and in an oven in the preceding project are shown in Table B.1. The tests lasted for two, three and four weeks [1].

Table B.1: Measured disbondment of coating in mm for coating OCR-400 of CD tests done on a hotplate and in an oven in the preceding project [1].

| *Panel no.* | *HP2w* | *OVN2w* | *HP3w* | *OVN3w* | *HP4w* | *OVN4w* |
|---|---|---|---|---|---|---|
| *1* | 7.1 | 3.8 | 7,5 | 12.5 | 13.1 | 14.1 |
| *2* | 5.8 | 4.0 | 11.9 | 14.4 | 12.8 | 15.6 |
| *3* | 6.0 | 3.2 | 5.3 | 14.5 | 9.4 | 13.0 |

# Appendix C: Film thickness

Film thickness of coating in micron for the panels used in the CD tests are shown in Table C.1.

Table C.1: Film thickness of coating in micron for the panels used in the CD tests.

| Panel no. | *HP1* | *OVN1* | *HP2.1* | *OVN2.1* | *HP2.2* | *OVN2.2* | *HP3* | *OVN3* | *HP4* | *OVN4* |
|---|---|---|---|---|---|---|---|---|---|---|
| *1* | 319 | 323 |  |  | 345 | 346 | 350 | 351 | 354 | 361 |
| *2* | 332 | 333 |  | 360 | 360 |  | 396 | 400 | 381 | 382 |
| *3* | 342 | 345 |  |  | 384 | 390 | 455 | 458 | 419 | 419 |
| *4* | 355 | 358 | 410 |  |  | 411 |  |  | 440 | 449 |
| *5* | 387 | 388 | 435 | 439 |  |  |  |  | 306 | 307 |
| *6* | 410 | 411 | 472 | 477 |  |  |  |  | 390 | 397 |

# Appendix D: Disbondment of coating

Measured disbondment of coating in mm for the panels used in the CD tests are shown in Table D.1. Table D.2 shows disbondment front in mm for the panels that were checked for further loss of adhesion after the initial disbondment front.

Table D.1: Measured disbondment of coating in mm for the panels used in the CD tests.

| Panel no. | *HP1* | *OVN1* | *HP2.1* | *OVN2.1* | *HP2.2* | *OVN2.2* | *HP3* | *OVN3* | *HP4* | *OVN4* |
|---|---|---|---|---|---|---|---|---|---|---|
| *1* | 4.1 | 12.8 |  |  | 14.8 | 15.7 | 4.6 | 10.2 | 7.7 | 11.2 |
| *2* | 4.5 | 3.6 |  | 13.6 | 13.9 |  | 3.4 | 2.3 | 12.3 | 15.1 |
| *3* | 3.5 | 12.6 |  |  | 4.7 | 15.5 | 2.7 | 3.0 | 4.3 | 4.5 |
| *4* | 5.0 | 12.6 | 5.5 |  |  | 14.5 |  |  | 11.9 | 3.2 |
| *5* | 4.4 | 12.3 | 3.2 | 13.4 |  |  |  |  | 5.5 | 12.6 |
| *6* | 12.4 | 15.9 | 2.4 | 15.0 |  |  |  |  | 4.6 | 4.0 |

Table D.2: Measured disbondment front in mm for the panels checked for further loss of adhesion.

| Panel no. | *HP1* | *OVN1* | *HP2.1* | *OVN2.1* | *HP2.2* | *OVN2.2* | *HP3* | *OVN3* | *HP4* | *OVN4* |
|---|---|---|---|---|---|---|---|---|---|---|
| *1* | 14.4 |  |  |  |  |  |  |  |  |  |
| *2* |  | 11.6 |  |  |  |  |  |  |  |  |
| *3* |  |  |  |  |  |  |  |  | 12.1 | 14.3 |
| *4* |  |  |  |  |  |  |  |  |  | 14.1 |
| *5* | 13.8 |  | 11.7 |  |  |  |  |  | 16.0 |  |
| *6* |  |  | 11.2 |  |  |  |  |  | 14.3 | 12.4 |

# Appendix E: Temperature

Temperature measured manually in the holiday for all the cells in test 1, 2.1, 2.2 and 4 are shown in Figure E.1-4. Logged temperature in the steel for the cells in test 1, 2, 3 and 4 are shown in Figure E.5-8. Logged temperature in the interface between the steel and the coating for the cells in test 1 and 2 are shown in Figure E.9 and E.10. Logged temperature in the solution for the cells in test 1 and 2 are shown in Figure E.11 and E.12.

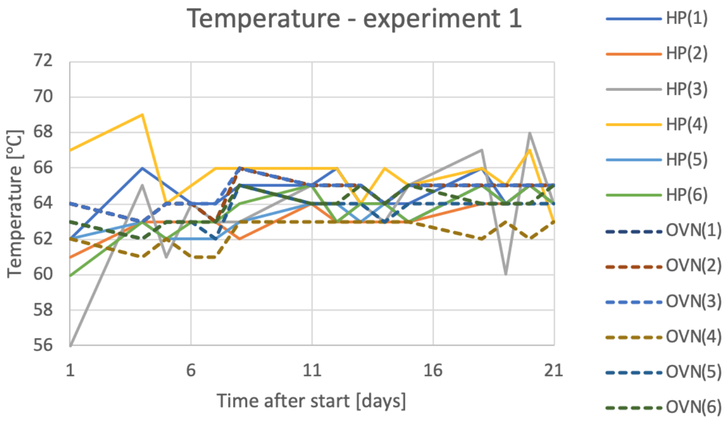

Figure E.1: Plot of temperature measured for experiment 1.

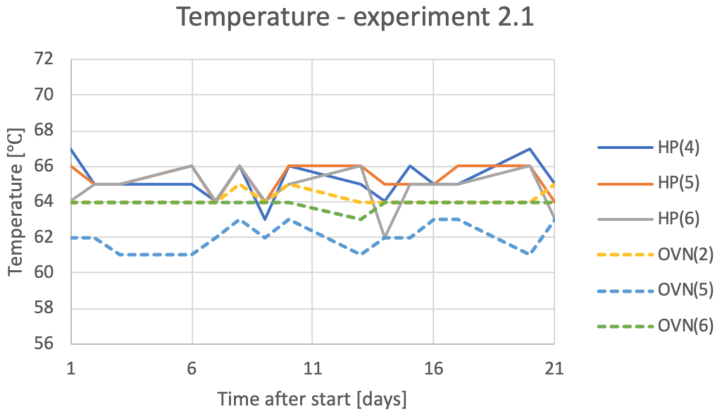

Figure E.2: Plot of temperature measured for experiment 2.1.

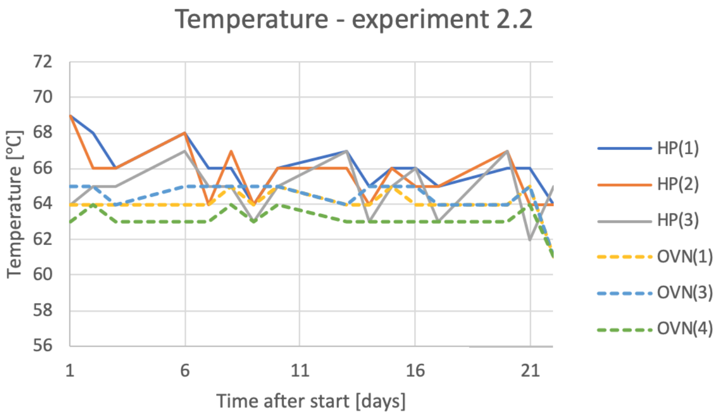

Figure E.3: Plot of temperature measured for experiment 2.2.

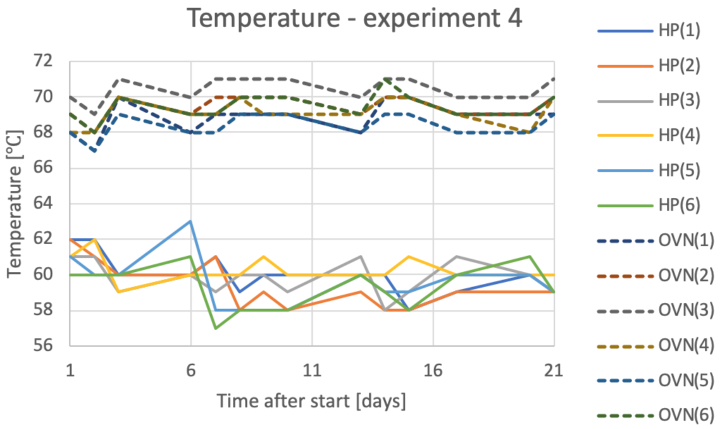

Figure E.4: Plot of temperature measured for experiment 4.

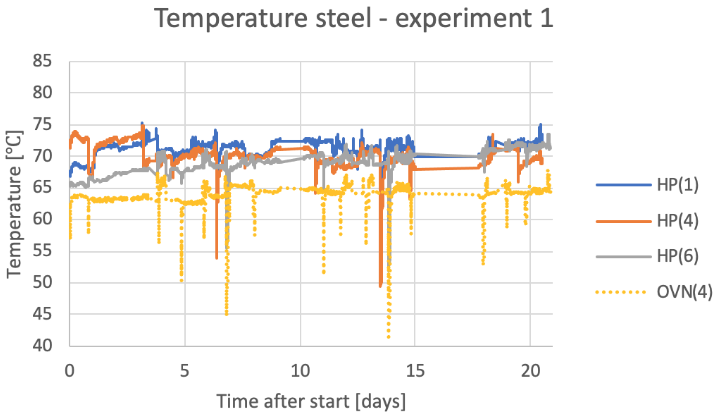

Figure E.5: Plot of temperature in the steel logged for experiment 1.

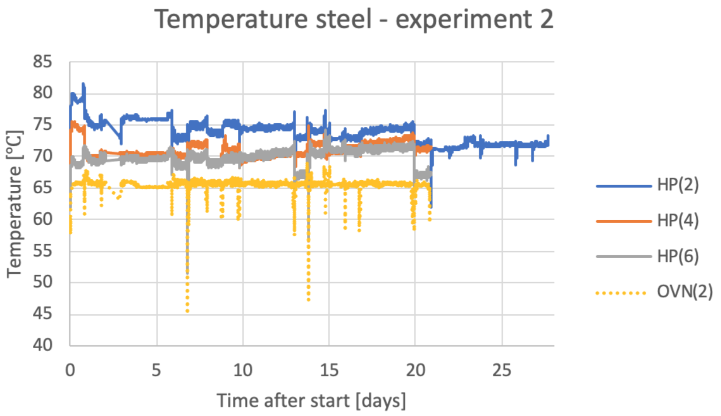

Figure E.6: Plot of temperature in the steel logged for experiment 2.

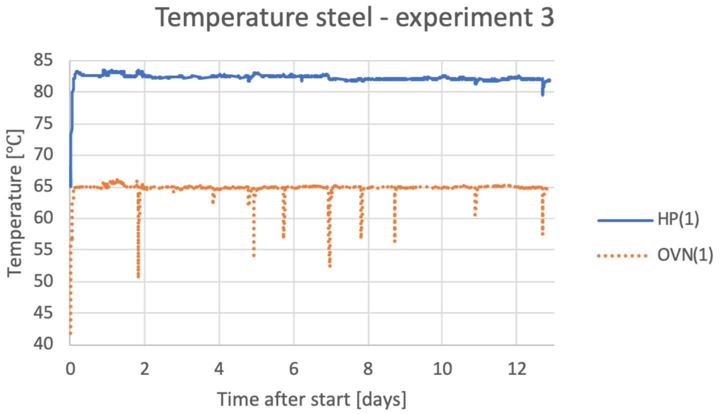

Figure E.7: Plot of temperature in the steel logged for experiment 3.

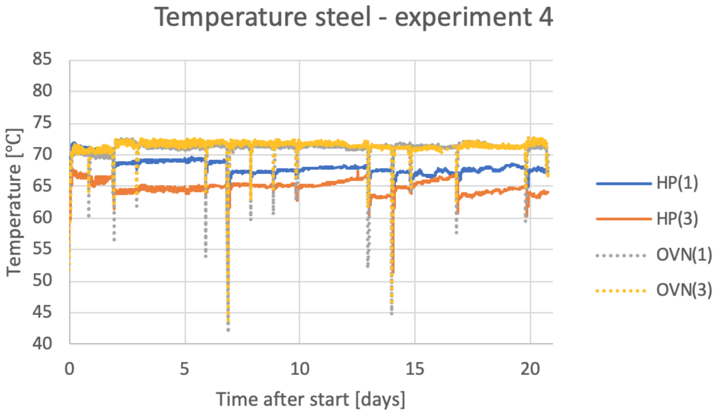

Figure E.8: Plot of temperature in the steel logged for experiment 4.

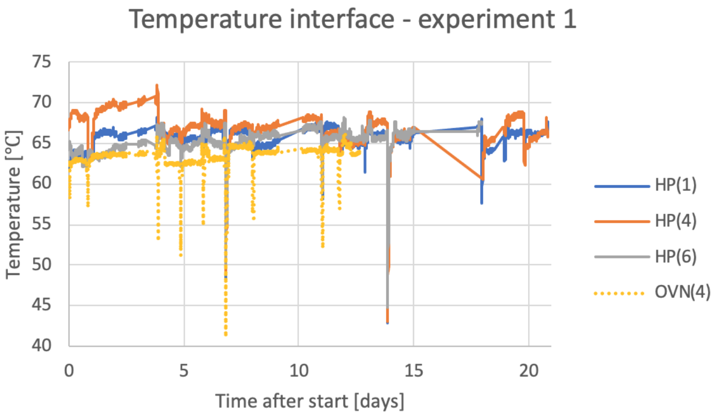

Figure E.9: Plot of temperature in the interface between the steel and the coating logged for experiment 1.

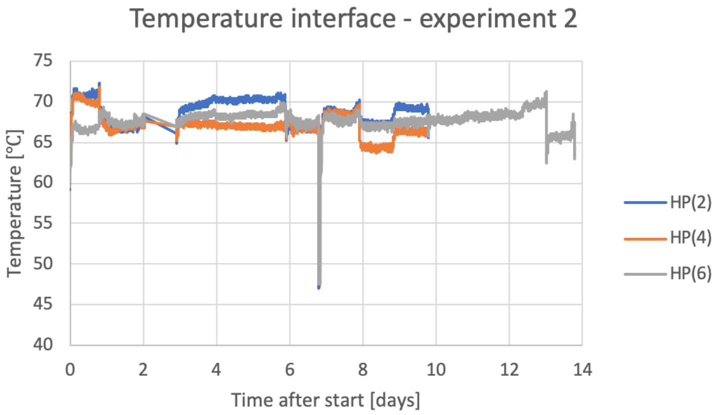

Figure E.10: Plot of temperature in the interface between the steel and the coating logged for experiment 2.

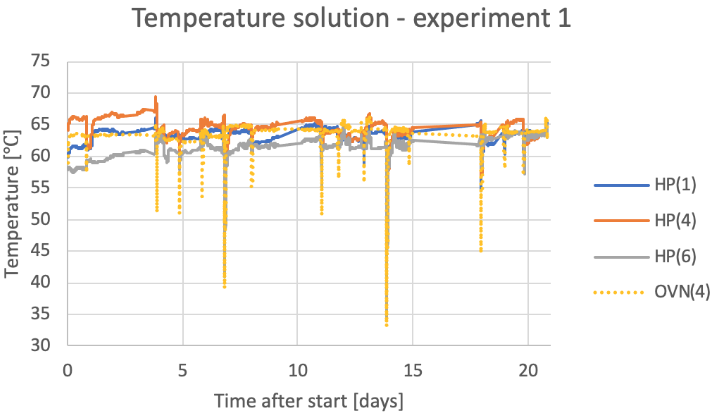

Figure E.11: Plot of temperature in the solution logged for experiment 1.

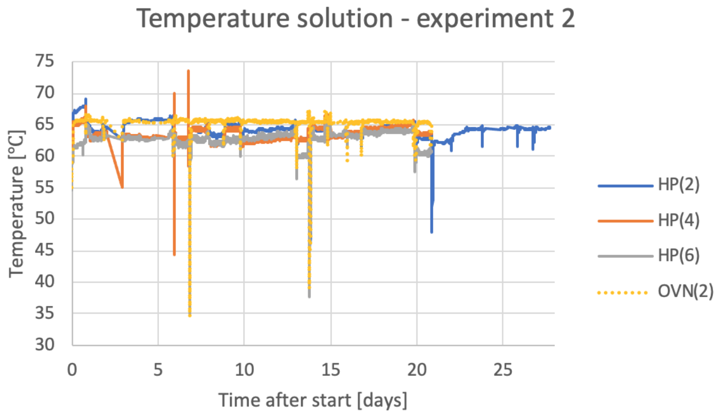

Figure E.12: Plot of temperature in the solution logged for experiment 2.

# Appendix F: Thermocouple sensors

Temperatures measured with thermocouple sensors compared with temperatures measured with a calibrated termometer are shown in Table F.1.

Table F.1: Temperatures measured with thermocouple sensors compared with temperatures measured with a calibrated termometer.

| *Thermocouple sensor no.* | *Temperature [°C]* | *Temperature calibrated termometer [°C]* | *Difference* |
|---|---|---|---|
| *1* | 58 | 57 | 1 |
| *2* | 66 | 64 | 2 |
| *3* | 59 | 57 | 2 |
| *4* | 66 | 63 | 3 |
| *5* | 58 | 56 | 2 |
| *6* | 64 | 62 | 2 |
| *9* | 57 | 56 | 1 |
| *10* | 57 | 56 | 1 |
| *11* | 57 | 55 | 2 |
| *12* | 55 | 55 | 0 |
| *13* | 56 | 55 | 1 |
| *14* | 56 | 54 | 2 |
| * | 59 | 58 | 1 |

# Appendix G: Potential

Potential measured manually for all the cells in test 1, 2.1, 2.2 and 4 are shown in Figure G.1-4. Logged potential in the holiday for the cells in test 1 and 2 are shown in Figure G.5 and G.6.

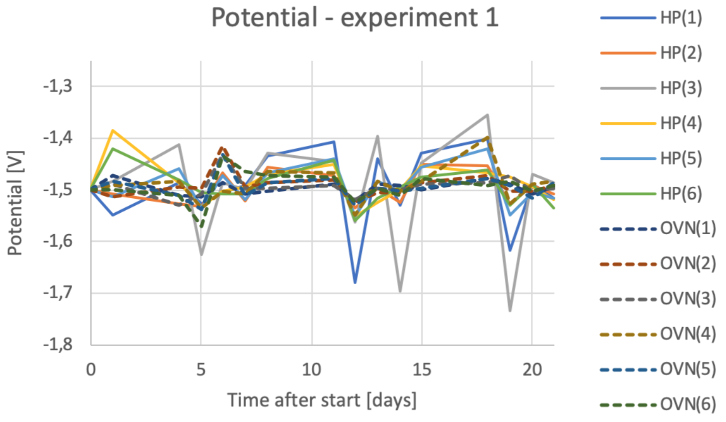

Figure G.1: Plot of potential measured for experiment 1.

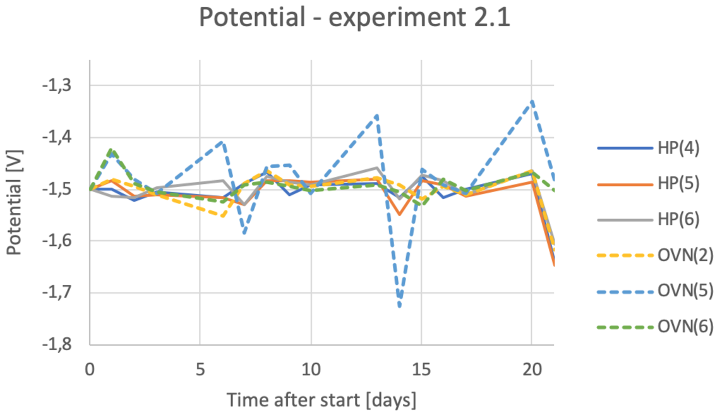

Figure G.2: Plot of potential measured for experiment 2.1.

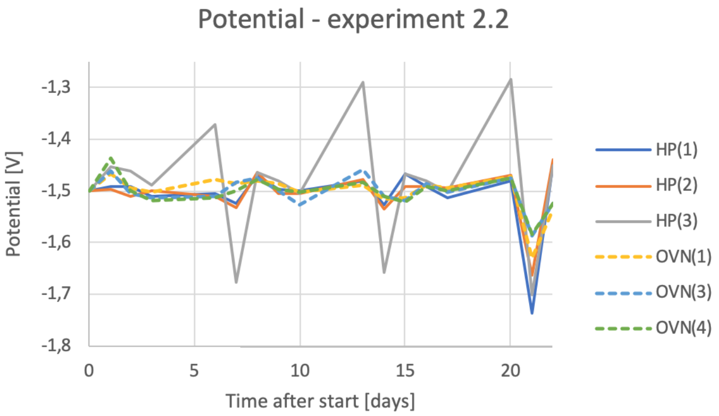

Figure G.3: Plot of potential measured for experiment 2.2.

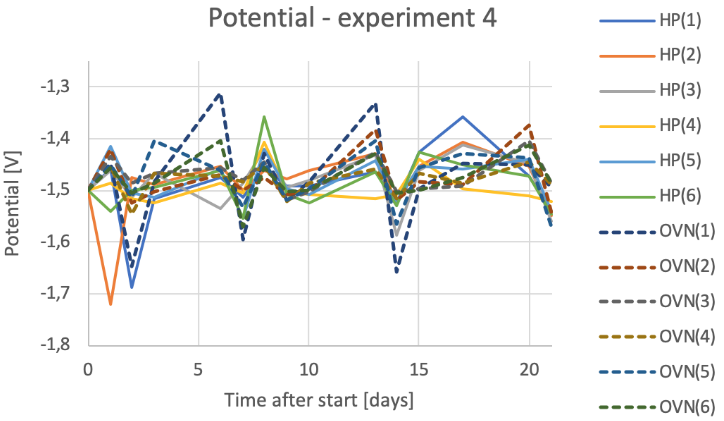

Figure G.4: Plot of potential measured for experiment 4.

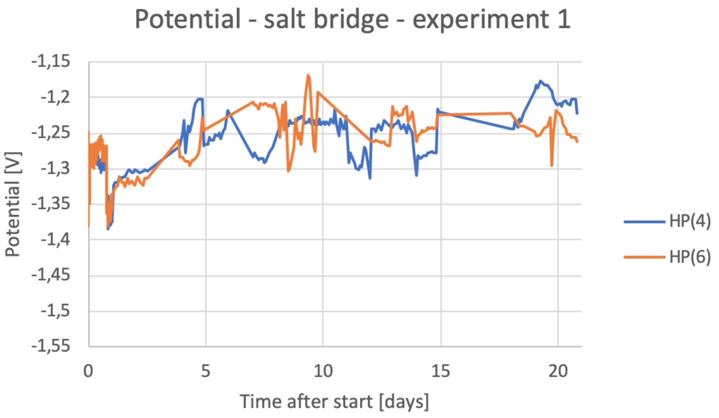

Figure G.5: Plot of potential logged for experiment 1.

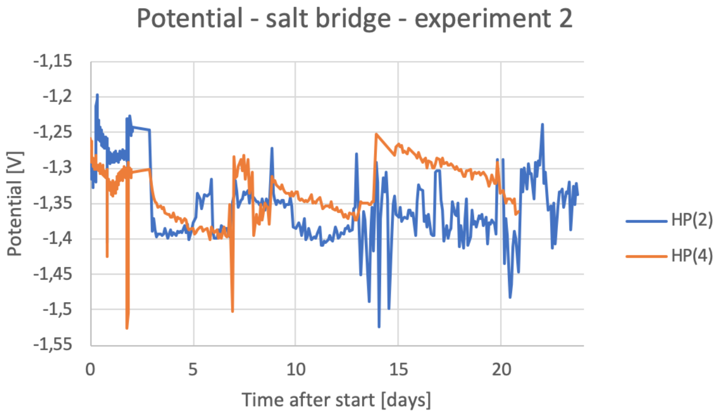

Figure G.6: Plot of potential logged for experiment 2

# Appendix H: Current

Average current logged for test 1, 2, 3 and 4, with average current of all measurements are shown in Figure H.1-4. The average current value for the cells tested on a hotplate for test 1, 2, 3 and 4 were -10.1 mA, -10,3 mA, -6.8 mA and -8.7 mA, respectively. The average current value for the cells tested in an oven for test 1, 2, 3 and 4 were -14.7 mA, -8.8 mA, -7.4 mA and -15.3 mA, respectively. Current logged for the cells in test 1, 2, 3 and 4 are shown in Figure H.5-8.

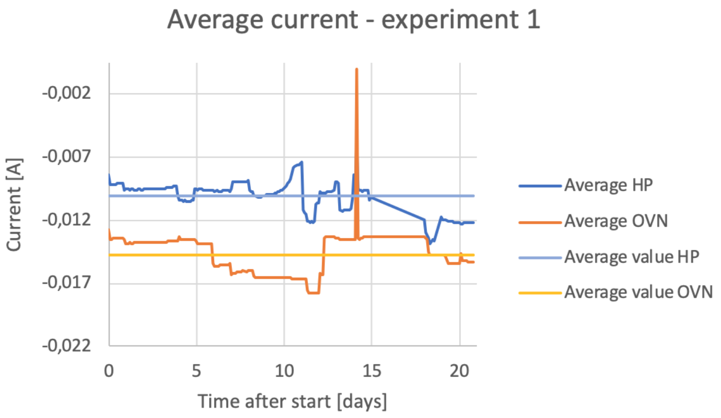

Figure H.1: Plot of the average current logged for experiment 1, with average current of all measurements.

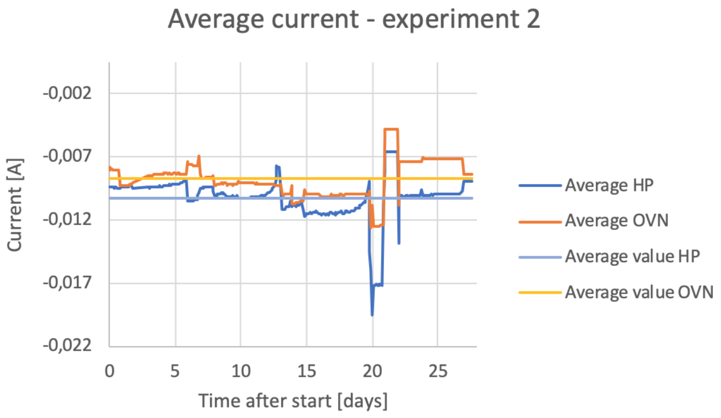

Figure H.2: Plot of the average current logged for experiment 2, with average current of all measurements.

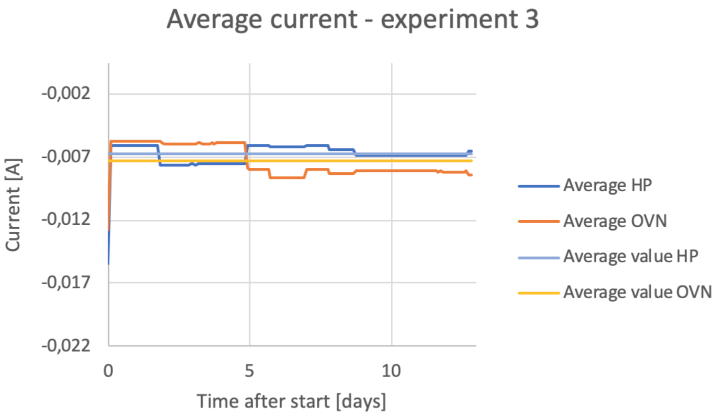

Figure H.3: Plot of the average current logged for experiment 3, with average current of all measurements.

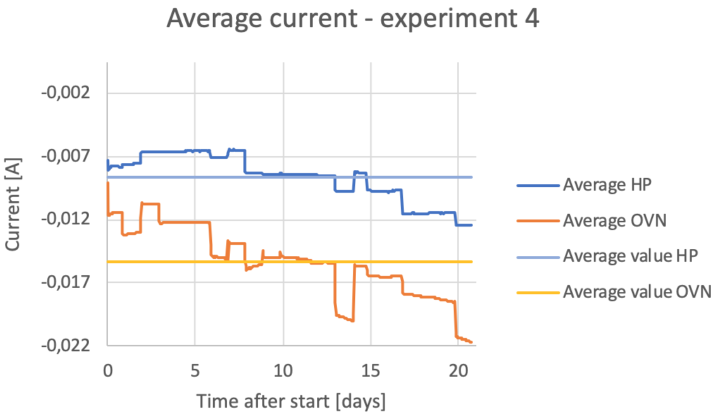

Figure H.4: Plot of the average current logged for experiment 4, with average current of all measurements.

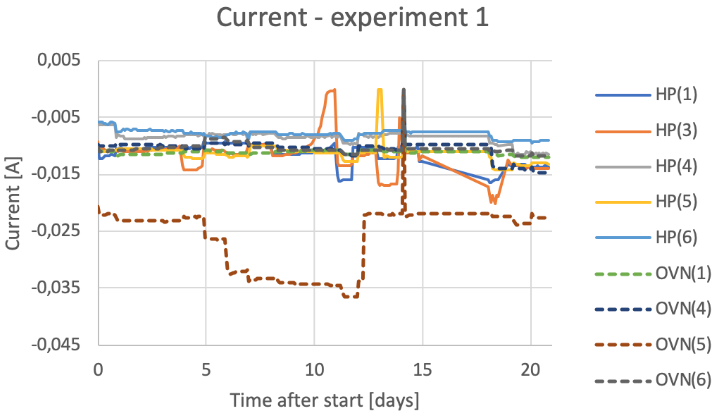

Figure H.5: Plot of current logged for experiment 1.

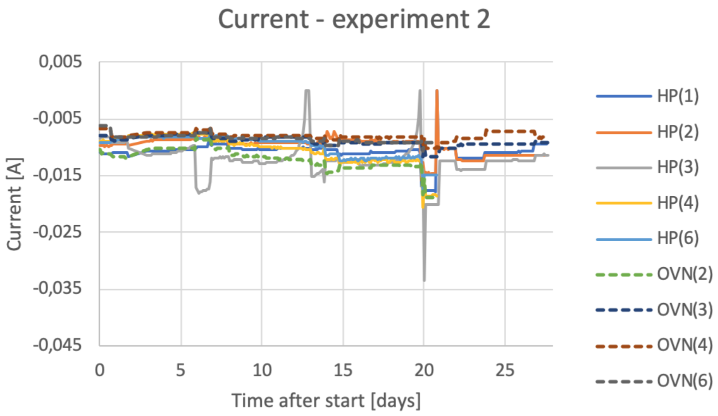

Figure H.6: Plot of current logged for experiment 2.

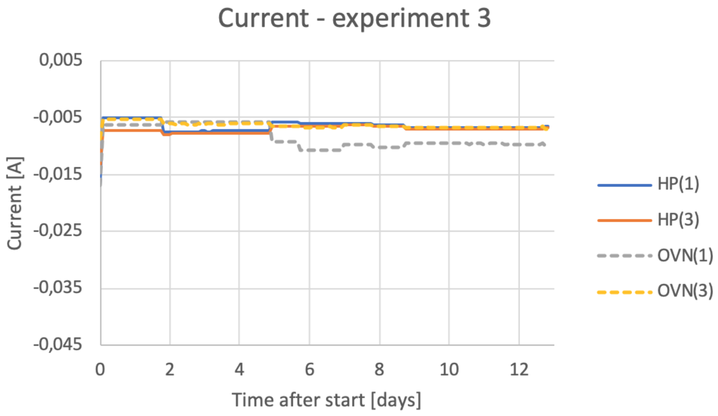

Figure H.7: Plot of current logged for experiment 3.

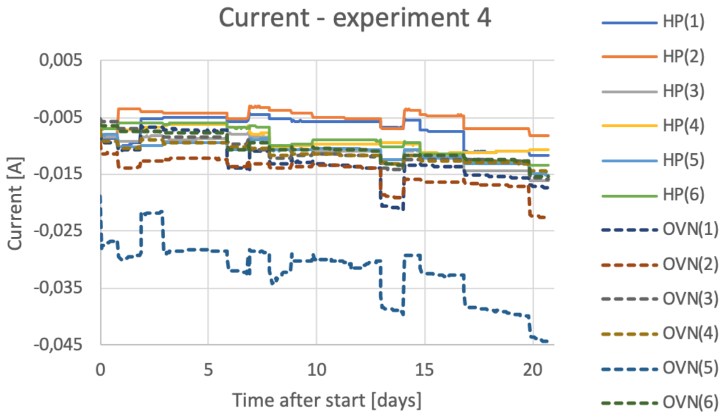

Figure H.8: Plot of current logged for experiment 4.