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Summary

The lasts development in remotely operated vehicles, ROV, have led to the introduction of Resident ROVs that is supposed to stay submersed for longer periods without the frequent maintenance. The increased time between planned maintenance introduces new challenges, and perhaps most important one, is corrosion challenges. This thesis is both a study of the corrosion challenges on IKM Subsea's Merlin UCV resident ROV that is intended to be placed on the seabed below Snorre B, and a more general study of corrosion challenges relating to longer ROV operations.

To protect against corrosion, the most common mitigation measure is to use coatings, cathodic protection and corrosive resistant metals/alloys by following standards. The perhaps most common standard for offshore steel and aluminium structures, is the DNV RP-B401 standard. This was developed to help companies install effective cathodic protection so that the protected structure was safe for several years. However, the standard is made on the assumption that the protected structure is submersed for a far longer period than a resident ROV currently is intended to.

The DNV standard have differentiated between the anode consumption in an initial phase, a mean phase, and a final phase. This is because the anode consumption is much larger in the beginning prior to polarization, while averaging at a lower mean value before it goes back up at the end of the anodes lifetime. It recommends that one uses the mean value to estimate the total anode consumption, while the initial and mean helps make sure the anodes are capable of higher short term consumption.

In terms of corrosion resistive alloys and metals that is getting more and more popular due to lower prices and normally high reliability, challenges relating to especially galvanic and crevice corrosion is important to overcome or at least understand. In the industry one have for a long time used isolators to reduce the possibility of galvanic corrosion, but quite often ended up with crevice corrosion. This makes it important to understand the mechanisms behind.

During this study, it has become apparent that metal combinations should be better understood. The lack of experience with more complex material combinations is perhaps because it usually works well for short term operations, while one avoid them at longer operations due to the risk of problems.

As a result of an experiment performed during the writing of this thesis, and study of literature, all metal parts on a resident ROVs should be under cathodic protection. One should dimension the anodes to be in the initial phase throughout its design life, and one should find anodes with a slightly higher potential to work better on more noble alloys and metals.

Some of the challenges faced during this thesis was to find ways to predict the important and relevant corrosion processes that one needs to overcome for the given material combination, material complexity and time frame. This is because some of the corrosion processes that are important for short time operation, might not be important over time and vice versa.

Another problem has been to gather relevant information and to get help from experienced persons with relevant expertise. Most literature deals with long term corrosion challenges that

is not always directly transferable, while most people in the industry have limited experience in ROV operations of more than a few weeks.

List of abbreviations

AC	alternating current
CRA	Corrosion resistant alloys
CP	cathodic protection
DC	direct current
DNV	Det Norske Veritas
DNV-GL	Det Norske Veritas – Germanisher Lloyd
EN	European Standard (Norm)
HAZ	heat effected zone
HISC	hydrogen induced stress cracking
HSP	hydrogen's standard potential
ICCP	impressed current cathodic protection
IT	Isolated Terra
KLA	Knife Line Attack
MIC	microbial induced corrosion
NACE	National Association of Corrosion Engineers
NORSOK	Norsk Sokkels Konkurransesituasjon
POM	polyoxymeethylene
ROV	remotely operated vehicle
RROV	resident remotely operated vehicle
RP	recommended practice
SCC	stress corrosion cracking
SCE	standard calomel electrode
SHE	Standard hydrogen electrode
SRB	sulphate-reducing bacteria
SS	stainless steel
SSC	Silver/silver chloride
TN	Terra Nautral
UID	Underwater Intervention Drone

List of Symbols

A	Anode surface area [m²]
A_c	surface area of the cathode that is exposed to the electrolyte [m²]
A_1	-173,4292 (constant)
A_2	249,6339 (constant)
A_3	143,3483 (constant)
A_4	-21,8492 (constant)
a	constant in coating breakdown factor
α	ratio factor to state the anodic part of the polarisation
B_1	-0,033096 (constant)
B_2	0,014259 (constant)
B_3	-0,0017000 (constant)
b	constant in coating breakdown factor
C_a	(individual) anode current capacity [Ah]
$C_{a\,tot}$	total anode current capacity [Ah]
c_B	Cathodic Tafel constant
D	diffusion coefficient
D_{O_2}	diffusion coefficient, oxygen
δ	Nernst diffusion boundary layer
$E_a{}^\circ$	design closed circuit anode potential [V]
$E_c{}^\circ$	design protective potential [V]
E'_c	global protection potential [V]
E'_a	(actual) anode closed circuit potential [V]
η	total polarisation
ε	anode electrochemical capacity [A/kg]
F	Faraday's number 96494 C/mol
f_c	coating breakdown factor
f_{ci}	initial coating breakdown factor
f_{cm}	mean coating breakdown factor
f_{cf}	final coating breakdown factor
I_a	(individual) anode current output [A]
I_{ai}	(individual) initial anode current output [A]
I_{af}	(individual) final anode current output [A]
$I_{a\,tot}$	total anode current output [A]
I_c	cathode current demand [A]
I_{ci}	initial current demand [A]
I_{cm}	mean current demand [A]
I_{cf}	final current demand [A]
i_a	current density [A/m²]
i_c	design current density [A/m²]
i_{corr}	current density/corrosion (unprotected/free potential) [A/m²]
i_L	diffusion-limiting current density [A/m²]
i_p	current density/corrosion for the given polarisation cathodic to E_corr [A/m²]
L	anode length [m]
L	Anode life [years]
l	distance from flow in plane in the flow direction [m]
M_a	Required anode mass [m]

m_a	(individual) net anode mass
m_{ai}	(individual) initial net anode mass
m_{af}	(individual) final net anode mass
N	number of anodes
$[O_2]$	oxygen concentration [mL/L]
Q	constant (in water)
R	Universal gas constant; 8,314 J/(mol*K)
R_a	Individual anode resistance [ohm]
S	salinity [‰]
ρ	seawater resistivity in ohm*m
T	Temperature measured in Kelvin [K]
t_f	design life [years]
u	anode utilisation factor [ ]
v	kinematic viscosity
v_∞	relative velocity between electrode and the liquid at infinite distance from the electrode surface
w_W	Waste rate by weight [kg/(A*years)]
Z	Number of electrons transferred in the corrosion reaction
z	number of electrons per mol oxygen reacting

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1. Introduction

1.1 Background

1.1.1 General

Resent years' development towards more and more subsea production, and the urge to reduce costs, have introduced a need for more permanent ROV services subsea. The benefits of using a resident ROV, RROV, is amongst other, that one is not weather restricted, one does not need a vessel for every operation, one does not need offshore pilots, one increases the safety by shorter respond time, and the time between a failure and the solution to the problem.

The development of resident ROVs will introduce challenges that have not been significant for short term ROV operations. Amongst the more likely challenges that one must overcome, is the risk of corrosion. Up until now, the increasingly more complex metal combinations have been working due to some galvanic isolation, the short time submersed, and perhaps a bit of luck. To be submersed over several months, one cannot rely on luck to ensure proper protection against corrosion.

1.1.2 Merlin UCV – IKM Subsea

IKM Subsea has been awarded a contract for ROV and subsea service for Statoil's Visund and Snorre B assets. The contract value for IKM is up to 750mill NOK for a 10 years period, with the possibility of extending it another 15 years.

The big difference between this contract and prior ROV contracts (with IKM or other ROV operators), is that for the the first time Statoil an IKM are going to develop a RROV concept where the ROV is being controlled from a control centre on land, and when not in use, is parked on the sea floor. [1]

The RROV (showed in Figure 1), that is going to be used on Snorre B, shall be based on excising proprietary Merlin ROV technology with RROV technology developed throughout the contract. However, there is a lot of challenges relating to the use of excising ROV technology when it is to be submersed for a longer period of time. This will to some extent relate to the increased possibility of leaks due to the longer period in water, but the main challenge will be the problem of corrosion. This id due to the large amount of different materials that is used together to make up the RROV.
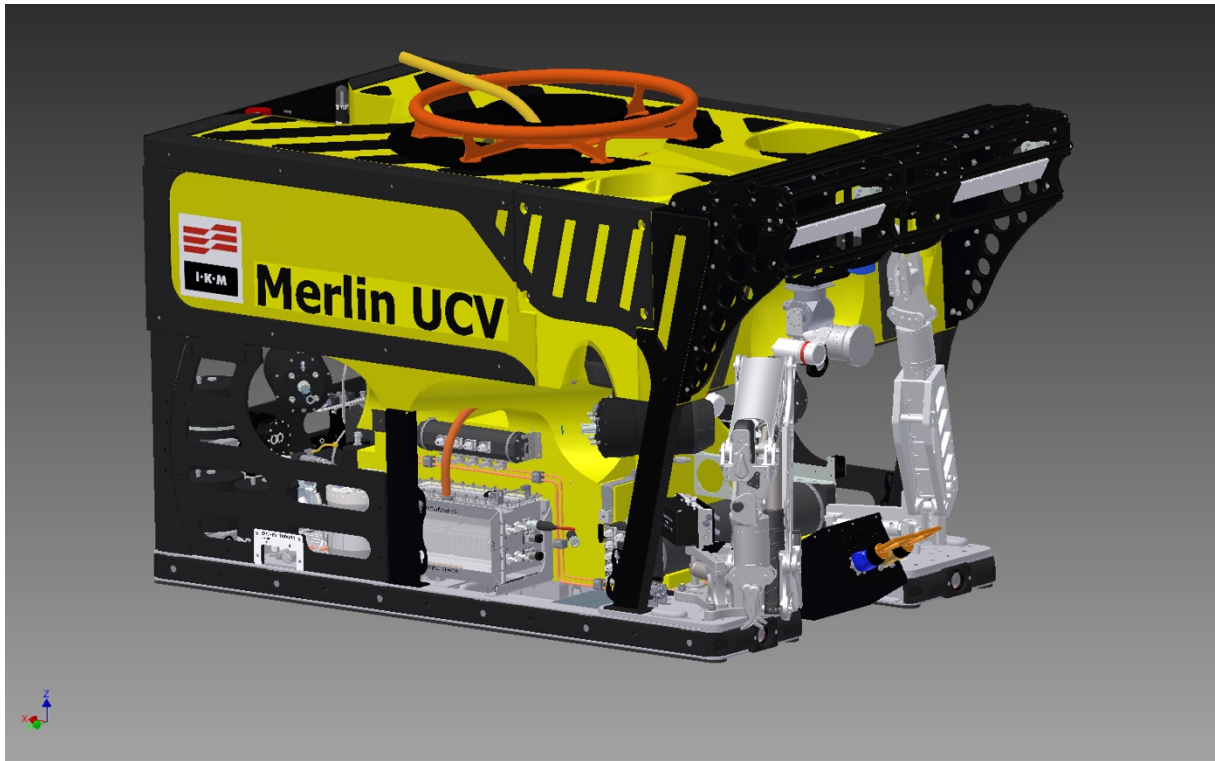
Figure 1 - Merlin UCV RROV

When the RROV is submersed for a longer time, one does not have the ability to check components susceptible to corrosion for early sign of corrosion or deterioration. There is also an increased risk of the cathodic protection to fail due to its inherent complexity (multi-material combinations) or simply faults.

1.2   The problem

In this thesis, the corrosion challenge for IKM Subsea's Merlin UCV was the main goal to study. There are other factors that could limit its performance over time, but it is assumed that corrosion it by far the most important factor. There are (depending on literature) around 8-12 different types off corrosion mechanisms, they are all presented in this thesis and evaluated for relevance to resident ROVs in this thesis.

The thesis has been limited to a theoretical study of the different corrosion mechanisms, where literature, studies, reports, articles and discussions with people in the industry have made the basis for the conclusion and recommendations, while the anode consumption calculated for the Merlin UCV is calculated according to DNV PR-B401, but with some modifications.

An experiment was performed to validate the assumption done in the anode consumption calculations. The experiment should ideally have been performed with several identical setups to eliminate errors and give the results greater validity.

1.3   Map over the thesis

The thesis is built up of eight chapters, succeeding this introduction chapter with a chapter where "state of the art"- corrosion protection is presented to give an overview of how challenges related to corrosion is dealt with, and how one design to reduce the possibility of corrosion in the first place.

The theory chapter is divided into a subchapter about the different corrosion processes in addition to hydrogen induced stress corrosion, HISC, although the latter on is not per definition a corrosion process, a subchapter about factors controlling the rate of corrosion, one on the effect of metal combinations, another one about protective measures against corrosion and finally a subchapter where the anode consumption of the Merlin UCV is calculated according to standard.

In the analysis chapter, an experiment was performed to study the effect of combining several metals together in a joint-anode system, and the influence the relative surface area of the different metals plays on the current density.

Further in the analysis chapter, the risk of crevice corrosion and stray current corrosion is being studied in relation to the Merlin UCV ROV. Both crevice corrosion and stray current corrosion is more likely to be a problem for a resident ROV than for a short term operating ROV and should be studied.

The result chapter, contains the results from the experiment. It is presented with graphs, while the raw data is placed in appendix. It shows how the current density is effected by both the anode configuration and how it is effected when the surface area is relative to the Merlin UCV surface area.

In the discussion chapter, the current density variations are discussed with respect to the mentioned factors and to the predicted behavior by the DNV RP-B401. The current density is compared between the different anode configurations, the possibility for the different corrosion mechanisms are discussed together with a discussion of the anode consumption for the Merlin UCV.

In the following chapter, a conclusion based on the discussion on the overall discussion is made. A recommendation for the choice of design current density phase is made. This is followed by a chapter where suggestions for further work is presented.

2. State of the art

Ever since the development of ROVs, they have always only been in continuous use for a short time period. The operations have typically been from a few hours to a few weeks where the vehicle has been submerged the whole time.

In terms of corrosion protection of ROVs today, there are several measures that is in use with great success. Amongst the most popular measures is to use corrosion resistant alloys, isolate metals/alloys with different potential, use coatings/paints, use cathodic protection, use few metal combinations and so on.

In order to avoid excessive corrosion in the form of uniform attack and/or pitting, there have been a tremendous evolution in the development of corrosion resistive alloys the last decades. The introduction of alloys like duplex and super duplex, several stainless steels and titanium alloys, have made it possible to avoid many of the problems one experienced in the early phase of subsea/marine operations. A huge, and often complex, mixture of materials has been used to specialize materials for each given task.

The introduction of different alloys and metals with different potentials have introduced a lot of new problems relating to the interaction between different materials. So far, the most popular way of treating this problem have been, and still is, to try to isolate these materials so that electrical contact between them is avoided. An isolator is typically placed between the two different materials, and hence the galvanic corrosion is eliminated.

Another way of dealing with corrosion is to isolate the metal that is in risk of corrode by a coating or paint. These materials work by (somewhat simplified) electrically isolated the seawater from the metal. Even though no coating is said to be perfect, they will at least lower the effective surface area, and therefore reduce the need for anodes, given that a cathodic protection system is used.

Cathodic protection is a type of protection used all over the world for numerous tasks and in a wide spectre of industries. It was developed by Humphrey Davy for the British navy and has ever since been used on almost everything subsea. Even alloys said to be resist corrosion, have in later years been equipped with a cathodic protection system. This has been done to cope with corrosion like crevice corrosion.

In terms of anodes for cathodic protection, there have been a shift from only using zinc or magnesium, to use anodes made from aluminium. This have been done partly because one have acknowledged the problem of cathodic overprotection and partly because of aluminium anodes superior durability.

The use of multiple metals and alloys in the same system have caused several problems, and in turn engineers have shifted slightly over from "only" find materials that is optimized for its function without regard for its interaction with other materials, to reduce the number of metals to avoid the complexity of having mixed materials.

The principle of finding materials for a part that not only will secure the integrity of the part alone, but also secure its function when working together with others, is gaining more and more focus. Perhaps it is due to failures that has been traced back to poorly material selection.

One of the reasons that we rarely hear about failures relating to insufficient corrosion protection of ROVs might be partially due to the short time in service. Between each dive, one have the opportunity to do maintenance and service to ensure the integrity of the corrosion protection. The later urge to make resident ROV will create problems that previously have been neglectable.

Long term corrosion protection is nothing new, and there has been a huge development in technology to cope with even the most extreme corrosion environments. Standards like NACE RP0169 and RP0675,BS CP1021 and EN12474, DNV TNA703, RPB401 and RPF103 to mention a few, have been developed to ensure the integrity of subsea structures. However, they do not tackle the challenge of several metals used in the same system. So far, this challenge has not been a huge issue, but recent demands for stationary ROVs will make us face those problems.

3. Theory

3.1 Deteriorative mechanisms

Almost all materials experience, to some extent, interaction with a large number of diverse environments. These interactions often have the ability to alter the materials mechanical properties like ductility or strength or other physical properties. In most situations, we experience a deterioration of the intended properties. The process of deterioration of materials are generally divided into three processes; degradation, material loss and oxidation.

Degradation is a process frequently happens to polymers, like for example O-rings or seals, and is a process where the polymers can be dissolved when exposed to a liquid solvent or it can absorb the solvent and swell. In this category, we can also talk about electromagnetic radiation (primarily ultraviolet) and heat that might cause alteration in their molecular structure. In Figure 2, a nylon water-heater valve has been degraded through the contact with chlorinated water, and it is clear that it has deteriorated from the inside.
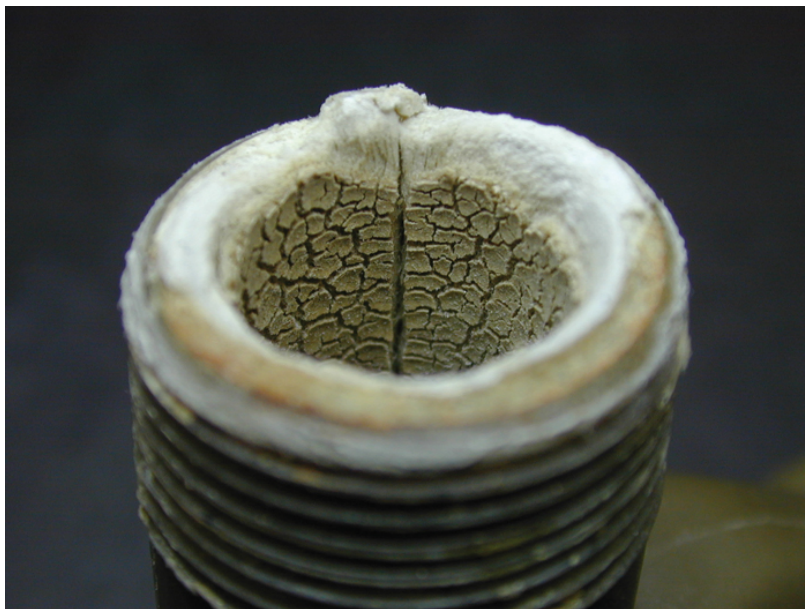
Figure 2 - Nylon water-heater valve degraded through contact with chlorinated water [2]

For metals, we have actual metal loss in a process known as dissolution (corrosion) and the process where non-metallic scale or film (oxidation) is formed mainly on the metals exposed surface. These two processes are frequently mixed up or assumed to be the same process, but has distinct differences. [3] In general we say that a metal first react with its surroundings to make a protective oxide-layer in a reduction-oxidation process, and that the dissolution (the oxide is being dissolved) of this oxide-layer is the corrosion process.

More specific we have that oxidation is a half-reaction that has to be coupled with a reduction-reaction in a reduction-oxidation process. This is an electrochemical process; hence we have a transfer of electrons. [3]

The process we usually call corrosion sometimes involves oxidation, but does not necessarily have to. We can have a corrosive process where an acid dissolves a solid metal or an oxide layer without the formation of oxide, but on a daily basis, we often refer to all degradation of

material as corrosion. For the rest of this thesis corrosion is used as a general term for both dissolution and oxidation if not stated otherwise.

Redox reactions
When talking about corrosion, we are talking about a branch of reduction-oxidation reactions (shortened "redox") which is a chemical reaction in which the oxidation states of atoms are changed. In general, we have that oxidation is a loss of electrons (anode) while reduction is a gain of electrons (cathode). [4] The oxidation and reduction process occurs simultaneously and cannot happen independently of one another even though we for the sake of simplicity sometimes divide the reaction equations into half-reactions.

For de corrosion to occur, we need a reductant to transfer electrons to an oxidant. A substance that has the ability to oxidize another substance is called an oxidizer, while a substance that has the ability to reduce another substance is called a reducer. In term of corrosion we mean the metals (like iron, aluminium, titan, nickel, chromium etc.) when we talk about reducers, and mainly oxygen (including H_2O and CO_2) and nitrate when we talk about the oxidizers.

Standard electrode potential
"Corrosion is the degradation of a metal by an electrochemical reaction with its environment". [5] When metal is "produced" or more accurately called "reduced from its oxidized form" one has to introduce energy into the process. For iron this is done by heating iron oxide together with charcoal to about 1600-2000 degrees Celsius, the reaction can be described by the following process:

Carbon from the charcoal reacts with oxygen to form carbon monoxide:

$$2\,C + O_2 \rightarrow 2\,CO$$
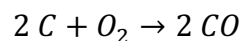
The carbon monoxide reduces the iron oxide to iron and carbon dioxide (the carbon monoxide is oxidized):

$$Fe_2O_3 + CO \rightarrow 2\,Fe + 3\,CO_2$$
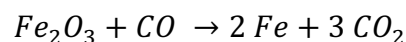
While some of the iron oxide reacts directly without gone via the carbon monoxide step:

$$2\,Fe_2O_3 + 3\,C \rightarrow 4\,Fe + \,CO_2$$
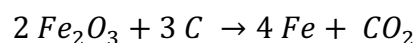
In this reduced state, the iron has taken up a lot of energy that it has a tendency to try to give back to the surroundings, but this can only happen with the help of a redox-reaction. Now the iron is in its reduced form and wants to be oxidized. Like all metals, there is a measure of how great this tendency to be reduced is. There is no possible (accurate) way to measure the absolute value of this tendency but it is measured against a standard electrode called a "Standard hydrogen electrode".

The hydrogen's standard potential (HSP) is defined as zero volts (although estimated to be 4,44 ± 0,02 V at 25 degrees Celsius) at ALL temperatures in order to be used as a reference value. This reaction is described by the redox half cell:

$$2\,H^+\,(aq) +\,2\,e^-\,\rightarrow\,H_2\,(g)$$
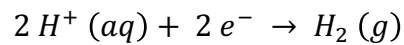
The reduction potential E^0_{red} (the potential when the half reaction happens at the cathode) is the measure against the HSP, so metals with a larger (positive) E^0_{red} has a greater tendency to stay in its reduced ("metallic") form, while metals with a lower E^0_{red} has a tendency to corrode. An example of a metal with high E^0_{red} is gold with a $E^0_{red} = 1,68\,V$ for the half reaction:

$$Au^+ +\,e^-\,\rightleftharpoons Au$$
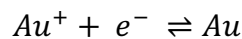
Gold is a metal found in its reduced form in nature, so it gives sense that this has e strong tendency to stay reduced. On the other hand, iron has an $E^0_{red} = -0,44\,V$ for the half reaction:

$$Fe^{2+} + 2\,e^-\,\rightleftharpoons Fe\,(s)$$
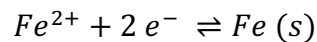
This explains why we don't see iron in its pure form naturally in the nature, and hence has to reduce it.

Thermodynamics of corrosion reactions
Thermodynamics is a part of science that deals with temperature, energy and entropy, and how this relates to work. The factor that governs the reactions and decides whether or not a reaction is spontaneously is called "free energy" or "Gibbs free energy". "All interactions between elements and compounds are governed by the free energy changes available to them". [5]

It is common to express the individual free energy as G, and the net change of energy ΔG. For a reaction to be spontaneous the reaction has to go from a higher energy state to a lower energy state, and hence release energy. Since energy is leaving the system, we can say that ΔG has to be negative in order to be spontaneous. On the other hand, if ΔG is positive, we are adding energy to the reaction. Most chemical compounds of metals, have at room temperature, a lower value of G than the uncombined metals and therefor has a tendency to corrode. [5]

Although ΔG says a lot about a metals tendency to corrode, it does not say anything about the corrosion rate. In reality, most of the metals we use in machinery and construction have already corroded to some degree. By this we mean not all the way through, but exposed to the elements is often built up an invisible layer of oxidation that render the surface less prone to corrosion. This property is called "passivation" and a good example of that is the thin oxide layer that forms on the surface of aluminium when exposed to air. This layer is invisible to the naked eye, but offers a remarkable protection against further corrosion. The standard reduction potential for the aluminium half cell is $E^0_{red,Al} = -1,67$ V with the reaction:

$$Al^{3+} + 3\,e^- \rightleftharpoons Al$$
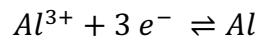
This is relatively low, and should indicate that aluminium would corrode very quickly, but the passivation saves the metal from further oxidation.

Kinetics of corrosion reactions

While the thermodynamics can explain the tendency for a material to corrode, it does however not tell us a lot about the rate it corrodes. As long as corrosion reactions is not in equilibrium, it causes a current to flow, and there is a flow rate that has to be described by kinetics. An example of this is aluminium's tendency to rapidly form a protective oxide layer, however once this is formed, the corrosion rate suddenly drops down, and the corrosion rate can in some circumstances be looked at as zero.

When studying the kinetics of corrosion, we are interested in the current flow (electrons) that flows from the anode to the cathode. The absolute current, I, is measured in ampere while the current density, i, is measured in ampere per square meter. Throughout this thesis, the lower case "i" will be used to denote the current density, i_a and i_c for the magnitude of the anodic and cathodic current densities which is in line with most published material, standards (DNV-GL) and books on corrosion (for electric current density one often use "J" or "q" if it is in vector form). [5] [6]

An important factor in terms of kinetics is the free energy, ΔG, and the energy barrier, $\Delta G_a^{\ddagger}$, which both are variable because they are dependent on the nature of the materials on each side of the metal/electrode interface and these change. Take for example a piece of copper and put it into pure water. In the beginning, there is sufficient available energy in the system to cause copper atoms to overcome the energy barrier, $\Delta G_a^{\ddagger}$, and thereby oxidize from Cu to Cu^{2+} while giving away 2 electrons in the process (redox-reaction).

At the same time as the copper atoms are getting oxidized, the concentration of Cu^{2+}-ions in the surrounding water is increasing and hence the thermodynamic energy in the metal atoms and the adjacent ions tends to approach each other. The tendency of copper to corrode decreases as the current increases from zero, and hence the net free energy, ΔG, goes rapidly down a long with the potential. As we can see from Figure 3 [5], ΔG is high when the concentration of CU^{2+}-ions is low (or theoretically non-existing), and diminishes as the concentration gets into an equilibrium state.
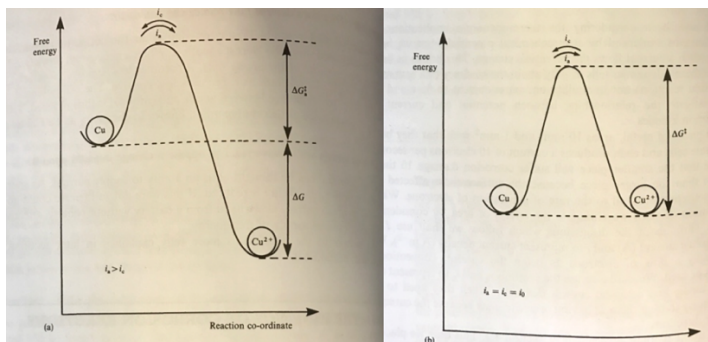
Figure 3 - Energy profiles for copper

(Original Text: "Fig. 4.6 (a) An energy profile for copper in pure water ia > ic. (b) An energy profile for copper in equilibrium with a solution of its divalent ions; $i_a = i_b = i_0$.)

In more general term, we can for a divalent metal use the equation below, where M represent the reduced metal and M^{2+} is the ion form (dissolved).

$$M \underset{i_c}{\overset{i_a}{\rightleftharpoons}} M^{2+} + 2e^-$$
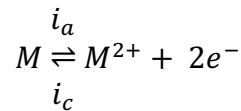
If, or when, we achieve a state of equilibrium in the system (globally or locally) we have $i_a = i_c$, and a net $i_{measured} = 0$. In this state there is current (I_0), but the current is equal and opposite and cannot be measured.

3.1.2   Types of corrosion

3.1.2.1   *Uniform attack*
Uniform attack is a form of corrosion that, as the name suggests, acts uniformly on the surface of the metal exposed. The process is electrochemical and happens with the same intensity all over the exposed surface area and both the oxidation and reduction process occurs randomly all over the area and at the same rate. [5] [7] In Figure 4, an example of uniform attack is shown.

Figure 4 - Uniform attack [8]

Uniform attack is relatively easy to both predict and measure and hence failures relating to uniform attack is rare. In situations where we have uniform attack, it is usually accepted due to its limited damage potential (almost purely esthetical), and the corrosion rate can be calculated relatively precise. [9]

To reduce uniform attack, both cathodic protection and coatings/paints are well established mitigation measures that will, if done correctly, drastically reduce the corrosion rate. No mitigation measures are trusted to stop this form of corrosion completely, but for engineering purposes one can by these measures almost assume perfect protection. However, other corrosion problems can result from trying mitigation measures intended to reduce the uniform attack (will be discussed later).

3.1.2.2 *Galvanic*

Galvanic corrosion is a type of corrosion that occurs when two or more metals (with different cell potential) are electrically coupled and are exposed to an electrolyte. Unless an active voltage to opposite the cell potential is forced, the metal that has the lowest potential will corrode. One example of this is the corrosion we can see when iron screws are used to join brass plates in a marine environment. The iron corrodes violently, while the brass is unaffected as long as there is iron left to corrode. [10] In Figure 5, there is an iron bolt fastened by a more noble material (perhaps a stainless steel). The figure shows how the bolt have corroded much more than the nut.

Figure 5 - Galvanic corrosion [11]

In addition to the cell potential, the surface area exposed to the electrolyte (seawater in this context) and the relative ratio of this for the metals that are effected by galvanic corrosion is of great importance. For a system where a cathode with a surface area (exposed), a smaller anode will corrode faster than a bigger one. This is directly related to the current density and the rate, r, is given by:

$$ r = \frac{i}{n * \mathfrak{F}} $$

where i is the current density (A/m^2), n is the number of electrons associated with the ionization, and $\mathfrak{F}$ 96500 C/mol. [3]

To reduce the effect of galvanic corrosion one can choose metal combinations that are close together in the galvanic series, avoid unfavourable anode-to-cathode surface are ratio, or electrically insulate dissimilar metals from each other. A fourth measure is to use a sacrificial anode as an extra metal that has a lower galvanic potential as a form of anodic cathodic protection.

3.1.2.3 *Crevice Corrosion*

Crevice corrosion is corrosion that typically occur for example in deposit, fissure, gasket, interface, poultice, water-line and wedge corrosion. A good definition of crevice corrosion is:

"The attack which occur because part of a metal surface is in a shielded or restricted environment, compared to the rest of the metal which is exposed to a large volume of electrolyte." [5].

Crevice corrosion is corrosion where in the initiation phase of the corrosive attack is acting uniformly over both the outside of the crevice and inside. Here the electrolyte is assumed to be uniform. For some time, the reaction is counterbalanced in the sense that the generation of positive metal ions is balanced electrostatically by the creation of negative hydroxyl ions (OH^-).

As the corrosion continues to consume dissolved oxygen at both the outer surface and inside the crevice, the level of dissolved oxygen inside the crevice will, due to its confinement, be reduced while the level on the outside will remain the same. This impedes the cathodic process and generation of hydroxyl ions is diminished. [12]

The production of excess positive ions in the crevice makes the crevice a positive cathode, and in order to compensate for this electro potential, negative ions from outside the crevice diffuses in. This will in turn make it possible for the metal in the crevice to dissolve further and the process goes on.

The negative ion induced, as often in the case of seawater is chlorine ions, Cl^-. Cl^- is an excellent electrical conductor, and at the same time reduces the pH (formation of H_3O^+) and thus increases the rate of corrosion. The active crevice corrosion cells are autocatalytic which means that once they have started, they do not need any external drive to continue.

When effected by crevice corrosion, it is not the iron in the stainless steel that is the main problem, it is rather the chromium that dissolves and subsequent hydrolyse that is thought to lead to the major pH decrease. As seen when compared the two reactions below:

$$Fe^{z+} + H_2O \rightarrow Fe(OH)^{(z-1)+} + H^+$$
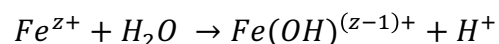
where z is mainly 2 or 3

$$Cr^{3+} + 3H_2O \rightarrow Cr(OH)_3 + 3H^+$$
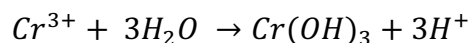
From these two reactions, we can see that a dissolved chromium atom causes 3 times as many H^+-ions than the iron atom, and due to the small electrolyte volume inside the crevice, this has a huge effect the corrosion rate. Two examples of crevice corrosion are shown in Figure 6. Here, an axle and a flange, that have been covered by a form of seal, have experienced severe crevice corrosion.

Figure 6 - Crevice corrosion on axle and flange [13] [14]

A possible mitigation measure is to reduce or eliminate the possibility of crevice corrosion is to ensure circulation of the oxygen rich sea water. By this measure, the metal surface can build up a protective oxide layer.

3.1.2.4 Pitting Corrosion

Pitting is a type of corrosion that, according to K Trethewey & J Chamberlain, occurs where there is

"A surface scratch or mechanically induced break in an otherwise protective film

An emerging dislocation or slip step caused by applied or residual tensile stress

A compositional heterogeneity such as an inclusion, segregate or precipitate" [5].

Pitting is initiated by metallurgical factors alone, and is a very local form of corrosion that leads to the formation of small holes in the metal surface. The initiation process is autocatalytic and happens when metal oxidation causes local acidity maintained by a spatial separation of the cathodic and anodic half reactions. This causes an electro mitigation of ions into the pit driven by the induced potential gradient. For example, when a metal like steel, that primary is made up of iron (Fe), is submersed into seawater (for the sake of simplicity a solution of dissolved NaCl) the pit acts like a positive anode. At the same time, the rest of the surface of the metal acts like a cathode and we have a local positively charged pit and a negatively charged surrounding area. In the pit Fe^{2+} attracts Cl^-ion and forms MCl molecules which in turn reacts with water to form HCl (hydrogen chloride). HCl is a strong acid forming H_3O^+ and thereby accelerating the pitting. [15]

The process can be quite strong if propagation is not stopped. Most of the nucleation current dies out and effectively hinders the propagation, but if the pit survives the nucleation, its survival is dependent on keeping an effective barrier to diffusion provided by a perforated cover of corrosion product over the pit mouth and is called "metastable". The propagation is in this stage dependent on a sufficient current to maintain the stage and if the pit survives, then stable pitting occurs. [5]

14

Figure 7 - Pitting Corrosion [16]

3.1.2.5   *Intergranular Corrosion*

Intergranular corrosion is a type of corrosion that occur between grains due to the presence of precipitates. The intruding elements is divided into two types; namely "intermetallics" and "compounds".

Intermetallics are also known as intermediate constituents, are formed from metal atoms and can be both anodic and cathodic.

Compounds are formed between the metals and the non-metallic elements hydrogen, carbon, silicon, nitrogen and oxygen.

Any metal can be susceptible to intergranular corrosion if it has intermetallics or compounds, but it has been most often reported for austenitic stainless steels, but can also happen for ferritic and two-phase stainless steels, as well as nickel-base corrosion-resistant alloys. In Figure 8, the dark areas are areas affected by severe intergranular corrosion (cross-section). [5]
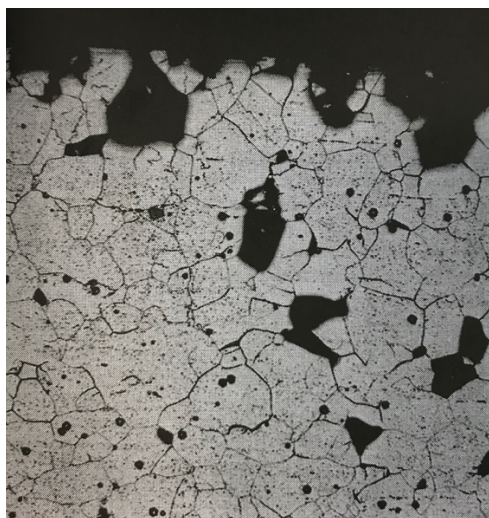
Figure 8 - Intergranular corrosion of 304 stainless steel [5]

When making aluminium, the strength is determined by the precipitates at the grain boundaries and within the grains. Some common precipitates are $CuAl_2$, $FeAl_3$, Mg_5Al_8 and $MgZn_3$. The presence of these inhibitors will, based on whether they are cathodes or anodes in the surrounding aluminium ($CuAl_2$ and $FeAl_3$ are cathodic while Mg_5Al_8 and $MgZn_3$ are anodic) determine if the precipitates themselves are corroded (anodic) or the surrounding metal (cathodic). [5]

Weld decay

Intergranular corrosion is most frequently found in austenitic stainless steels, and are often called weld decay due to its frequent occurrence in association with the welding of materials, but the principles apply for any alloy system in which precipitates occur at grain boundaries. To avoid weld decay, one has three ways of reducing the susceptibility to intergranular corrosion; use low carbon steel (less than 0,03%), apply post-weld treatment to dissolve the precipitates or add titanium or niobium to form carbides preferentially.

An illustration of where one fine weld decay is shown in Figure 9. The intergranular corrosion associated with weld decay occurs at the heat affected zone marked with "Weld Decay" in the figure.
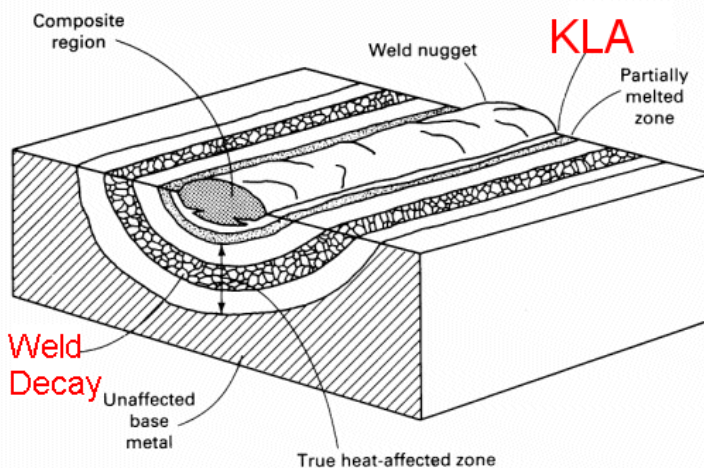
Figure 9 - Weld decay and knife line attack

Knife line attack

A steel alloy not susceptible to intergranular corrosion is known as "Stabilised stainless steel". One can stabilise an austenitic stainless steel by adding small amounts of titanium or niobium that forms carbides in preference to those of chromium and as a result the grain boundary area are not chromium-depleted.

In the adjoining area, along for example a weld, there is a great risk of knife line attack due to the effect of heating into the sensitization temperature range. Sensitization refers to the precipitation of carbides at grain boundaries in stainless steels or alloys, causing the steel or alloy to be susceptible to intergranular corrosion or intergranular stress corrosion cracking. [17] In Figure 9, a zone along the weld marked "KLA" is showed to illustrate an area highly susceptible to knife line attack due to the heat during welding.

3.1.2.6 *Selective leaching*

Selective leaching is a form of corrosion where we have net removal of one element in an alloy. It is known as dealloying or demetallification. This sort of corrosion can be both local and global to a metal surface. When the selective leaching is global the process removes a metal from the alloy "evenly" all over the surface. This will leave the overall geometry unchanged, but the surface is often porous and virtually without any mechanical strength. When the effect is locally, like for example along a veld, we can get a perforation. The local selective leaching is a form of microscopic-scale galvanic corrosion and is shown in Figure 10. The dark area is where the less noble metal is being corroded while leaving the surrounding metal unaffected.
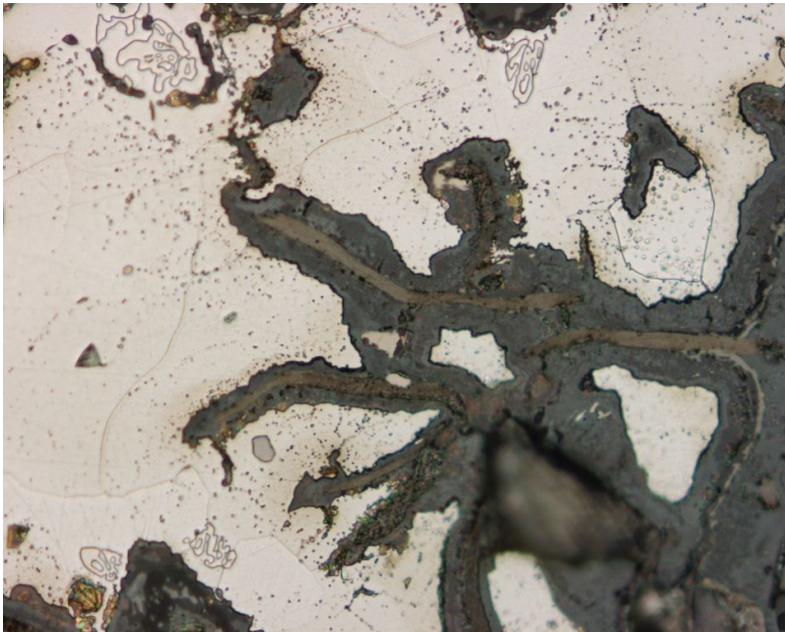
Figure 10 - Selective leaching (500x magnification) [18]

Over the years, the biggest problems relating to selective leaching has been with brasses, where it corrodes and looses zinc in the process known as dezincification. Components like valves, taps, condensers and pipes have been susceptible to this when used in fresh- or seawater. Although the problem had been most common for zinc it is also possible for other metals like aluminium, nickel and tin. [5] [7]

3.1.2.7 *Flow-induced corrosion (erosion-corrosion)*

Flow-induced corrosion is the acceleration of corrosion due to the relative motion between the metal surface and the electrolyte fluid. There is an electrochemical process occurring, but the main corrosive driver is mechanical. The effect is closely linked to the nature of the fluid where a solution is more erosive-corrosive than a pure fluid, bubbles or suspended (suspended particulate if in air) solids enhances the rate.

All metals are to some degree susceptible to flow-induced corrosion, but metals that passivate by forming a protective layer of surface film is especially exposed. The film might be eroded away, leaving an exposed surface of unprotected bare metal. At this stage, the metals corrosion resistance if determined by its ability to rapidly form a new protective film, and if

not the corrosion could be severe. An example of erosion corrosion is shown in Figure 11. The figure shows a heat sink that used recycled water to cool the underlying electronics severely affected by erosion corrosion. The attack would most likely be reduced if the cooling fluid had contained more oxygen to maintain the protective oxide layer.
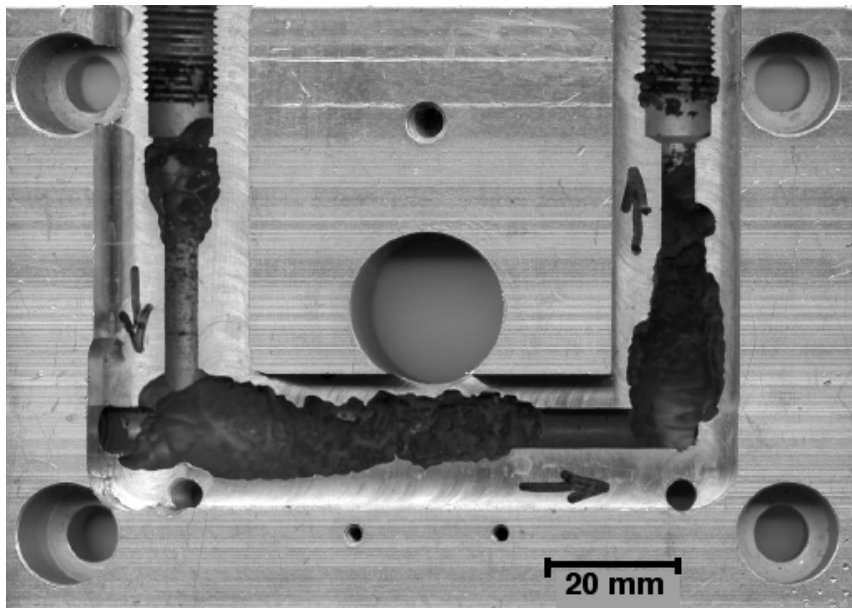
Figure 11 - Erosion Corrosion [19]

Flow-induced corrosion in laminar flow can be the result of the fact that when the fluid is flowing, the (cathodic/anodic) equilibrium might not be established. The ions are removed from the system due to the fluid flow. This cause the surface to be positively charged and the corrosion continues. However, in practice this is rarely the cause of accelerated corrosion. Systems susceptible to general corrosion suffers accelerated corrosion due to enhanced transport of oxygen. [5]

Factors that will affect the protective film layer is the rate of which oxygen and aggressive ions is replenished or solid particles that might scour the surface. The oxygen is needed by the metal in order to replace the eroded surface film (usually oxide). A good example of this is stainless steel, that has very good protection as long as there is sufficient amount of oxygen to maintain the oxide films. In this case, we could reduce the rate of corrosion by reducing the flow rate, while for the replenishment of aggressive ions we could increase the flow to get the contact time down.

For scouring there is both a positive and a negative side of the present particles in the flow. On one hand, they can scour the metal surface and make it susceptible to corrosion where the protective layer is damaged, but on the other hand the particles might help prevent deposition of silt or dirt that in turn could result in even more aggressive corrosion.

Although laminar flow can cause erosion-corrosion to some degree, the problems gets a whole lot worse when we have a turbulent flow. Turbulence does not have to be a problem, but in terms of flow-induced corrosion, it is usually a more complex situation. The turbulence effects the metal surface by the fact that the fluid flows directly onto the surface and back again, and some of the causes of turbulence is geometrical factors.

A typical form of flow-induced corrosion caused by turbulence is the grooves, rounded holes or gullies one sometimes can observe in areas when a flow has gone from a larger diameter pipe to a smaller. The effect can be reduced by reducing the speed of the fluid flow, change the geometry or smoothen the surface finishing.

Impingement is a more extreme form of severe turbulent effect. In normal turbulence, we can look at the flow as more parallel to the metal surface on the majority of the fluid and perpendicular only on the are rarely close to the surface. When we have impingement, we see that molecules of fluid impinge directly upon the metal due to the large bulk of fluid moving at this direction. Impingement can in short time cause extreme corrosion in critical places.

Yet another form of flow-induced corrosion is "cavitation". Cavitation is a result of the formation, and more importantly, the proceeding collapse of bubbles and vapour near metal surfaces. The bubbles normally form due to a high relative speed between the fluid and the metal surface, this can be for example on the surface of a propeller (see Figure 12), impeller or hydraulic turbine gear. The vapour is formed when localized hydrodynamic pressure drops, the next stage is the pressure increase that effectively condenses the vapour. This rapidly condensing of vapour cause a considerable force that can, in some sense, be looked at as a small, but intense explosion. This again can, if the metal surface cannot withstand the pressure, cause corrosion.

Figure 12 - Erosion corrosion caused by cavitation [20]

3.1.2.8 *Stress-corrosion Cracking (SCC)*

"Stress-corrosion cracking is a term given to the intergranular or transgranular cracking of a metal by the conjoint action of a static tensile stress and a specific environment" and is said to be a well understood type of corrosion. [5] Despite this, it continues to be a huge problem in the industry.

SCC often occur well below the materials tensile stress limit, and in environment where it is not particular to corrosion caused by the surrounding chemicals. SCC is usually hard to detect due to the fact that the corrosive environment is often just mildly corrosive, but together with

the stress and the material, cracks can propagate rapidly. "Cracking of a particular metal is observed only for relatively few chemical species in the environment, and these need not to be present in large concentrations." [5]

For most steels, a temperature of about 100°C is necessary for SCC to be a problem, but this possibility is effectively reduced by the use of cathodic protection. [7] An example of SCC is shown in Figure 13

Figure 13 - Stress-corrosion cracking

3.1.2.9   Microbial induced corrosion (MIC)

Microbial Induced Corrosion is a result of biofouling on the surface of metals. There has been a debate about whether or not MIC is a specific form of corrosion or if it simply causes local changes in the environment that again causes other forms of corrosion. Either way, micro-organisms like fungi, algae and diatoms, and bacteria creates chemicals as by-products of their metabolism and again cause corrosion.

Fungi, algea and diatoms typically leads to pitting or other localized attack. The pitting usually happens due to the formation of differential aeration and concentrations cells, or is related to the acids excreted during metabolism.

MIC caused by bacteria usually happens in small defects (cracks) in the metal surface. The bacteria are typically in the range from 0,2-5 μm wide and 1-10 μm long, but compared to a typical crack that might be several hundred times as big, the bacteria can easily develop optimum conditions to thrive.

Different types of bacteria have adapted to live in different temperatures, pH-levels, nutrient level and combinations, and at various oxygen-levels. They are divided into aerobic and anaerobic bacteria, where the aerobic need oxygen to survive, while the anaerobic ones, need an environment free of oxygen. In Figure 14, the "invisible" microbes have eaten away metal from the inside of the oil pipe.
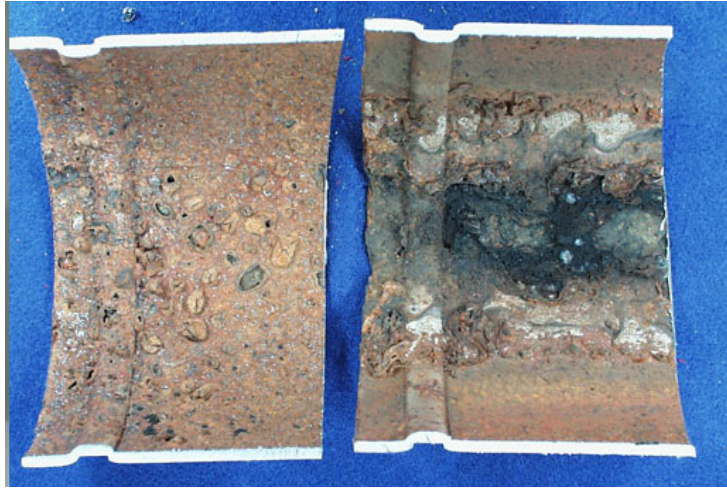
Figure 14 - Microbial induced corrosion in an oil pipeline [21]

Some of the bacteria are called sulphate-reducing bacteria (SRB) and cause the most aggressive corrosion of iron and steel. They have been reported to corrode as much as 2 inch per year. [22]. They are anaerobic bacteria that obtain energy by oxidizing organic compounds or molecular hydrogen while reducing sulphates SO_4^{2-} to hydrogen sulphide H_2S that is highly corrosive. [5]

3.1.2.10 High-temperature corrosion

By high-temperature corrosion we mean corrosion at temperatures in excess of about 500 degrees Celsius and without a liquid electrolyte. In general, we then talk about oxidation of metals in contact with oxygen (even though nitrogen also react with chromium, aluminium, titanium, molybdenum and tungsten at very high temperatures). For machinery used subsea, this is an neglectable form of corrosion.

3.1.2.11 Hydrogen embrittlement

Hydrogen embrittlement is strictly speaking not corrosion, but is a phenomenon that often happens in relation to corrosion. It is a process where hydrogen atoms penetrate into the metal (usually a high strength metal alloy) and reduces its ductility, and hence makes it brittle. The hydrogen that is induced in the crystal lattice, can be in concentrations as low as just several parts per million can lead to cracking. In most cases the cracks fractures have been transgranular, but have in some alloys been observed to be intergranualar.

The phenomenon is similar to stress corrosion, but while stress corrosion can be reduced or ceased by the use of cathodic protection, hydrogen embrittlement can be initiated or enhanced by the same protection. Hence, one have to balance the level of cathodic protection in order to supress stress corrosion, but not induce hydrogen embrittlement.

The presence of hydrogen is a must for hydrogen embrittlement to occur, and there are several ways for it to form. Pickling (a procedure where one use hot sulphuric or hydrochloric acid to remove oxide scale from steel), electroplating and the presence of "poisons" such as sulphur and arsenic compounds. [3]

There is a strong relation between a steels susceptibility to hydrogen induced embrittlement and its strength. High-strength steels tend to be much more susceptible than low-strength steels. Martensitic steels are most vulnerable, while bainitic, ferritic and spheroidic steels are more resilient along with ductile steels.

Figure 15 shows a cross-section picture of a crack caused by hydrogen embrittlement. The hydrogen induced into the high-strength steel.

Figure 15 - Hydrogen embrittlement [23]

Methods used to reduce the likelihood of hydrogen embrittlement to occur is to reduce the metals tensile strength using e heat treatment, remove the source of hydrogen where one can use "baking" to drive out hydrogen from the alloy, or substitute the metal to a more hydrogen embrittlement resistant metal.

3.2   Rate of corrosion

3.2.1   Materials (standard electrode potential)

One of the most important factors in corrosion rate is the standard electrode potential. The standard electrode potential is the voltage one can measure between two (or more) dissimilar metals that is submersed in an electrolyte. The potential is not static and will normally vary over time, mostly due to the formation and deration of oxide forming on the anode, but still, the potential can tell us a lot about where in a system of metals the oxidation and reduction will occur.

In general, we can say that the corrosion rate is dependent on the electrode potential between metals, but this is very vague and not accurate due to the protectiveness of oxide film on some metals (like aluminium), the ratio between the surface area of the cathode and the anode, salinity, temperature and so on.

The displacement of electrode potential from its equilibrium is called polarization. This is when the two half-cells are short circuited together so that we get a differential potential called overvoltage. The term polarization is, in electrochemistry, a collective term for certain mechanical side-effects by which isolating barriers develops at the interface between an electrolyte and an electrode. We distinguish between activation and concentration polarization. [3]

Activation polarization has to do with the accumulation of gasses (or other non-reagent products) at the interface between electrode and electrolyte. As an example of activation

polarization, we can study the process in where hydrogen ions, H$^+$, gets reduced to hydrogen molecules in a 4 step process [3]

1. Adsorption og H$^+$ ions from the solution onto the metals surface
2. Electron transfer from the metal to form a hydrogen atom

$$H^+ + e^- \rightarrow H$$
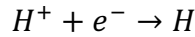
3. Combining of two hydrogen atoms to form a molecule of hydrogen

$$2H \ \rightarrow \ H_2$$
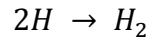
4. The coalescence of many hydrogen molecules to form a bubble.

The slowest of these steps are the one that determines the overall rate of the reaction, and is the limiting factor in terms of activation polarization and the relationship between overvoltage, η_a, and current density i is

$$\eta_a = \ \pm\beta \ log\frac{i}{i_0}$$

where

η_a overvoltage [V]
β constant for given half-cell
i_0 exchange current density, constant for given half-cell (no net current exchange) [A/m^2]
i current density [A/m^2]

The oxidation and reduction can be given by [3]

$$r_{res} = r_{oxid} = \frac{i_0}{n\mathfrak{F}}$$

where

r_{res} reduction rate
r_{oxid} oxidation rate
i_0 exchange current density, constant for given half-cell (no net current exchange) [A/m^2]
n number of electrons associated with the ionization of each metal atom
$\mathfrak{F}$ Faraday's number 96494 C/mol

Concentration polarization exists when the reaction is limited by diffusion in the solution. This happens when the solution/electrolyte in the vicinity of the metal surface changes. This can be a built-up of H$^+$ ions due to an unbalanced diffusion rate from the electrolyte to the interface of the reaction. The mathematical relation between overvoltage and the current density is given by [3]

$$\eta_c = \frac{2,4RT}{n\mathfrak{F}}\log\left(1-\frac{i}{i_L}\right)$$

where

η_c	overvoltage [V]
R	universal gas constant; 8,314 J/(mol*K)
T	absolute temperature [K]
$\mathfrak{J}$	Faraday's number 96494 C/mol
i	current density [A/m^2]
i_L	limiting diffusion current density [A/m^2]

3.2.2 Salinity

Dissolved salt, in the form of ions, makes the water more corrosive than fresh water. This is because of the increased conductivity of the free ions, and the penetrating effect of chloride ion through the surface films on a metal surface. Together with temperature and oxygen concentration, the chloride concentration is the most important parameters that effects the rate of corrosion.

A 3,5% salt content (mainly Cl$^-$ and Na$^+$) is believed to be the most corrosive even though the increase in chloride ions in theory should increase the rate further. The reason for this the that as the salinity level increases, the oxygen saturation goes down. At 3,5% the oxygen and chloride level is at its peak value, and hence, the corrosion rate is at its biggest. [24]

In 1978 "The Practical Salinity Scale" was developed and is a complex function related to the ratio (K) of the electrical conductivity of a seawater sample to that of a potassium chloride (KCl) solution with a mass fraction in KCl of 0,0324356 at a constant temperature and pressure. The salinity is given by

$$S = 0,0080 - 0,1692K^{0,5} + 25,3853K + 14,0941K^{1,5} - 7,0261K^2 + 2,7081K^{2,5}$$

where

S	salinity
K	electrical conductivity of measured solution divided by a KCl solution of the same temperature and pressure at 15°C

The salinity here is based on measurements, and is important when calculating the oxygen saturation level see page 26.

3.2.3 Temperature

In general, all reactions occur at a higher rate when the temperature gets higher. This is because reactions need energy to run. We often separate between exothermic and endothermic reactions where the exothermic reactions give of energy, and endothermic reactions absorbs energy. However, there is a need for an activation energy regardless of the net total energy transfer. This is energy that needs to be present even for exothermic reactions, but after each reaction, the total energy transfer is negative (meaning it has given away more energy than it has spent). [5]

The effect of temperature is, according to Bardal, most significant for the diffusion-limiting current density, i_L, and is given by [25]

$$i_L = D_{O_2} \, z \, F \, \frac{c_B}{\delta}$$

where

i_L	diffusion-limiting current density
D_{O_2}	diffusion coefficient
z	number of electrons per mol oxygen reacting
F	Faraday's number $\approx$ 96500 C/mol e-
c_B	Cathodic Tafel constant
δ	Nernst diffusion boundary layer

The diffusion coefficient, D_{O_2}, is again given by

$$D_{O_2} = A * e^{-\frac{Q}{RT}}$$

where

A	constant (in water)
Q	constant (in water)
R	universal gas constant
T	temperature, absolute [K]

From this we can see that since the diffusion coefficient is strongly dependent on temperature and therefor also the diffusion-limiting current density. As T increases, "e" will get increasingly closer to 1, which is the highest value it can have given the negative sign.

The temperature also changes the viscosity of the water, so when studying the mathematical model of the Nernst diffusion layer given by Vetter for laminar flow 90° towards the edge of a plane electrode given by [25] [26]

$$\delta_{lam} = 3 \, l^{1/2} \, v_\infty^{-1/2} \, v^{1/6} \, D^{1/3}$$

where

l	distance from flow in plane in the flow direction
v_∞	relative velocity between electrode and the liquid at infinite distance from the electrode surface
v	kinematic viscosity
D	diffusion coefficient

It is clear that while the viscosity reduces, the diffusion coefficient increases, so the effect on the boundary layer, δ, is relatively small.

3.2.4 Oxygen

In open air, where the water is in equilibrium with the atmosphere, the concentration of oxygen is determined by the saturation concentration of air in water. A relationship has been derived from which the equilibrium concentration of dissolved oxygen can be calculated [24]

$$ln[O_2](mL/L)$$
$$= A_1 + A_2(100/T) + A_3 \ln(T/100) + A_4(T/100)$$
$$+ S[B_1 + B_2(T/100) + B_3(T/100)^2]$$

where

$[O_2]$	oxygen consentration [mL/L]
A_1	= -173,4292
A_2	= 249,6339
A_3	= 143,3483
A_4	= -21,8492
B_1	= -0,033096
B_2	= 0,014259
B_3	= -0,0017000
S	salinity [‰]
T	absolute temperature [K]

The equation shows that the oxygen concentration is strongly dependent on the temperature. However, it is not a very "elegant" equation, and is somewhat complex.

The main driver for dissolution of oxygen is the air-water exchange with oxygen in the atmosphere, which leads to a saturation within 5%. However, there can be deviations due to biological processes. The dissolved oxygen can be consumed by biochemical oxidation of organic matter which in turn can lead to the water being under-saturated and production of CO_2 and acidification of the water. This process strongly depends on the availability of nutrients and dissolved oxygen and can cause a low oxygen concentration below the zone of surface mixing. [24]

Another phenomenon, is the supply of oxygen rich cold water by deep oceanographic currents, but these are strongly dependent on local conditions and season. An example of this is the extension of the mixed zones to the bottom due to the effect of storms in the winter, while in the summer the same water may become stratified like in some areas of the North Sea. [24]

3.2.5 pH

The effect of pH is interrelated with both temperature and dissolved oxygen. On local scale, the pH-level can become a lot lower or possibly higher than the surrounding electrolyte (sea water in this case) as for in pitting and crevice corrosion, but for the average pH around an ROV, it is believed to be constant. The relation between pH, temperature and dissolved oxygen can be seen in Figure 16. The relationship is valid at 1 atmosphere pressure and 25ºC. The corrosion rate is believed to double for each 10 ºC. However, due to the reduced oxygen content at elevated temperatures, the corrosion rate is to some extend limited.
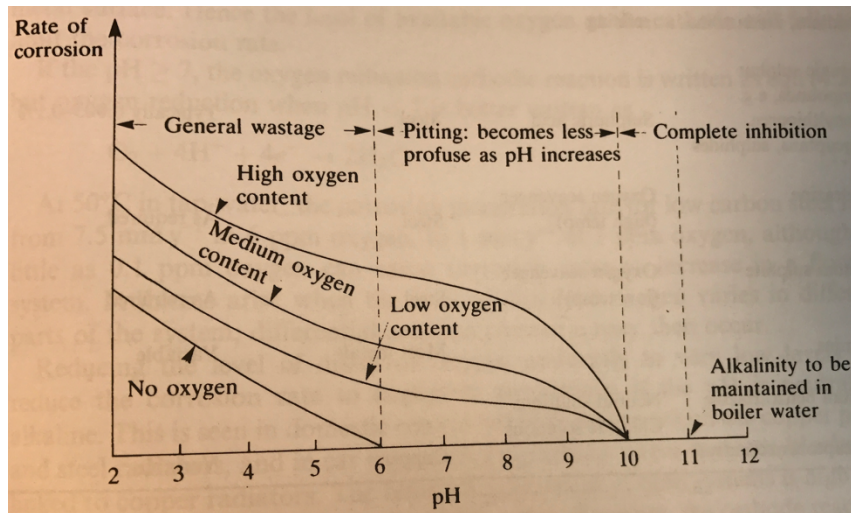
Figure 16 - Relationship between corrosion rate, pH and dissolved oxygen content

From Figure 16, it is clear that the corrosion rate follows a more or less linear negative relationship to the pH (it should be noted that the pH scale is logarithmic) below pH of 6, and that the corrosion rate is zero over pH of 10, when pH is the only varying factor.

3.2.6 Protective layer

The corrosion rate for most metals depend on its ability to form oxide layer and its ability to withstand erosion or solubility. This is a natural process that occurs instantly to exposure of oxygen. Paint and galvanizations on the other hand, are treatments made to imitate that process while also sometimes give additional properties.

The principle of corrosion protection by coatings is to cause one or more of the following main mechanisms [25]

i)   Barrier effect, where any contact between the corrosive medium and the metallic material is prevented.

ii)   Cathodic effect, where the coating material acts as a sacrificial anode.

iii)   Inhibition/passivation, including cases of anodic protection.

3.2.7 Relative surface area

The rate of corrosion when galvanic connected to other metals with different potential is strongly dependent on the relative ratio of exposed surface area. Like for a sacrificial anode that has a very small area compared to the cathode it is to protect, a metal with a more negative potential than its coupled metal, will corrode more rapidly if its surface area is smaller relative to the other metal.

If we study the formula for current demand (cathode), I_c, we have that it is given by [6]

27

$$I_c = A_c * i_c * f_c$$

I_c	is the cathode current demand
A_c	is the surface area of the cathode that is exposed to the electrolyte
i_c	is the design current density
f_c	is the coating breakdown factor

Here we can see that (except for the coating breakdown factor), the current demand is a product of the exposed surface area and the current density for the given metal. For the anode, the equation is the same, except for that the anode should not be coated (this would increase this effect). The current demand for the anode would therefore be given by

$$I_{a\,tot} = A * i_a$$

where

$I_{a\,tot}$	is the anode current output
A	is the anode area
i_a	is the current density

Since I_c and $I_{a\,tot}$ must be the same, we can set the two expressions against each other and find that

$$A_c * i_c * f_c = A * i_a$$

$$i_a = \frac{A_c * i_c * f_c}{A}$$

If we introduce a factor for the ratio $A_{c/a\ ratio} = A_c/A$ that is the relative ratio between the cathode surface area and the anode surface area we have

$$i_a = A_{c/a\,ratio} * i_c * f_c$$

And a larger $A_{c/a\ ratio}$ will give a larger current density, i_a, on the anode. This is directly linked to the corrosion of the anode and should be avoided if the anode is not to be scarified. The current is the same, so when the anode area goes down, the anode current density goes up.

3.3 Metal combinations

3.3.1 Combinations with joint grounding

ROVs and subsea equipment are made up of materials that on its own makes well engineered components, but they might not work as well when they are galvanic connected in a system. This development is perhaps a result of trying to enhance the performance of each individual part without thinking of where it will be used.

Ideally, all components in a subsea system should be made up of the same material, or made with a galvanic isolator between the different types of metals/alloys that has the possibility to react with each other. However, this is rarely possible, or it might be extremely expensive to do.

An experiment was carried out by E. B. Shone and P. Gallagher for Shell Research Ltd. To study the galvanic compatibility of selected high alloy stainless steels in seawater. In the experiment they tested 7 different metal/alloys in combination with each other. The test confirmed that both the maximum galvanic current and the corrosion was larger for alloys with greater potential difference. [27]

3.3.2 Combinations without joint grounding

If we use a galvanic isolator to isolate all the different metals (that has different potential), we would have a system where there is no joint grounding. In this system, we could use anodes for metals that is susceptible to corrosion, while drop it for metals that are passive in the given environment. It would be easier to find a suitable cathodic protection system that were designed for each given metal and function, rather than one for the whole ROV.

This is however not easy or practical to do. An ROV is usually so complex, that to isolate every metal with an isolator would be very expensive, complicated and quite possibly induce more complex corrosion challenges than the one we have with multi-metal combinations.

3.3.2.1 Use anode on all parts

The principle behind the sacrificial anode is possible to use on all part in a system, but is very expensive since there is a lot of parts, and most of them are small. These would require small anodes that is purpose made for the individual part, and would require a lot of work to calculate both its potential, size and weight.

Unlike for a joint grounding system, one can use anodes of variating size in this type of configuration since each anode only gives away electrons to its galvanic connected part. This way, small anodes (given correct dimensions) would be "eaten" at the same rate as bigger anodes on other part of the system.

3.3.2.2 Use on critical parts (material dependent)

A more realistic and cheaper solution to cathodic protection would be to only apply it on parts that was especially susceptible to corrosion. This would often require a whole lot less anodes since many metals are sufficient resistant to most critical corrosions, or are thick enough to accept some degree of corrosion.

Other metals like titanium, and most aluminium parts, does not require CP protection on its own if not due to special circumstances or requirements. Examples of this would be the risk of crevice corrosion inside gaskets etc.

3.4   Protection

3.4.1   Surface treatment

Surface treatment is one of the most widely used measures to reduce the rate of corrosion of a structure. The idea behind a surface treatment is to either function as a barrier, by prevent contact between the corrosive medium and the metallic medium, cathodic protection, where the coating function as a sacrificial anode for the metal, or passivation, where the coating or inhibitors causes passivation. Some coating combine these mechanisms. [25]

Metallic coating

Metallic coatings are a type of corrosion protection where one in most cases use a coating based on a metal with a different potential than the protected metal. The metallic coatings are divided into two groups, namely cathodic coating and anodic coatings.

Cathodic coating

We call it cathodic coating when the coating is more noble then the protected material (often called substrate). This type of protection will normally act as a barrier against the corrosive electrolyte, but for some substrate it is possible to act as a cathode that helps passivate the substrate one exposed.

The corrosion can, for a metal that is coated by cathodic coating, be intensive due to the possibility for galvanic corrosion close to the interface between the coating and the substrate at locations of holidays or defects. This is illustrated in Figure 17. Here we can see that the metal below a defect in the coating has corroded. However, there is also the possibility of the cathodic coating to help passivate the metal below. This is often the case for metals like aluminium, titanium, stainless steels and other metals that normally forms protective oxide layers.
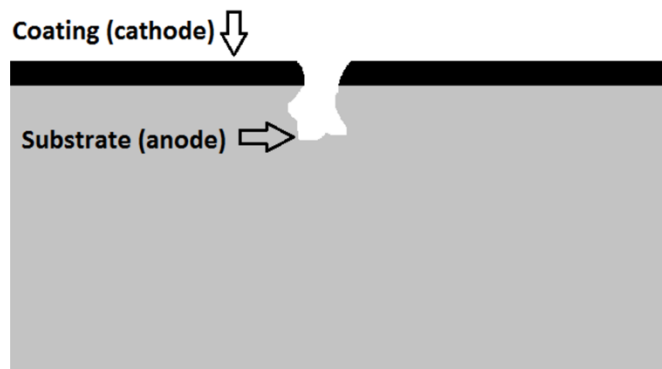
Figure 17 - Cathodic Coating

Anodic coating

Anodic coating are coatings that are less noble than its substrate and will usually both function as a barrier against the electrolyte, and as a cathodic protection for holidays. The coating in this case will work as a barrier for all the metal that is covered, but where there is a holiday or defect in the coating the coating will function as a sacrificial anode. This process is a galvanic corrosion process, but unlike for the cathodic coating, here the coating will be corroded instead of the protected metal.

As illustrated in Figure 18, we can see that the corrosion does not corrode further down into the metal, but rather keep corroding the coating. A special benefit of this type of metal coating

is that due to the protective potential of this form of cathodic protection, the metal will remain (to some degree) protected as long as parts of the coating is intact. In other words, the coating does not have to be perfect for it to work.
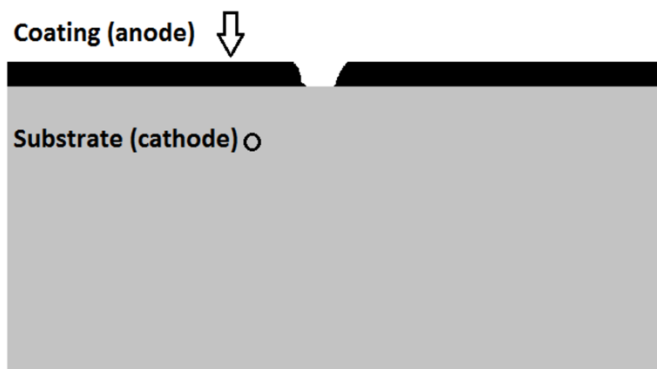
Figure 18 – Anodic Coating

Inorganic coating
Inorganic coatings that is not metals and are often enamels or glass linings. It is often applied in the form of a powder, and then heat treated to form a seal around the protected metal. For this type of coating, one can make the coating highly resistant to various types of chemicals and corrosive environments. However, this type of coating is often highly sensitive to deformation due to its brittle characteristics, and does often not withstand local heat exposure well.

Paint coating
Among the surface treatments to prevent or reduce corrosion, the most widely used is paint coating. [25] The point of paint coating is to work as a barrier that keeps the electrolyte and air away from the protected metal. Paints used for corrosion preventions is often impermeable to ion such as chloride, sulphate and carbonate, but no paint is complete barrier to oxygen or water. Oxygen and water will in time always find a way to penetrate, and the paint cannot hinder the cathodic protection. To compensate, one can maintain the protected structure by apply new paint like the worker does in Figure 19.

Figure 19 - Paint coating [28]

A paint or coating system consists of a vehicle that gives the paint its fluidity and evaporates to form a solid film, a pigment that controls the corrosion reaction or the rate of diffusion of the reactants through the film, and additive/fillers that accelerate the drying process or better enable the dry coating to withstand the working environment. [5]

The pigments serve several roles. The most obvious is that it colours the paint, but more importantly in a primer, it controls the corrosion process at the metal surface, either by inhibiting the reactions or providing sacrificial protection to the substrate metal. And in the finish coat (the outer layer), inert pigments increase the length of the diffusion path for oxygen and moisture penetrating the film.

In important aspect of paint coatings is the possibility of paint failure. Given that the type of paint is selected to match the environmental conditions, the most common cause of failure is either poor or inadequate surface preparation or that the paint is applied under unsuitable atmospheric conditions or by inappropriate methods. [5]

3.4.1.1 Organic coating (other than paint)

Other organic coating can be rubber coating, asphalt or coal tar. These serves as barriers and together with a textile or mineral net, or lately polyvinyl chloride or polyethylene with adhesive on one side, serves as a relatively long lasting protection against corrosion.

3.4.1.2 Anodization

Anodization is the process of creating a protective oxide layer that will reduce the current density so much that the corrosion rate is almost halted and this type corrosion mitigation can be divided into three categories. The first on is anodic protection with impressed current, and is strictly speaking not a surface treatment, but rather a "reverses" cathodic protection.

The second one is the formation of local cathodes on the metal surface. This process is primarily used on materials with a high hydrogen overvoltage to avoid acid corrosion. In this process, the goal is to achieve passivation.

The third category includes passivating inhibitors that acts by either or both reduce the passivating current density by encouraging passive film formation or/and raise the cathodic partial current density by their reduction.

3.4.2 Cathodic protection (CP)

Cathodic protection is a very effective type of protection against corrosion and can be used to protect from all types of corrosion. In the process of cathodic protection one exploits a sacrificial anodes lower galvanic potential in a way that makes the anode corrode, while at the same time supplying the protected cathodic metal with electrons.

In order to understand the principle behind both cathodic and anodic protection it is beneficial to understand the E/pH-diagram for the metal that needs protection. An example of a E/pH-diagram is shown in Figure 20. [5]
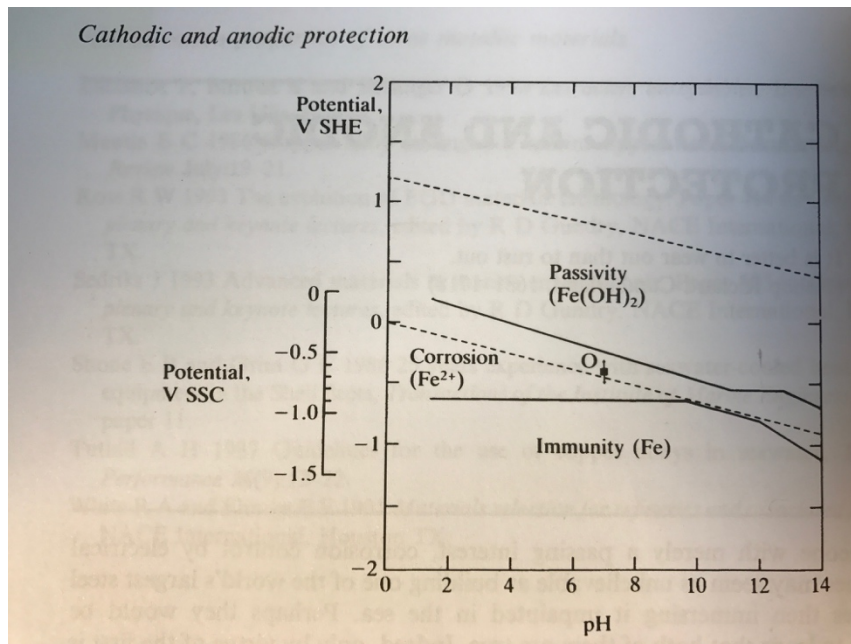
Figure 20 - E/pH diagram for iron in water

From the figure we can see that there is four ways of changing the corrosion potential. One can decrease the pH in the electrolyte, but this will not decrease the rate of corrosion (in fact it will increase it, but this is not shown in Figure 20).

One can to some extent increase the pH to over 11, and if the SHE-potential is greater than -0,600V, the iron passivated. This is as a solution subsea not possible, since we cannot alter the pH of the whole ocean.

A more negative potential can be added, and hence move the iron over to a more passive state. For iron submerged into seawater, a potential of less than -0,800V should be sufficient for pH between 1 and 9. This does not mean that corrosion is not possible, it can still happen on a smaller scale, but the overall iron will be cathodic.
A more positive potential can be used to bring the iron into the passivity region. In this region, there will be formed oxide that could (but certainly not necessarily) keep the iron (that is now an anode) from further oxidation. This concept works better for aluminium and titanium

When designing a CP system, the engineer starts by stating the maximum acceptable corrosion rate (by weight), r_p, and use a graph, such as in Figure 21 (for steel) or a standard to obtain a value of current density, i_p, that leads to the desired corrosion rate. From the graph one moves horizontally to the left from the desired r_p until one hits i_p.

Fig. 16.2 Schematic diagram showing the variation of cathodic potential with current density for steel in sea-water, and the correlation with corrosion rate measured by weight-loss data.
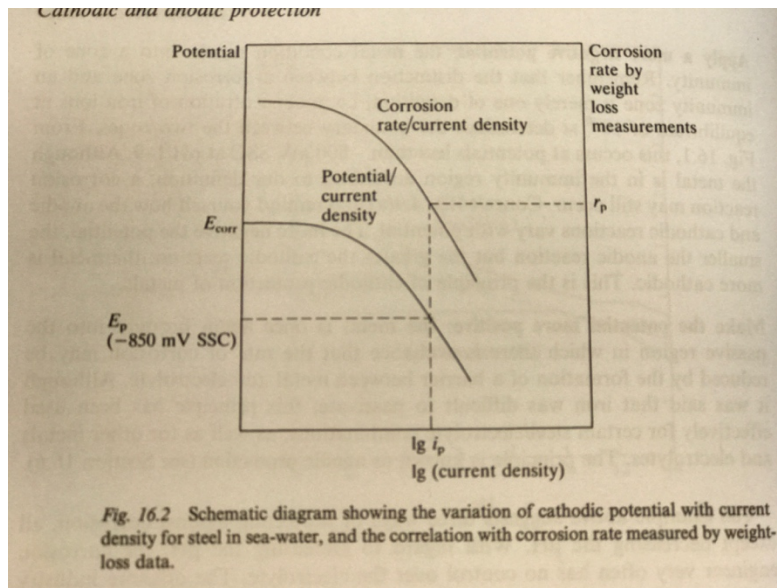
Figure 21 - Schematic diagram showing the variation of cathodic potential with current density for steel in sea-water, and the correlation with corrosion rare measured by weight-loss data. [5]

Then we go down vertically until we hit the Potential/current density line and fine the protective potential E_p, but it is important to beware of that this is not always ideal. The actual protection is highly dependent on the applications. A common protection potential for steel is said to be more negative than -0,800V SSC and as a general rule between -0,800V and -0,900V SSC. The corrosion rate is given by [5]

$$i_p = i_{corr}\, e^{\left(\frac{\alpha \eta Z F}{RT}\right)}$$

where

i_p	is the current density/corrosion for the given polarisation cathodic to E_{corr}
i_{corr}	is the current density/corrosion (unprotected/free potential)
α	ratio factor to state the anodic part of the polarization
η	total polarisation
Z	Number of electrons transferred in the corrosion reaction
F	Charge transported by one mole of electrons; value of 96494 C/mol
R	Universal gas constant; 8,314 J/(mol*K)
T	Temperature measured in Kelvin [K]

It is possible to use potential more negative than -0,900V SSC, but this can be a problem due to the evolution of hydrogen that may cause hydrogen embrittlement, and the fact that large currents can cause high local concentrations of hydroxyl ion. Hydroxyl ions can cause excessive chalking or damage barrier coatings such as paint.

It is important in designing the CP system to acknowledge that the current density will vary during the lifetime of the protected structure. For this reason, the system has to be designed in a way that ensures the current density over the lifetime of the anodes (between maintenance).

3.4.2.1 Impressed current cathodic protection

Impressed current cathodic protection (ICCP) works by the same underlying principles as those of sacrificial anode method, but there are some important differences:

The first main difference is that while for sacrificial anode protection one can connect the cathode structure directly to the anode in order to create sufficient protective potential, for the impressed current protection one must isolate the direct contact between the anode and the cathode. This is mainly because we need to control the impressed current that flows between the anode and the cathode.

In ICCP one can use non-consumable electrodes that instead reacts with water and oxidates it. The process is known as water splitting, and is described by the anode equation

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
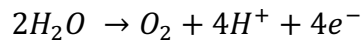
while in sea-water it is found that oxidation of chloride ions to chlorine gas is the favoured anode reaction, and is described by the anode equation

$$2Cl^- \rightarrow Cl_2 + 2e^-$$
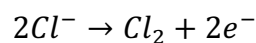
The last big, and perhaps the most important difference, is the use of control electronics. Electronics enable control over the systems corrosion rate. This is a big advantage over the sacrificial anode protection system, where one have to rely on the potential to stay within a given interval without the possibility to control it, is that with ICCP we directly control the potential and the current.

As for sacrificial anode protection ICCP is also susceptible to damage if a large current density is in vicinity of an anode could cause damage to many types of coating. For this reason, one should use several anodes and space them apart from each other.

3.4.2.2   *Sacrificial anode protection*

Sacrificial anode protection is a type if CP in which we find a metal with a lower/more active potential that we couple together to the metal that needs protection in order to make this the cathode. By this approach we assure that the oxidation happens at the sacrificial anode.

Even though this approach stops oxidation (as long as it has sufficient protective potential) on the cathode, it might cause other problems. If the protection potential is too great the current density can become too high, a result of this could be damage to paint coating or hydrogen embrittlement.

In theory one could use any of the materials in the galvanic series that has more active potential, but in practice one find that some of them are highly reactive to water. If we for example were to use sodium to protect a steel structure, it could result in a violent explosion.

There are two general approaches when designing a cathodic protection system. In the first, one defines a protection potential, E_p, and design a system to achieve this potential all over the structure. In this method, one have to take the CP calculation into the very first stage of the planning phase, everything is in a way built around the CP design.

In the second approach, assumptions are made about the current density required to protect the structure and the area of steel which will be exposed to the sea. The exposed area is highly

effected by coating (given that it is applied), the quality of the coating both in terms of its defects and coating breakdown. Together with this, and the material(s) that is to be protected, one can choose the anode material and calculate the needed anode mass.

When determining the sacrificial anode material, an important factor is the capacity, that is, the number of ampere-hours that can be supplied per kilogram. The current per unit of exposed area, due to the importance of exposed area in the calculation. The wastage rate, which is a measure of the rate of eater volume or mass loss, and the last important parameter is the throwing power. Throwing power is a description of how the corrosion protection level is affected by the distance from the anode to the cathode in which it is to protect.

The required anode mass required to maintain cathodic protection throughout the design life is calculated by DNV to be [6]

$$M_a = \frac{I_{cm} * t_f * 8760}{u * \varepsilon}$$

where (where to find in DNV-RP-B401)

M_a	Required anode mass [m]	(7.1.1)
I_{cm}	Mean current demand [A]	(7.4.2)
t_f	design life [years]	(6.4.4)
u	Anode utilisation factor [ ]	(6.8)
ε	Design electrochemical capacity [A/kg]	(6.5)

Table 1 - Recommended Anode Utilisation Factors for CP Design Calculations

Table 10-8 Recommended Anode Utilisation Factors for CP Design Calculations	
Anode Type	Anode utilisation Factor
Long slender stand-off L ≥ 4r	0,90
Long slender stand-off L < 4r	0,85
Long flush mounted L ≥ 4 width and L ≥ 4 thickness	0,85
Short flush-mounted, bracelet and other types	0,80

Table 1 have been taken from DNV RP-B401 [6]

The mean current demand, I_{cm}, can be calculated by (DNV-RP-B401 (7.4.2))

$$I_{cm} = A * i_{cm} * f_{cm}$$

where

A	Anode surface area [m^2]	(Table 10-8)
i_{cm}	Design mean current density [A/m^2]	(6.3.5)
f_{cm}	Mean coating breakdown factor	(6.4.4)

Due to the fact that there are usually several sacrificial anodes in a CP system, it is convenient to calculate the individual current output, I_a. The total and individual anode current output. [6] (7.8.2)

$$I_c = N * I_a = \frac{N(E_c{}^\circ - E_a{}^\circ)}{R_a} = \frac{N * \Delta E^\circ}{R_a}$$

where

I_c	Current demand [A]	(7.4.2)
N	Number of anodes	(7.8.1)
I_a	Individual anode current output [A]	(7.8.2)
$E_c{}^\circ$	Design protective potential [V]	(7.8.2)
$E_a{}^\circ$	Design closed circuit anode potential [V]	(6.5.1)
R_a	Individual anode resistance [ohm]	(6.6.1)

Hence, the individual anode current output is given by

$$I_a = \frac{(E_c{}^\circ - E_a{}^\circ)}{R_a}$$

By the use of the anode output (individual or total) we can together with the chosen anode mass, M_a(net total) or m_a(individual), the anode utilisation factor, u, the waste rate by weight, w_w, calculate the anode life time. [5] (16.4)

$$L = \frac{M_a * u}{I_a * w_W}$$

where

L	Anode life [years]	(16.4) - Chamberlain
M_a	Required anode mass [m]	(7.1.1) - DNV
u	Anode utilisation factor [ ]	(6.8) - DNV
I_a	Individual anode current output [A]	(7.8.2)
w_W	Waste rate by weight [kg/(A*years)]	dependent on the specific anode

Anodic protection

Anodic protection is a type of corrosion protection where one exploit a metals ability to passivate. If the potential is made (by the use of an impressed current, but opposite of that of ICCP) more positive than E_{corr}, and if passivity is possible for the given metal, a point is reached at which current density falls to an extremely low value, i_{pass}, and the corrosion rate is comparably low. A problem for anodic protection is that if the potential wanders even slightly outside the intended range, the corrosion can be worse than if it were cathodic protected, close monitoring is for this type of corrosion control important.

3.5   Current Demand at resting position
3.5.1   Protective potential

When applying cathodic protection to a system, it is crucial to know the current demand in order to calculate the anode mass requirement. If the anode were to be totally corroded, the system would be left without cathodic protection, and hence the designed protection will be

worthless. There exist a lot of literature on how to calculate the anode requirement, and there are a variety of parameters that one should take into account in the calculations.

One example of a parameter is the protective potential. The potential can and will vary over both the life time of the anode and the protected cathode. This variation does not have to be linear in time, and it can be effected by the formation of oxide. [29]

However, in practice one can somewhat simplify certain assumptions, and like DNV, use max, mean and minimum for parameters like protective potential, anode current output, coating breakdown factor etc. For the protective potential DNV states that:

"5.4.2 For a correctly designed galvanic anode CP system, the protection potential will for the main part of the design life be in the range - 0.90 to - 1.05 (V). Towards the end of the service life, the potential increases rapidly towards - 0.80 (V), and eventually to even less negative values, referred to as 'under-protection'. The term 'over-protection' is only applicable to protection potentials more negative than - 1.15 (V). Such potentials will not apply for CP by galvanic anodes based on Al or Zn." [6]

For the UTC Merlin RROV one has decided to use aluminium based anodes, and according to DNV a closed circuit potential, $E_a{}^\circ$, of -1,05V (Table 10-6). The potential of the protected object (the cathode) is the design protective potential for the given material. For C-steel and low-alloy steel the potential is said to be -0,80 V. [6]

3.5.2 Design current densities

Current density, i_c, refers to the cathodic protection current unit per surface area, and are hence given in A/m^2 where A is ampere, and m is meter. Due to the fact that the current density is expected to vary over time, one usually defines i_{ci} to be the initial design current density, i_{cf} to be the final current density, and i_{cm} to be the mean. These values are given in DNV-RP-B401. [6]

For the depth (>300m), location ("Arctic") and temperature (<7 degree Celsius) of where the RROV shall operate, the value for the current densities are given as [6] (Table 10-1 and Table 10-2)

$$i_{ci} = 0,220 \; A/m^2$$

$$i_{cm} = 0,110 \; A/m^2$$

$$i_{cf} = 0,170 \; A/m^2$$

These also apply for any stainless steel or non-ferrous components of a CP-system which includes components in carbon steel or low-alloy steel. For calculations of anode current output, a protective potential of -0,80 V shall then also apply for these materials. [6]

For components that are heated to a temperature above 25 degrees Celsius, one should

increase the design current density by 0,001 A/m² for each degree above 25 degrees Celsius. On the UCV Merlin RROV, there components will not exceed this temperature over time, and most likely not at all. [6] (6.3.9)

For component made of aluminium, or coated with either aluminium or zinc, the design current densities are all (initial, final and mean) 0,010 A/m². [6] (6.3.11).

3.5.3   Coating Breakdown Factor for CP Design

The coating breakdown factor, f_c, is a factor used to describe the anticipated reduction in the cathodic current density due to the insulating effect of an applied electrically insulating coating. In accordance with DNV, a $f_c = 0$ indicates that the cathode is 100% electrically insulated from the surrounding electrolyte (seawater), and a $f_c = 1$ indicates no coating at all. [6] It should be noted that an apparently perfect coated surface may allow for a significant passage of current, and vice versa.

The coating breakdown factor is a function of coating properties, both operational parameters and time. According to DNV, one can for engineering purposes, use the formula [6]

$$f_c = a + b * t$$

where

f_c is the coating breakdown factor

a and b constant in coating breakdown factor

The constants a and b should preferably be specified by the owner, but when not specified, values given in DNV-RP-B401 Table 10-4 should be applied. The effect of marine growth is highest in the upper 30 meters where the wave force may further contribute to coating degradation. The UCV Merlin RROV will operate on a depth of over 30m, hence a and b is [6]

$$a = 0,10$$

$$b = 0,05$$

The values are only applicable for "Category I" described by DNV-RP-B401 (6.4.6) as "One layer of epoxy paint coating, min. 20 μm nominal DFT" (dry film thickness) [6]. The mean and final coating breakdown factors are hence given by

$$f_{cm} = a + b * \frac{t_f}{2} = 0,10 + 0,025 * t_f$$

and

$$f_{cf} = a + b * t_f = 0{,}10 + 0{,}05 * t_f$$

3.5.4 Galvanic Anode Material Design Parameters

The CP design parameters related to anode material performance are design electrochemical capacity, ε (Ah/kg), and design closed circuit anode potential, $E°_a$(V). These values shall, if not specified by owner, be found in Table 10-6 if calculated according to DNV-RP-B401. [6]

$$\varepsilon = 2000 \ Ah/kg$$

$$E°_a = -1{,}05 \ V$$

Both values are for aluminium based anodes in seawater.

3.5.5 Anode Resistance

The individual anode resistance is the shape and size dependent resistance in the anode. It shall, unless otherwise specified, be calculated using the shape applicable formula in Table 10-7 in DNV-RP-B401. The anodes used for the UCV Merlin RROV is of the type "Short flush-mounted, bracelet and other types" and the individual anode resistance is given by [6]

$$R_a = \frac{0{,}315 * \rho}{\sqrt{A}}$$

where

ρ is the seawater resistivity in ohm*m

A   is the anode surface area.

The seawater resistivity is a function of seawater salinity and temperature. In open water the salinity does not vary significantly, and temperature is the main factor. According to DNV-RP-B401 (6.7.4) the value to use in temperated regions (annual average surface temperature of 7-12 degree Celsius)

The anodes intended to use on the Merlin UCV is a product from Skarpenord Corrosion A. S named CORAL A-12-1. Dimensions is given in Appendix A. This gives an area of 0,034760 m^2 and given the assumed seawater resistivity, $\rho_{seawater}$, of 0,3 ohm*m the anode resistance is

$$R_a = \frac{0{,}315 * \rho}{\sqrt{A}} = \frac{0{,}315 * 0{,}3}{\sqrt{0{,}034760}} = 0{,}50686 \ ohm * m$$

3.5.6 Anode utilization factor

The fraction of the anode material that may be utilised for the calculation of the net mass required to sustain protection throughout the design life of a CP system is given by the anode utilization factor, u. The value should be, unless otherwise agreed, be according to DVN-RP-B401 Table 10-8.

$$u = 0,80$$

for short flush-mounted, bracelet and other types. [6]

3.5.7 Surface area calculations

When calculating the net anode mass required for the cathode protection to be sufficient, on need to know the current demand. The current demand, I_c, is dependent on the coating breakdown factor, the design current density and the surface area that is exposed to the electrolyte (in this case seawater).

It is convenient to divide the protected object into sub-units. The division could be based on depth zones, physical interface of the protected object, or it could be that parts of the system is galvanic isolated from other part of the system.

According to DNV-RP-B401 (7.3.1)-(7.3.2), one can use some simplifications in the calculation of the surface area, but is has to be within an accuracy of -5/+10%, or for smaller components it might be lowered depending on whether or not a coating will be applied. [6]

The surface area in this thesis are calculated by individually checking the surface area of the parts in Inventor. The area calculated is the area that is exposed to the seawater once submerged, and the accuracy should be well within the requirement stated above.

Table 2 - Surface area Merlin UCV

	Titanium	Stainless Steel	Aluminium	Steel
Uncoated main	3,3827	6,5101	33,2183	0,6587
Coated main	4,9610	0,3084	3,1124	0,8346
Uncoated iso	0,1195	2,2431	0,7107	0,0145
Coated iso	0	0,0754	0	1,4154

In Table 2, "uncoated main" refers to uncoated surfaces that is connected to the CP system, "coated main" refers to coated surfaces of the CP system, "uncoated iso" and "coated iso" refers to parts of the electric system (no CP on these).

The material categories consist of:
Aluminium: Aluminium, Aluminium-5052, Aluminium-6061 and Aluminium-6082-T6
Steel: S165, S355J2G3, Steel (high strength) and Steel (mild)
Stainless Steel: Stainless Steel 316L, Duplex, Super Duplex, Stainless Steel 440C and Stainless Steel
Titanium: Titanium and Titanium Gr.2

3.5.8 Current demand

The current demand, I_c, is given in ampere and is directly related to the speed of which the sacrificial anode is being used. The current demand will vary over the lifetime of the anode, and is given by

$$I_c = A_c * i_c * f_c$$

I_c is the cathode current demand
A_c is the surface area of the cathode that is exposed to the electrolyte
i_c is the design current density
f_c is the coating breakdown factor

It is important to also include all items that are exposed to the electrolyte and that are electrically connected to the system that is connected to a CP system. This is because although they might not require CP on their own, they will drain current from the CP system. [6]

Initial current demand, I_{ci}, is given by

$$I_{ci} = A_c * i_{ci} * f_c$$

Mean current demand, I_{cm}, is given by

$$I_{cm} = A_c * i_{cm} * f_c$$

Final current demand, I_{cf}, is given by

$$I_{cf} = A_c * i_{cf} * f_c$$

When calculating using I_{ci}, I_{cm} and I_{cf} from Table 10-1 in Annex A in DNV-RP-B401 based on the surface area given in Table 2 we get the current demand in Table 3

Table 3 - Current density/demand Merlin UCV

	Titanium	Stainless Steel	Steel	Aluminium	Total
Current density initial	0,220	0,220	0,220	0,010	
Current density mean	0,110	0,110	0,110	0,010	
Current density final	0,170	0,170	0,170	0,010	
Current demand initial uncoated	0,7442	1,4322	0,1449	0,3322	2,6535
Current demand mean uncoated	0,3721	0,7161	0,0725	0,3322	1,4928
Current demand final uncoated	0,5751	1,1067	0,1120	0,3322	2,1259
Current demand initial coated	0,1364	0,0085	0,0230	0,0039	0,1718
Current demand mean coated	0,0682	0,0042	0,0115	0,0039	0,0878
Current demand final coated	0,1054	0,0066	0,0177	0,0039	0,1336

3.5.9 Anode mass calculations

The total net anode mass, M_a, is the required mass of the anodes (total) to maintain the required cathodic protection throughout the design life, t_f (years). It is given by (7.7.1) [6]

$$M_a = \frac{I_{cm} * t_f * 8760}{u * \varepsilon}$$

where

M_a	is the total net anode mass
I_{cm}	is the mean current demand
t_f	is the design life in years
8760	is the number of hours in a year
u	is the anode utilisation factor
ε	is the anode electrochemical capacity

Due to deterioration of the coating applied to several parts on the RROV, there will be an increase in the current demand on those parts, and hence, there will be an increased anode consumption. This increase will be notable, but the uncoated parts makes up over 80% of the effective exposed area so the increase will not be huge. From the calculations presented graphically in the diagram below (Figure 22 - Anode consumption per year for the cathodic protected system), we see that the total anode consumption over the first year is about 8,6kg.
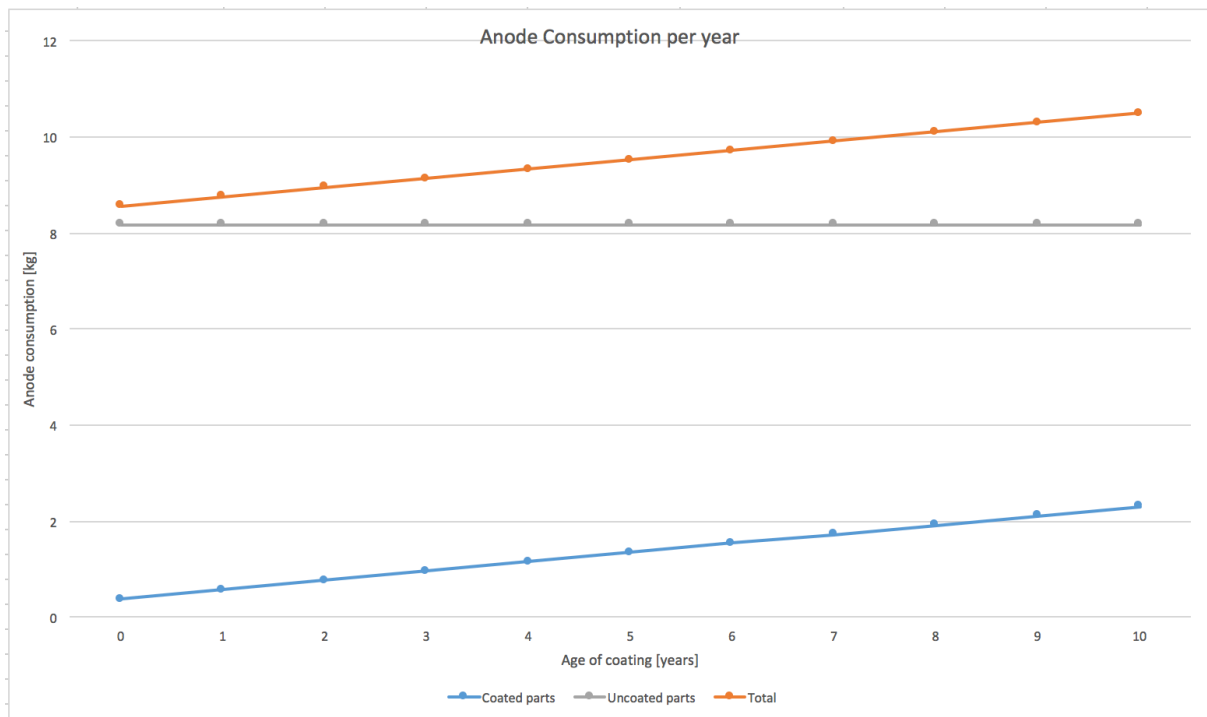
Figure 22 - Anode consumption per year for the cathodic protected system

As seen from the graph, the increase in anode consumption is about 0,19kg per year. This means that after 10 years, the coating used on parts of the RROV has deteriorated so much that the anode consumption from these parts has increase by 23%. This is however not based on measurements for this particular RROV, but calculated by the DNV-RP-B401 standard. The increase could be higher or lower, but due to the inherent conservatism of the DNV standard, it should not be significantly higher.

It should be noted that the graph (Figure 22) assumes a constant current density and are the estimated linear increase in anode consumption for each year. It does not take in to account that the initial consumption will be higher than the mean, or the increase at the end of the anode life.

The Merlin UCV are, in the beginning at least, supposed to operate for 3 months which would give a consumption of ¼ of that for one year. However, it will in the beginning consume a lot more than the initial value. In Table 4 one can see the calculated anode consumption for 3 months use under water. It should be noted that the coating breakdown factor is set to 0,125.

Table 4 - Anode consumption 3 months

Anode consumption [kg]	Titanium	Stainless Steel	Steel	Aluminium	Total
Initial	1,2053	1,9720	0,2298	0,4600	3,8671
Mean	0,6027	0,9860	0,1149	0,4600	2,1635
Final	0,9314	1,5238	0,1775	0,4600	3,0927

The consumption is, due to the chosen coating breakdown factor, the expected consumption for 3 months periods the first year. And it will be slightly smaller in the beginning whilst increasing to slightly above at the end (still this variation can be treated as neglectable).

It is also worth noticing that DNV does not give a timeframe of when the different stages of the consumption take place. One does not add together the initial, mean and final consumption, but rather see them as consumption given that consumption rate was stable. This means that if the CP system does not polarize within the first 3 months, the consumption rate would be close to the initial value, while closer to the mean if it fully polarizes within a short time after deployment.

3.5.10 Number of anodes

To calculate the number of anodes, the individual anode current output, I_a, together with the anode current capacity, C_a, shall be known. The individual anode current output required to meet the current cathode demand, I_c, is given by [6]

$$I_c = N * I_a = \frac{N(E_c^\circ - E_a^\circ)}{R_a} = \frac{N * \Delta E^\circ}{R_a}$$

where
I_c	current demand [A]
N	number of anodes [ ]
I_a	(individual) anode current output [A]
E_c°	design protective potential [V]
E_a°	design closed circuit anode potential [V]
R_a	(individual) anode resistance [ohm]
ΔE°	design driving voltage [V]

According to DNV, "As the design driving voltage is defined using the protective potential for C-steel, the initial/final design current densities that define the anode current output capacity, and hence driving voltage, refer to the required anode current output at this potential. Hence, the initial/final design current densities given in Table 10-3 (DNV-RP-B401

ANNEX.) are based on a protection potential of – 0,80 V. " [6] For more negative potentials, the design protective potential shall still be 0,80 V.

The individual anode current capacity, C_a, is given by [6]

$$C_a = m_a * \varepsilon * u$$

where
C_a current capacity [A*h]
m_a (individual) anode mass [kg]
ε anode electrochemical capacity [Ah/kg]
u anode utilisation factor [ ]

According to DNV-RP-B401, calculations shall be carried out to demonstrate that the following requirements are met (numbering in brackets are as in standard) [6]

Requirement (5):
$$C_{a\ tot} = N * C_a \geq I_{cm} * t_f * 8760$$

Requirement (6):
$$I_{a\ tot\ i} = N * I_{ai} \geq I_{ci}$$

Requirement (7):
$$I_{a\ tot\ f} = N * I_{af} \geq I_{cf}$$

where
$C_{a\ tot}$ total anode current capacity [Ah]
N number of anodes
C_a current capacity [A*h]
I_{cm} mean current demand [A]
t_f design life [years]
8760   number of hours in a year
$I_{a\ tot\ i}$ total initial current output [A]
I_{ai} (individual) initial anode current output [A]
I_{ci} initial current demand [A]
$I_{a\ tot\ f}$ total final current output [A]
I_{af} (individual) final anode current output [A]
I_{cf} final current demand [A]

This means that the requirements can be written as

Requirement (5):

$$\frac{N * C_a}{I_{cm} * t_f * 8760} \geq 1$$

Requirement (6):

$$\frac{N * I_{ai}}{I_{ci}} \geq 1$$

Requirement (7):

$$\frac{N * I_{af}}{I_{cf}} \geq 1$$

When checking these requirements, it is beneficial to use a spread sheet to see the difference when changing the number of anodes (the weight have been chosen and will not change). The calculations for the requirements is listed in Table 5 below.

Table 5 - Requirements 5, 6, and 7 according to DNV RP-B401 (excluding underside of anodes)

Req.\Anodes	1	2	3	4	5	6	7
Req. 5	0.37	0.74	1.11	1.48	1.85	2.22	2.59
Req. 6	0.55	1.11	1.66	2.22	2.77	3.33	3.88
Req. 7	0.74	1.47	2.21	2.94	3.68	4.41	5.15

4. Analysis

4.1 Current density test using multimetal cathodic protection

The Merlin UCV ROV is made up of several materials that can be grouped in four main categories; aluminium, stainless steel, steel and titanium. Even though there is used a few different aluminium and stainless steel alloys, there is not that big difference between them in turns of current density. However, there should be larger difference between the different types of metal.

There are two main goals for this experiment. The first is to see if there is a difference in the anode consumption between cathodes that are electrically isolated from each other to those that are in contact. The second one is to see if the relative surface area between the cathodes will affect the accuracy of the predicted anode consumption by DVN.

4.1.1 Equipment

6,8 m planks (48mm x 98mm)
Screws
Plastic board cut into pieces for "shelves" and for junction board
75 m copper wire (1,5 mm^2, 7 threads)
56 copper shoes (nickel plated)
112 M4 washers
36 M4 machine screws
36 M4 machine nuts
Battery box
Cargo fasteners
5 floaters (5 l cans)
Duct tape
Titanium plates, Gr. 2   200x200 mm x2 and 200x72 mm
Aluminium plates, 6082-T6   200x200 mm x2 and 200x599 mm
Stainless steel plates, SS 316L   200x200 mm x2 and 200x117 mm
Steel plates, s355   200x200 mm x2 and 200x14 mm
Bricks for ballast
Multimeter (Biltema Art. 15-276) including temperature probe

4.1.2 Literature

DNV-RP-B401 Recommended Practice, Cathodic Protection Design

4.1.3 Info

Assume temperature less than 11°C for the whole experiment
Assume sufficient circulation of water, but not so much that it creates erosion-corrosion
Assume no current between the plates other than intended through wires
Assume anodes have the same anode resistance
11 of the 12 plates are placed with equal 50mm distance between each other horizontally
The largest aluminium plate is placed vertically ~ 50 mm from the others

4.1.4 Equipment info

Plates

8 of the plates are equal in size while the remaining 4 has the same width, but different lengths to represent the surface area of the Merlin UCV Resident ROV.

The titanium used is grade 2, the same as for the titanium used on Merlin. There is not information about the grade of titanium used on the manipulators, but for seawater it is the most common.

The steel chosen is S355K2C, and it is meant to represent the steels used on the ROV. Although there in the CAD drawing are listed "Steel"," Steel, high strength"," S355J2G3" and "Steel, mild" the S355 should be representative for them all since none of them are corrosive resistive (relatively speaking).

For the stainless steel, the plates chosen are SS 316L. Almost all the stainless steel of the ROV is of this alloy except for a very small amount of duplex/super duplex. For this reason, the SS 316L should represent the stainless steel without any significant problems.

There are 3 different aluminium alloys used on the ROV, 6082-T6, 5052 and 6061, but the majority is 6082-T6 and hence the choice of this alloy to represent aluminium.

Plate size

The size of the plates was chosen so that a multimeter would be able to measure the current in mA. The multimeter chosen has a resolution of $0,1\mu A$ and should hence be able to measure current over in the lower part of the mA region. This in addition to weight limitations due to the practicality of the experiment, is the reason for the plate size of 200 mm x 200 mm.

The thickness of the plates was decided by the operator of the water cutting machine. The requirements for the experiment was that they were thicker than 2 mm to secure the mechanical properties during mounting, and that they were less than 6 mm thick due du weight limitations. The decided thickness ended up on 5 mm.

For the plates that is to represent the relative size of the surface area of the ROV, one first have to calculate the surface area off all parts on the vessel. This was done using an assembly file in Autodesk Inventor. Since Inventor does not have a built-in function to calculate the exposed surface area of an assembly, this has to be calculated by hand.

On the ROV there are about 2400 different parts that are exposed to seawater and hence have to be calculated. Some of the parts there were several of, but the final number of different parts are 530 in my calculations. There is a possibility that some of the calculated areas are slightly larger or smaller than in reality, and the possibility that a few parts have been left out should also be noted. DNV allows for simplification in calculations, but recommends being within -5 to +10% accuracy. [6] It is not feasible to check the accuracy, but it should be well within these limitations. However, for every single part the exposed surface area has been checked against the surface area calculation for the whole part given by Inventor to check for error.

When grouping all the parts according to whether- or whether not they are part of the cathodic protection, type of metal, and if they have coating or not, the surface area are summarized in Table 6 - Surface area.

Table 6 - Surface area

Metal	Stainless Steel	Steel	Aluminium	Titanium
Uncoated area	6,5101	0,6587	33,2183	3,3827
Coated area	0,3084	0,8346	3,1124	4,9610

The coated parts are coated with different coatings, and are not sufficiently good to be classified to any other than "Category I" according to DNV-RP B401. [6] In the experiment, none of the plates are coated, but the area of those parts has been reduced by a coating breakdown factor to compensate for this. The coating breakdown factor, f_{cm}, was calculating according to DNV-RP-B401 to be 0,125. The effective surface area is given in Table 7.

Table 7 - Total effective surface area

Metal	Stainless Steel	Steel	Aluminium	Titanium
Uncoated area	6,5101	0,6587	33,2183	3,3827
Eff. Coated area	0,03855	0,1043	0,3891	0,6201
Total area	6,5485	0,7630	33,6073	4,0028

The length of the plates was then calculated to maintain the total surface area of the 200x200 mm plates, while represent the relative size of the surface area of the metal combinations of the ROV. The width is 200 mm for all the plates while the width is given Table 8.

Table 8 - Length of plates, width is 200 mm

Metal	Stainless Steel	Steel	Aluminium	Titanium
Length 1 [mm]	200	200	200	200
Length 2 [mm]	200	200	200	200
Length 3 [mm]	117	14	599	72

Multimeter

The multimeter is a model from Biltema. The model is marked Art. 15-276 and has an accuracy of [30]

± (2,0% of displayed value + 1 digit) on the µA- and mA-range
± (3,0% of displayed value + 3 digit) on the 10A-range
± (1,2% of displayed value + 1 digit) on the voltage and a resolution of 100 µV

The resolution is stated to be 0,1µA. However, when measuring mill
i-ampere, the number of digits in the display gives a resolution of 0,1 mA. This will give an accuracy of 2,0% of the "read value" plus 0,1 mA. It is calculated by

$$uncertanty = counts\ of\ readings + counts\ of\ range$$

$$uncertanty = (\%\ of\ readings * applied\ value) + (counts * resolution)$$

where
% of readings	given statistical percentage accuracy (stated by instrument producer)
applied value	is the "read value" for the current
counts	is the counts of range (stated by instrument producer)
resolution	the "preciseness" of the read values (stated by instrument producer)

The display has 3 ½ digits with 3200 steps.

The analogue scale has 34 segments and measures 12 times a second. The analogue scale will however not be used.

The multimeter will indicate when the battery level is too low for its intended voltage.

The working environment of the multimeter is from 0 to 50°C and within a relative moisture of < 70 %.

The temperature coefficient is given as 0,2*(specified accuracy)/°C below 18°C and above 28°C (only valid within working environment conditions stated above). This coefficient will vary slightly due to the initial temperature of the multimeter that will cool down depending of on the outside temperature. However, this correction factor is for this multimeter relative low, so for the data it is assumed a "worst case scenario" of 0°C which gives a multiplication factor of 0,2/28 per degree Celsius away from the working environment. The temperature was measured for each measurement day, and not a single value below 6°C was found. 0°C should then be a reasonable value since the multimeter cannot fall below the outside temperature.

All calculations of uncertainties shall be calculated by MATLAB and Microsoft Excel. All data from the experiment is entered into Excel, which is used by MATLAB to create matrixes for uncertainty calculations. The uncertainty will then be used in the result chapter in the form of uncertainty bars in the plots.

4.1.5   Relevance to the Merlin UCV

Despite the fact that this experiment is carried out at a location far away from the location where the Merlin UCV RROV are supposed to operate and that important factors like salinity, oxygen level and depth are not the same, literature indicate that temperature is the major corrosion rate controlling factor in natural seawater systems. [27] [25] [24] [7]

A factor that might be of greater importance, is the time factor. The experiment is only supposed to last a month, and due to the variation of the potential over time, the corrosion rate does not necessarily represent the initial, mean and final conditions of the Merlin UCV RROV.

In the absence of sufficient coating, the initial current density will be significantly greater than both the mean and the final value. This is primarily because it takes time to achieve the long-term polarization, and it is for seawater, the activation polarization that governs (concentration polarization is to some extent meaningless in the case of corrosion in the huge ocean, except for in still standing water and in closed compartments).

The current density could potentially be in the initial phase throughout the whole experiment, or it could move over to the mean or final phase at the end. This should be visible in the data

gathered from the measurements, but it should be noted that this is not possible to determine with a 100% certainty as long as the duration of the experiment is so limited.

According to DNV, the initial current density of titanium, steel and stainless steel is assumed to be 220 mA/m^2 below 7 °C at depths greater than 300 meters, and 250 mA/m^2 below 7 °C from 0-30 meters. [6] This means that DNV assumes the current density in the initial condition is about 13,64% higher at the shallower location where the experiment takes place.

For the mean condition, the current density is 110 mA/m^2 below 300 meters and 120 mA/m^2 above 30 meters. [6] This gives an increased assumed current density of 9,09%, which will indicate that, given that the conservative assumption is realistic, the long term different is smaller for than the initial.

The final current density is for all depths (except for between 30 and 100 meters) assumed to be 170 mA/m^2. [6] Together with the initial and mean current density, it seems that the different in depth is more important in the beginning of the CP-phase, and that the difference diminishes more and more over time. It should be noted that this is only valid for temperatures below 7°C. [6]

4.1.6 Setup

To test the current density of the materials when subjected to cathodic protection together with other metals, a test where aluminium, stainless steel, titanium and steel shall be connected to a joint anode (aluminium anode). In Figure 16, one can see how the plates are installed inside the buoy, while the anodes are mounted on the outside of the buoy.

Figure 23 - Cathodes and anodes mounted on the buoy

The test is divided into three system so that different variables can be isolated. The main goal is to see if there is a difference between the current density of metals when they are galvanic isolated from each other and when they are interconnected. From Figure 24, on can see how each cathode (plate) is connected by a separate wire to the junction board. Each plate is "isolated" from physical contact so that the easiest way for electrons to travel between them is through the wires.
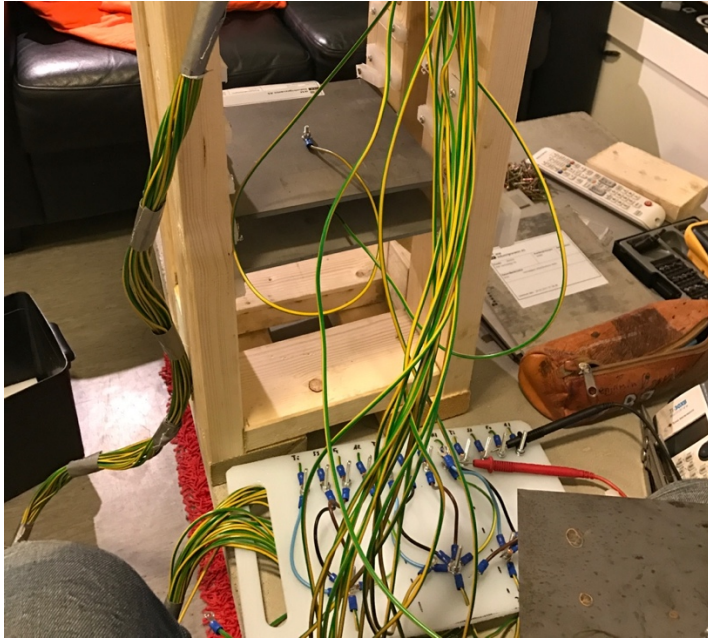

Figure 24 - Building the buoy

The potential shall be measured at deployment, and at a weekly interval till the 4th week. The last measurement at the 4th week does not necessarily represent the final current density, but will give an indicator of the development in the current.

During the test, there will not be connected ammeter/voltmeter and the wires will be shortcut at these points to ensure proper CP and current flow. This can be seen in Figure 25.
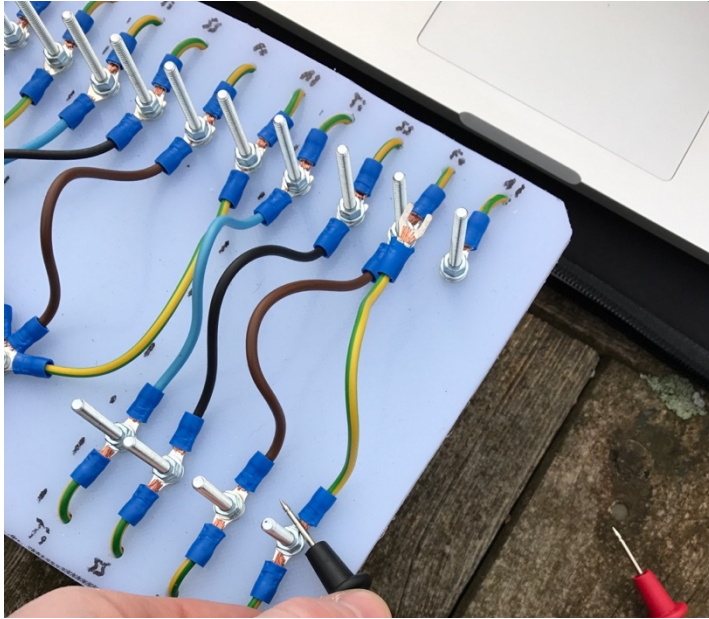
Figure 25 - Short cutting and current/voltage test

System 1

Here the four different materials are not in contact with each other, but rather connected to an anode each. The systems circuit is represented Figure 26. The resistors represented are the resistance in the wires.
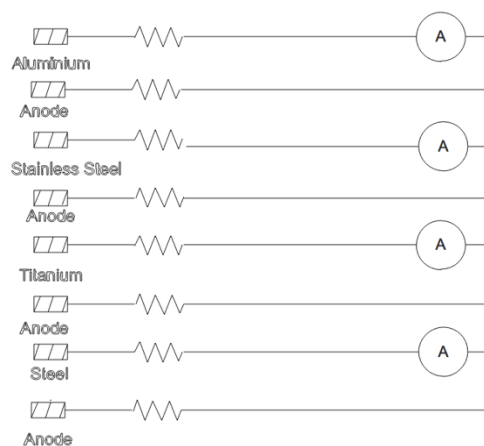

Figure 26 - System 1 current/voltage measurement

In this system, it is possible to measure the potential by removing the ammeter and place a voltmeter at the two points where the ammeter was connected. The voltmeter has a built-in resistor that is used to measure the voltage over.

The current demand has been calculated according to [6] and are given in Table 9. The values are said to be somewhat conservative, but should be close to the measured currents.

Since the plates must be submerged through all phases of the experiment, and due to the need for measure the current passing between the cathodes and the anodes, wires have been

connected from each individual cathode to a junction box, and back to the anode. For this reason, the resistance in the wires must be calculated/measured. The resistivity is given by

$$\rho = \frac{RA}{l}$$

where

ρ	resistivity [Ω*m]
R	resistance [Ω]
A	area [m²]
l	length [m]

Hence, the resistance is given by

$$R = \frac{\rho l}{A}$$

The resistivity of copper is 1,80*10^-8 Ω*m at 20°C [31], which gives a resistance, R, of 0,0112Ω per meter given a cross-sectional area of 1,5mm². This again will give a voltage drop that must be taken into account when calculating the real potential between the anode and the cathodes. The voltage drop is directly related to the current and the resistance of the wire. Hence [3]

$$U_{drop} = R_{per\ meter} * I_{wire} * l_{wire}$$

where

U_{drop}	voltage drop of wire [V]
$R_{per\ meter}$	resistance per meter [Ohm]
I_{wire}	current running through the wire [A]
l_{wire}	length of wire [m]

The voltage drop should be calculated for each single wire. The low voltage makes the influence of the resistance in the wiring higher than it would be for a higher voltage.

The design driving voltage is given by

$$\Delta E° = (R_a + R_{wires}) * I_{wire}$$

where

$\Delta E°$	design driving voltage [V]
R_a	(individual) anode resistance [Ω]
R_{wires}	wire resistance (total) [Ω]
I_{wire}	current running through wire [A]

since

$$\Delta E° = (E_c° + E_a°)$$

where

$E_c°$ design protective potential
$E_a°$ design closed circuit anode potential

The individual anode resistance is for a short slender stand-off anode given by [6]

$$R_a = \frac{\rho_{seawater}}{2*\pi*L}\left[ln\left\{\frac{2L}{r}\left(1+\sqrt{1+\left(\frac{r}{2L}\right)^2}\right)\right\}+\frac{r}{2L}-\sqrt{1+\left(\frac{r}{2L}\right)^2}\right]$$

$\rho_{seawater}$ seawater resistivity [Ω*m] $2,00*10^{-1}$
L length of anode
r radius

Since the anodes are not cylindrical, "r" have to be substituted by [6]

$$r = \frac{c}{2\pi}$$

where
c anode cross sectional periphery

Given that the dimensions of the anodes are approximately 15*15*20 mm, the c is 0,06 m. This gives us an r of $9,5439*10^{-3}$ and an R_a of 2,79 Ohm (after correcting for distance between anodes and cathodes). It should be noted that in system 3 the aluminium plate is placed further away from the anodes than the rest of the plates, but still within 0,3 meters.

The total resistance in the circuit is given by

$$R_{a\ circuit} = R_{a/j} + R_{c/j} + R_a$$

where
$R_{a/j}$ wire resistance between anode and junction point
$R_{c/j}$ wire resistance between cathode and junction point

The resistance in the cables, $R_{a/j}$ and $R_{c/j}$, are the same for all the cables due to the same length and is about 0,0448 Ohm.

Table 9 - Current Demand System 1

	Steel	Stainless Steel	Aluminium	Titanium
Area	0,084	0,084	0,084	0,084
Current 1 (initial) [mA]	21,00	21,00	0,84	21,00
Current 1 (mean) [mA]	10,08	10,08	0,84	10,08
Current 1 (final) [mA]	14,28	14,28	0,84	14,28

System 2

In the next system, all the materials are connected together in a joint-CP system. This way, the electrons are in theory free to move between the metals, but are of course governed by the potential between them. The system is presented in Figure 27.
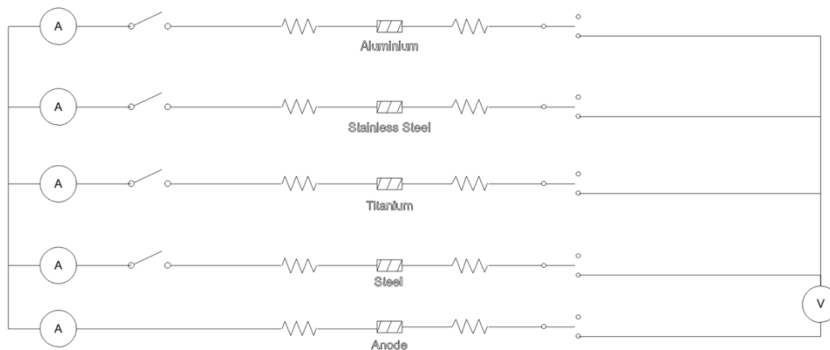

Figure 27 - System 2 current/voltage measurement

The resistors represented are the resistance in the wires. There will not be an individual wiring for the voltmeter, but it is illustrated by a separate set of wiring for illustration purpose.

The anodes here are joined together by a single wire, so that in theory all anodes will to some extend be consumed. However, usually the smallest anode will experience the highest corrosion rate.

Current drainage per metal is given in Table 10. The current drainage should according to DNV-GL be the same as for system 1.

Table 10 - Current Demand System 2

	Steel	Stainless Steel	Aluminium	Titanium
Area	0,084	0,084	0,084	0,084
Current 1 (initial) [mA]	21,00	21,00	0,84	21,00
Current 1 (mean) [mA]	10,08	10,08	0,84	10,08
Current 1 (final) [mA]	14,28	14,28	0,84	14,28

System 3

This system is in setup identical to "System 2", but the surface area of the cathodes is different in order to represent the relative surface area size used on the Merlin UCV ROV. The system is shown in Figure 28.
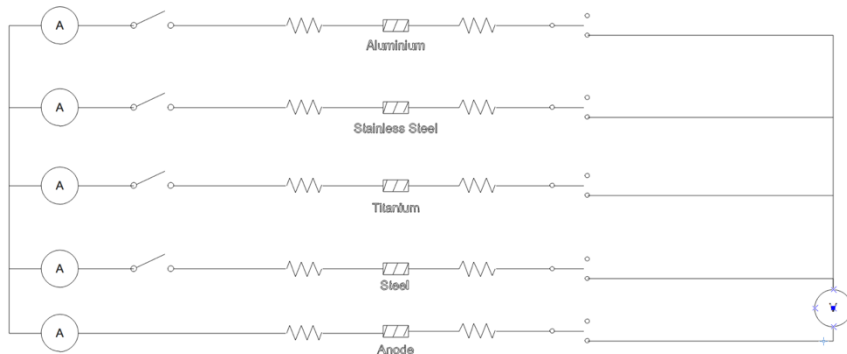
Figure 28 - System 3 current/voltage measurement

Current drainage per cathode is shown in Table 11 and differs from the other systems due to the different surface area. The current density should however be the same.

Table 11 - Current demand system 3

	Steel	Stainless Steel	Aluminium	Titanium
Area	0,0074	0,04997	0,24759	0,03152
Current 1 (initial) [mA]	1,85	12,4925	2,4759	7,88
Current 1 (mean) [mA]	0,888	5,9964	2,4759	3,7824
Current 1 (final) [mA]	1,258	8,4949	2,4759	5,3584

4.2 Risk of local corrosion due to crevice corrosion between metals and elastomers

On the UCV Merlin RROV, there is several possibilities for crevices to be filled with seawater. For example, the connectors that is mounted to the control flask has been mounted with an elastomer maid of POM (polyoxymethylene). Between the POM and both the connector and the surface of the flask, we have two interfaces where there is a metal surface and an elastomer surface in contact.

Typically, tighter crevices can be achieved between metal and elastomers than between two metal surfaces, while the corrosion rate would usually be higher between two metal surfaces due to the higher supply of metal ions. The main drivers for crevice corrosion are geometrical, environmental, electrochemical reactions and metallurgical. [32]

4.2.1 Geometrical

One of the most important factors for crevice corrosion is the geometry of the crevice. For crevice corrosion to occur, one needs to have a crevice that hinders circulation of electrolyte from the bulk electrolyte in a way that does not supply significant amounts of oxygen, and in the same way secures deoxygenation and acidification within the crevice. A crevice that is deep and tight, have a greater possibility for corrosion than a narrow and wide gap.

Another geometrical factor in terms of crevice corrosion, is the ratio between the external surface area to the internal. This have something to do with the polarization between the external and the internal area, this is in a way the same as the fact that a small anode will corrode faster than a large one in a CP system. [32]

4.2.2 Environmental

Environmental conditions in a subsea system harder to control. Factors like O_2 concentration, pH and chloride level, temperature and agitation are factors that is inherent to the bulk electrolyte (seawater) surrounding the crevice and are impossible to change.

Mass transportation, migration, diffusion and convection are factors that in some sense is closely linked together and will affect the local conditions in the crevice. Helped by the continually autocatalytic tendency of crevice corrosion, the electrolyte in the crevice will be under endless random motion that is known as diffusion. [33] The inherent need to balance the reactions inside the crevice known as the Le Chatlier's principle, which states that "Any change in status quo prompts an opposing reaction in the responding system" [34] and is the main driver for convection inside the crevice.

The change of pH level due to hydrolysis is a huge factor in crevice corrosion and are highly effected by the electrolyte anion, mostly chloride in seawater. Chloride has a very low tendency to associate with hydrogen ions in water and this cause the H^+ ions to bond with H_2O molecules instead and form H_3O^+ ions. The concentration (logritimic) of H_3O^+ ions is the definition of pH. [5] [32]

4.2.3 Electrochemical reactions

Factors related to electrochemical reactions are mainly metal dissolution, O_2 reduction and H_2 evolution. All of them are the result of continually corrosion. The metal dissolution makes it possible for oxygen to react with the base metal which due to the lack of oxygen diffusion into the crevice results in a reduction in oxygen level. At the same time, water molecules react with the metal ions and create metal hydroxide plus hydrogen ions that in turn react to create H_3O^+ ions. In total, all these factors contribute to the autocatalytic process. [5]

4.2.4 Metallurgical

Metallurgical factors, are factors like alloy composition where major and minor elements together with impurities (unintentionally added/occurring elements) will affect the susceptibility for crevice corrosion. [32] An example of inhibitors is nickel that will help reduce the susceptibility of crevice corrosion by the reaction with the oxidizing chloride ions to form nickel(II) chloride [35]

$$Ni^{2+} + 2Cl^- \rightleftharpoons NiCl_2$$
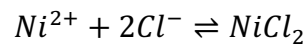
4.3 Risk of stray current at resting Depth

4.3.1 Description

Stray current corrosion is a type of corrosion caused by (unintentional) stray current. Stray current is current flowing in the electrolyte (sea water in this study) that is induced by an external potential source (usually an electric installation). [27] Or said in another way, stray current is those currents that follows paths other than their intended circuit. [36] In situations where metal has mysteriously corroded within weeks or months, we can usually attribute it to stray current.

There are mainly two factors that makes the stray current corrosion a potentially huge hazard; the potentially large voltage that easily can overcome the protective potential of the CP system, and the large current that can be transmitted over a small area that concentrate the corrosion to a local area. The electrons in a system tends to find the path with the lowest resistance, and whenever the current leaves or enter the structure it causes accelerated corrosion when it moves between the electrolyte and the metal structure.

Stray current corrosion is not, as for the other types of corrosion in the "Types of corrosion" chapter, dependent upon the potential between different metals, pH level or the rate of oxygen supply, but rather the impressed voltage and current on the local corroding area. [5]

In order to get stray current, there has to be at least two or more grounding points. For the UCV Merling, there is a joint ground for most of the installed equipment/parts and several components that runs on both AC and DC power. This rises the potential for stray current to occur. In addition, it will rest on a platform on the seabed which in turn can be problematic due to the potential of stray current to other CP protected installations at the given location of Snorre B.

4.3.2 Stray current due to internal electric

In literature, the focus of stray current corrosion is usually on problems related to subsea or buried pipelines, rail roads or power lines. Still, the problem can be just as problematic for an ROV. An ROV is in a way a system of several subsystems which in can be both galvanic connected or galvanic isolated from each other. The problem arises when current finds another path than the one intended by the designer. This can be due to insufficient grounding, faulty grounding or a short cut in one or several of the electric systems.

On the UCV Merlin, almost all of the ROV is intended to be grounded to a joint point. This is in order for the cathodic protection to function as intended and it means that the frame, the hydraulic system and both manipulator arms are jointly grounded. The "electric system" (camera, flask, transponders etc.), is galvanic isolated from the rest of the ROV, but draws power from the same source.

One of the ways stray current might occur is if a fault in the "electric system" caused a current to run through the sea water (electrolyte) and over to one of the components jointly grounded to the frame. Then we would have a closed circuit through the electrolyte, and depending on AC or DC current, a corrosion problem at the points of where the current enters and leaves it.

If the current leak is DC, then we would have a fixed local anode and cathode of which the electrons flow through the electrolyte from the anode to the cathode. This cause the anode to oxidize, while the cathode reduces.

If the current leak is AC, we will have the same problem, but the anode and cathode will alternate and we will have a much slower corroding rate. The rate now is in general believed to be approximately 1/100 of that for a similar DC current, but the problem can be just as severe since it now corrodes at two locations. [37]

4.3.3 Stray current due to other cathodic protected installations

For the main part of the stay subsea, the ROV will be connected through a TN power supply. This is to prevent a potential grounding fault that sends current through the grounding and through the water between the ROV and other subsea equipment.

Whenever there are divers in the water or when the ROV is lifted onto the deck, the power supply is switched over to IT. This is because one need a joint grounding to secure the safety of humans involved.

For the TN system, there is no grounding to the platform or the subsea equipment and this in turn should, when fully functional isolation, secure that there is no stray current between the ROV and other equipment. There is grounding through the seawater to the soil, but the joint grounding for the ROV is galvanic isolation to the top site and thereby to the rest of the subsea equipment. However, if there is a grounding fault, it could send a current through the water to other subsea systems.

In this system, there is a barrier (fuse) that cuts the power if the current leaking through the grounding is greater than 2,5A, and this in turn means that potentially there could be a leak of up to 2,5A.

For the IT system, there is an even greater risk of stray current. This is due to the joint grounding of both the ROV and the rest of the subsea equipment. If there were to be a fault in the grounding for any of the electric systems on board the ROV, it could potentially cause a huge current to flow through the water, and cause stray current corrosion. To secure that this does not happen, there is installed a fuse that shuts down the power if the current leak exceeds 0,5mA. This should secure that severe stray current does not occur.

5. Results

5.1   Results experiment

The results from the measurements with the multimeter has been taken roughly twice a week for 38 days. The uncertainties have been calculated according to the instruments manual and multiplied with relevant formula to get current density, mas consumption and so on, and then plotted as error bars. The raw data is given in Appendix .

The measurements (current [A]) from the first system has been divided by their respective surface area (cathode) to get the current density [mA/m^2]. It should be kept in mind that the current density in the beginning probably was somewhat higher than shown in Figure 29 trough Figure 31. This will be discussed in the discussion chapter.

In Figure 29 through Figure 36 the initial, mean, final values (in addition to the joint initial/mean/final value for aluminium) for the current density according to DNV RP-B401 has been plotted to serve as reference values for the measurements. It should be noted that these values are conservative and that when they indicate anode mass, it is the actual mass to be installed (no safety margin).

In Figure 29 the current density is plotted for each individual metal (all anodes connected individually to a separate anode). The rapid increase in current density after the 30th day was measured after observing that the cathode had started to corrode excessively.
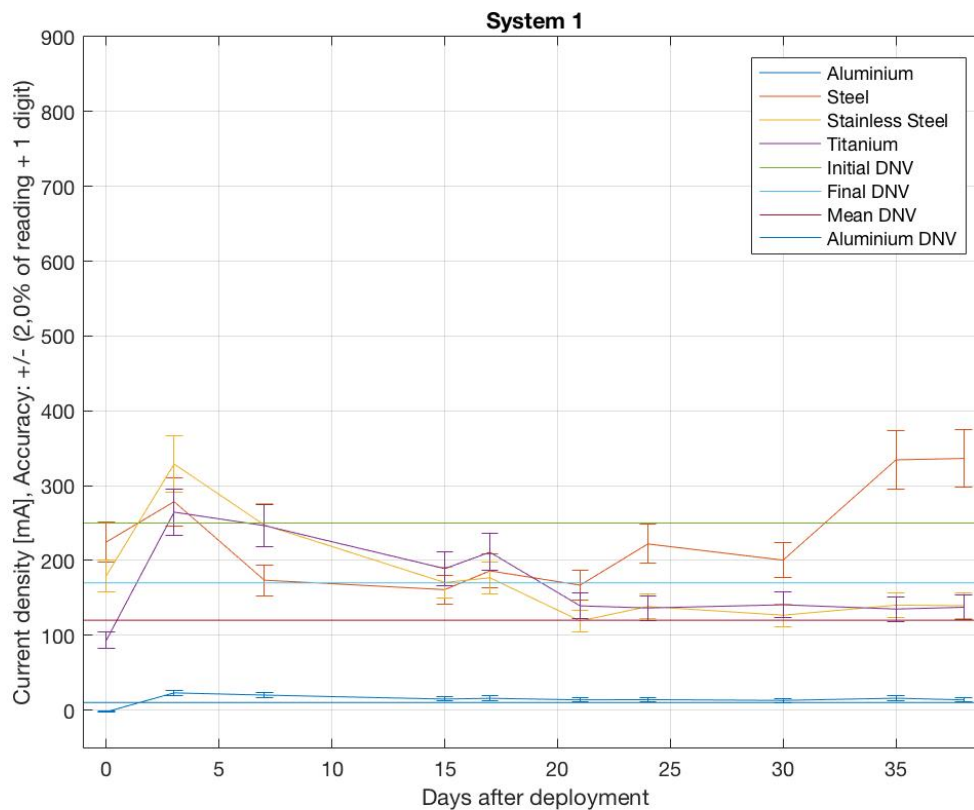

Figure 29 - System 1 Current Density

In Figure 30 the current density for each metal is plotted (connected to a joint anode). The values seem to correlate well with System 1, but perhaps somewhat smaller variations. It is also worth noticing that the steel cathode stayed under cathodic protection throughout the whole experiment and hence the difference at the end (compared to steel in system 1).
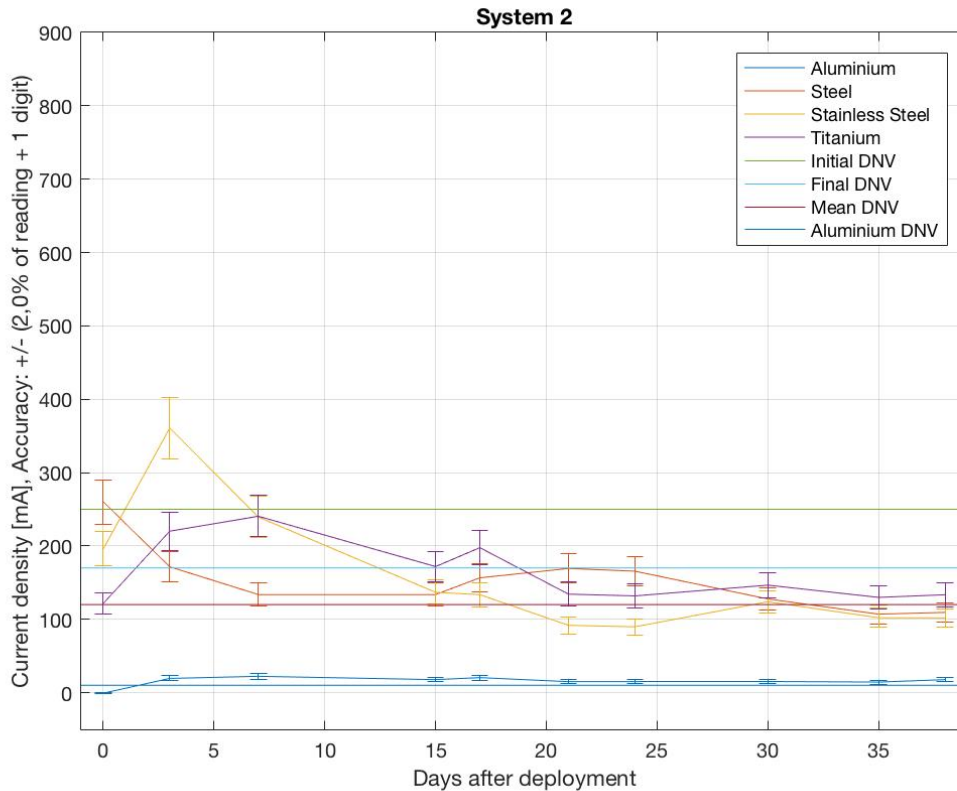

Figure 30 - System 2 Current Density

From System 1 and 2 where all the cathodes have the same surface area, we can see a huge difference in current density in Figure 31. The only difference in the setup between System 2 and 3 is that the relative surface area is different. However, the current density is a measure of current per square meter, so the values have been adjusted for the difference in size. Still the current density for all metals (except aluminium which will be discussed later) are higher than for the other two systems. The current density 7th day was measured to be 759,46 mA/m^2 which is more than 3 times as much as DNV states as the initial value for steel while both titanium and stainless steel was close to twice the initial value given by DNV (250mA/ m^2 for all metals except aluminium). [6]
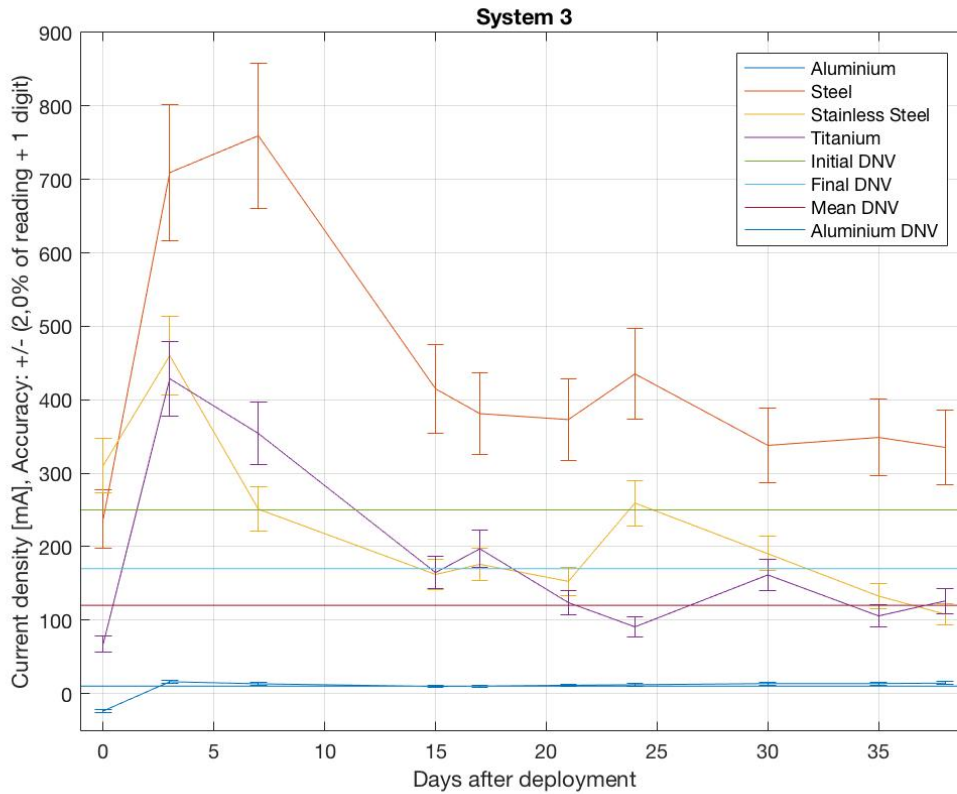
Figure 31 - System 3 Current Density

In the next 5 figures, the current densities have been plotted according to the type of metal to be able to compare the different systems effect on the current density. It should be noted that the values for any given metal should be the same regardless of the relative size of the anodes and the connection between them.

The current densities for aluminium was first plotted in Figure 32 so that the current densities could be compared to each other and still be compared to the other metals. However, it is not easy to see the difference between the different system setups so the values were also plotted to another scale in Figure 33.
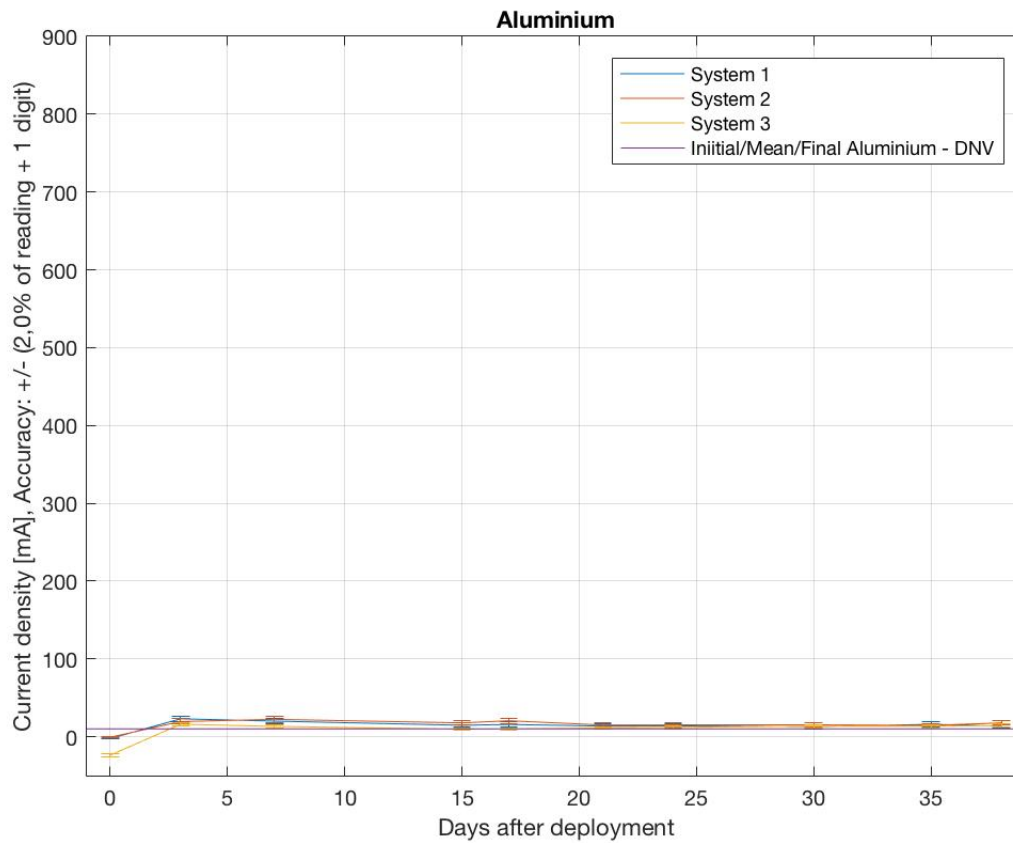
Figure 32 - Aluminium Current Density

In Figure 33, it is clear that the aluminium cathode actually functioned as anodes in the beginning of the experiment while stabilizing around 15-20 mA/m^2 after a few days. This is 50-100% than the initial/mean/final value of 10 mA/m^2 stated by DNV.
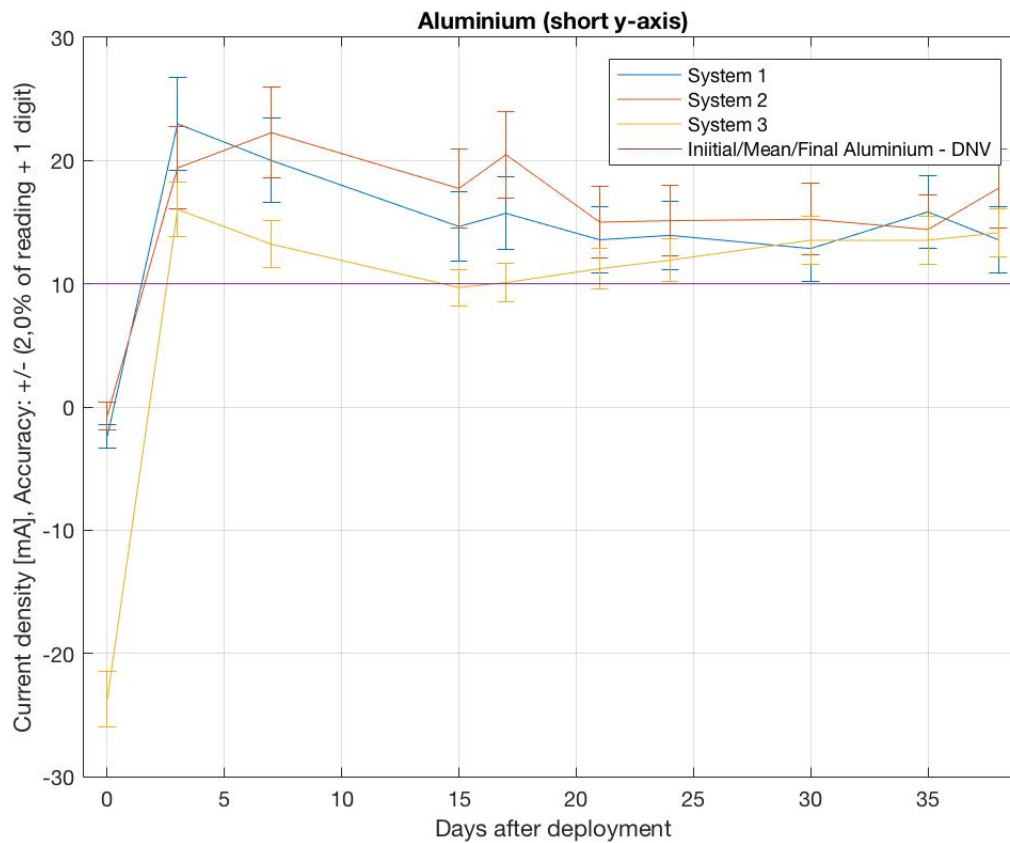
Figure 33 - Aluminium Current Density (short/adjusted y-axis)

For steel, as mentioned on page 53, we can see in Figure 34 that the current density of steel is significantly higher in system 3 where the surface area is a lot smaller than in the other two systems. Still, it looks like it is following the same trend as the other systems.
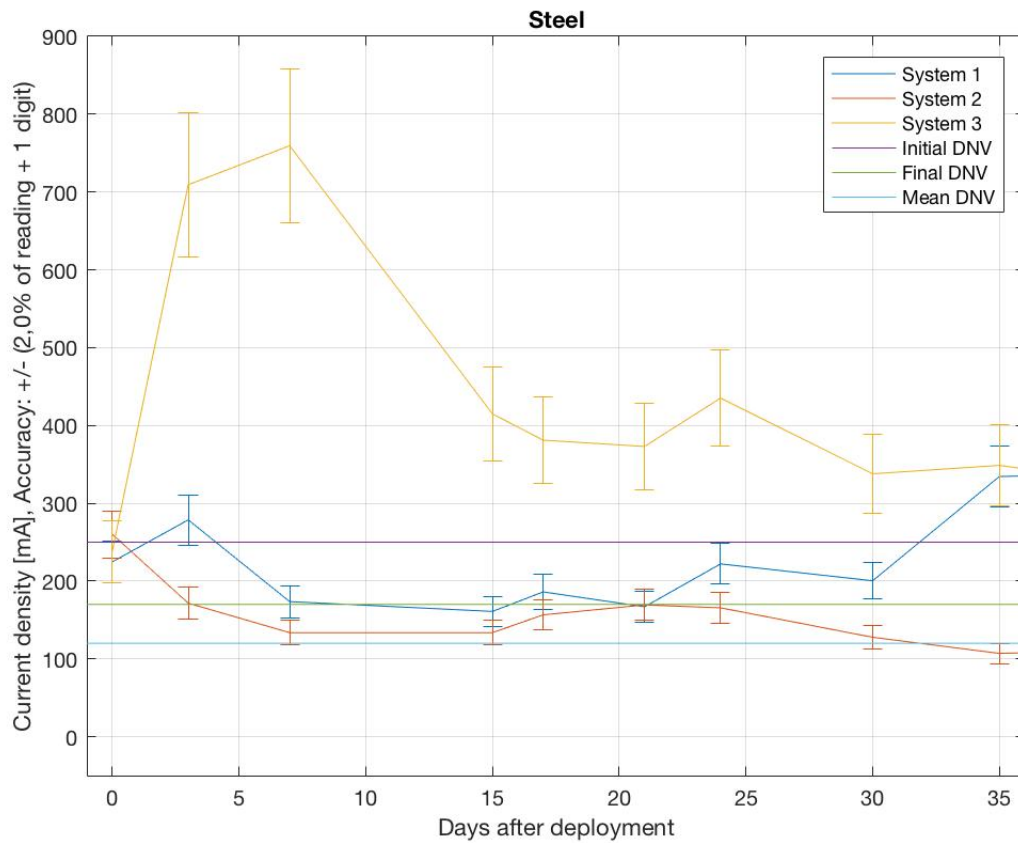
Figure 34 - Steel Current Density

In Figure 35 both system 1 and 2 have about the same current density. The variation is almost insignificant, while the current density for System 3 is notably higher at times.
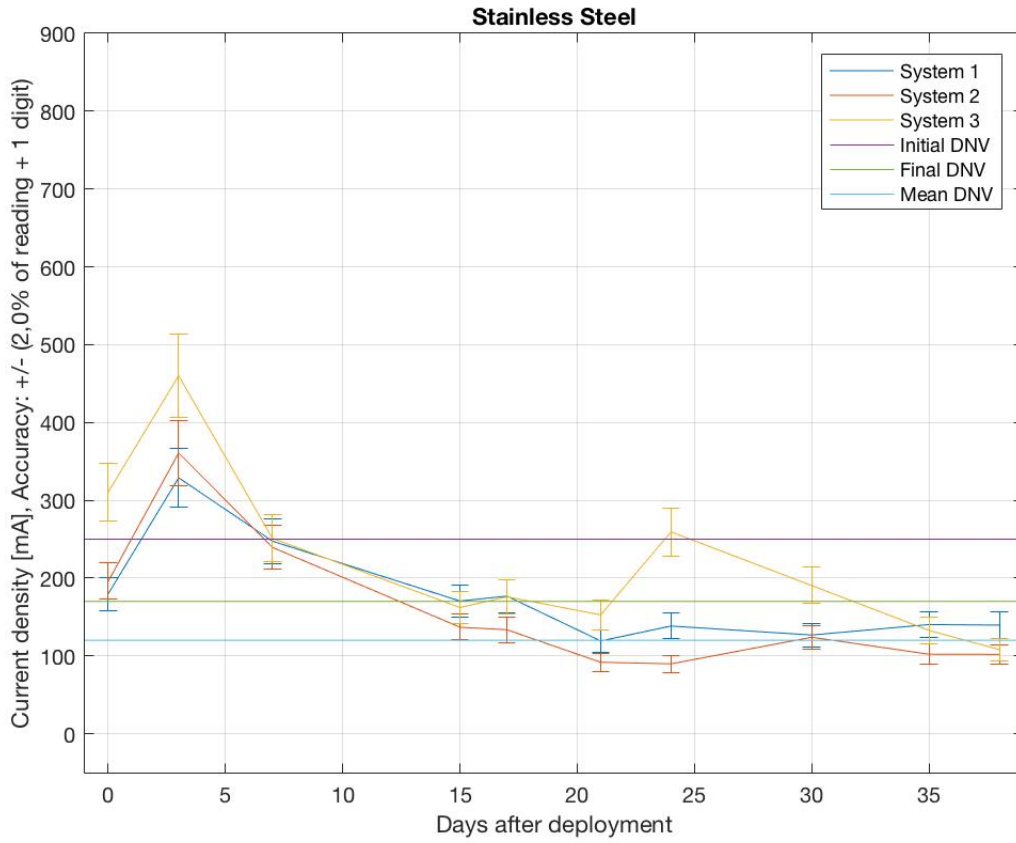
Figure 35 - Stainless Steel Current Density

For titanium, the current density is almost independent of anode configuration and relative surface area. However, in system 3, the current density is significantly higher in the beginning as seen in Figure 36.
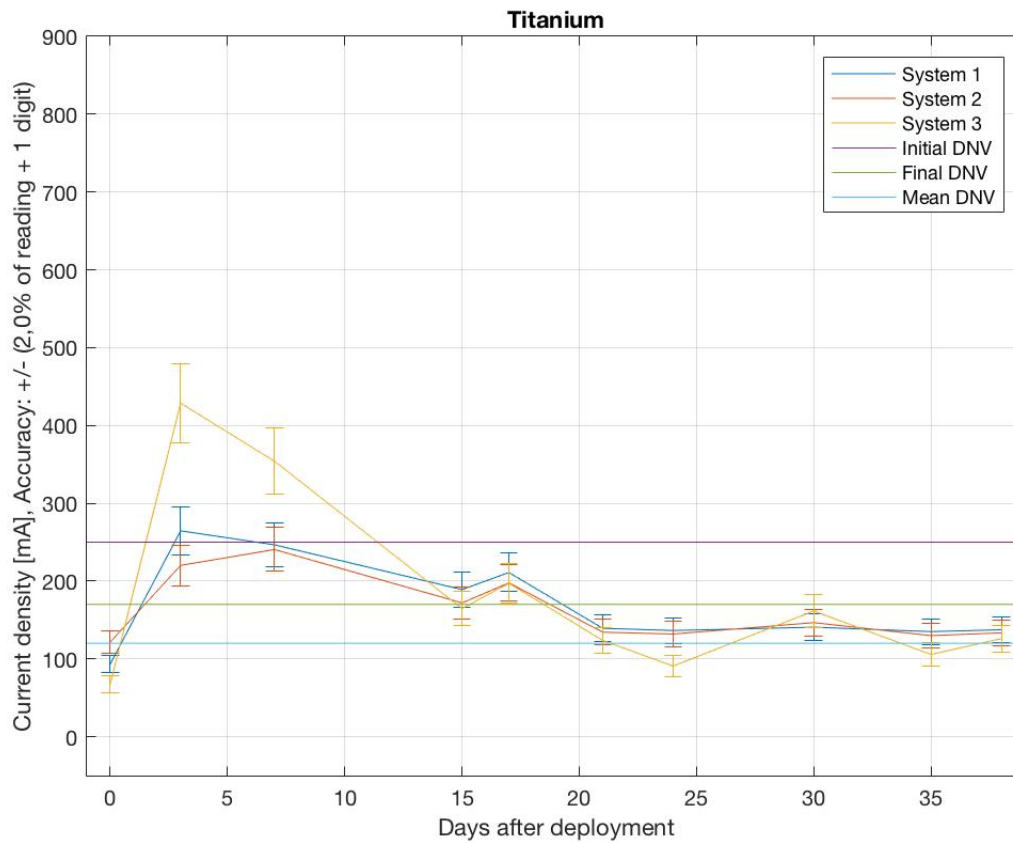
Figure 36 - Titanium Current Density

Regarding the anode consumption, all 3 systems calculated consumption based on the electrical measurements are plotted in Figure 37. The figure displays the actual measurements along with an interpolated graph that is supposed to represent the daily anode consumption. One can see that all 3 graphs has roughly the same shape, while it looks like there is an almost constant difference (except for the last 8 days of System 1).
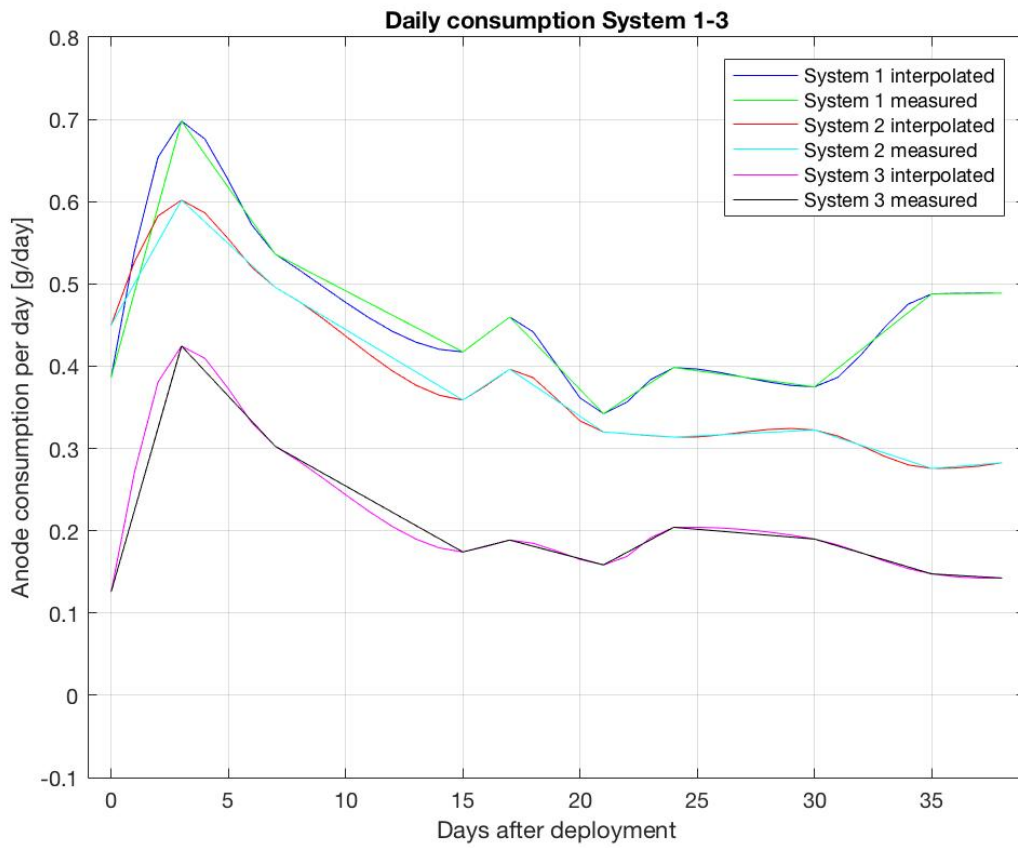
Figure 37 - System 1-3 Daily Anode Consumption

In Figure 38 the daily consumption has been plotted along with the calculated mean consumption based on the measured values and the mean based on the actual anode consumption. The increase of the anode consumption occurred at the same time as the oxidation was observed on the steel plate in this system. The mean value based on the anode weight before and after the experiment should be seen as more or less the reference value for the consumption.

When comparing the two different measures of mean consumption to the initial, mean and final values predicted by DNV RP-B401, we can see that the two means are roughly around the mean value of DNV by ± 2% (calculated in Matlab).
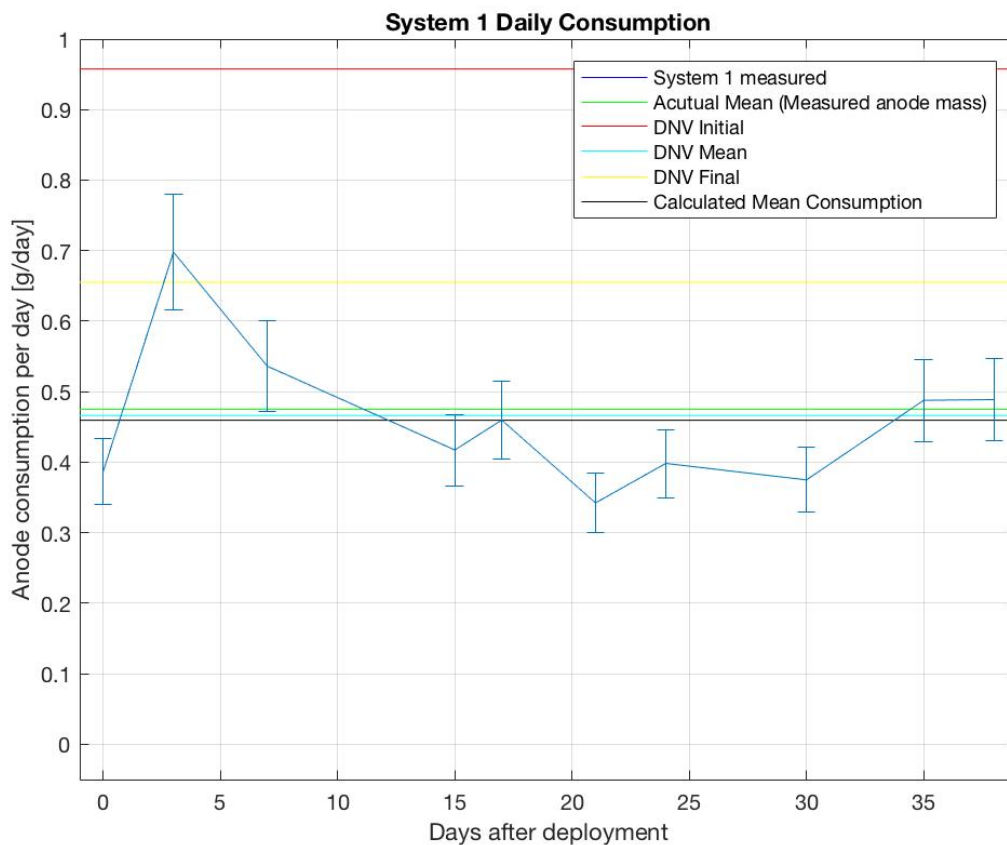

Figure 38 - System 1 Daily Anode Consumption

To compare the predicted consumption by DNV to the actual consumption in the test, the utilization factor, u, have been set to 1, and the anode current capacity, C_a, to 2.585 Ah/kg. The result of this is that the consumption based on the current densities can be compared without taking the utilization of the anodes or the possible lower anode current capacity into account. The result is shown in Figure 39, and it shows that the actual mean (found by weighing the anodes) is higher than the mean value given by DNV (red line versus the pink line).
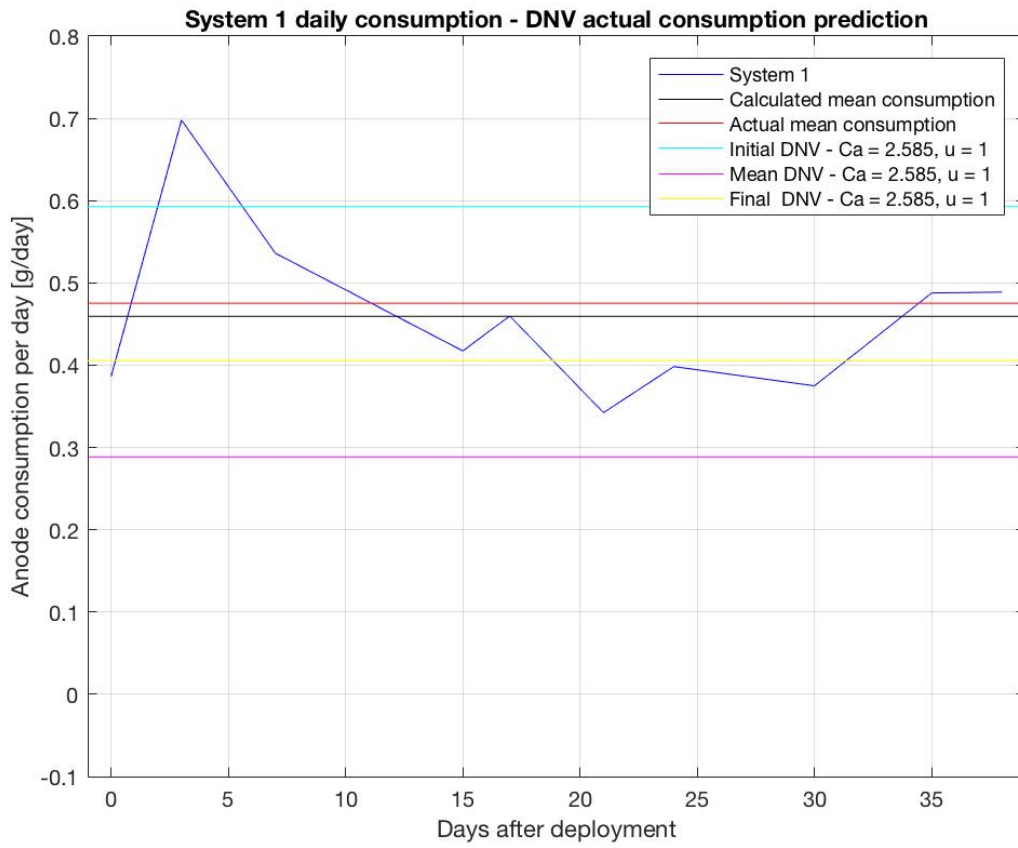
Figure 39 - System 1 daily consumption - DNV actual consumption prediction

In Figure 40, the daily consumption has been plotted for System 2 in the same manner as for System 1 in Figure 38. There is on the other hand a greater difference in the calculated mean based on the electrical measurements and the mean based on the weight of the anodes.

The calculated mean based on the electrical measures are even closer to the mean value (about -18% under) while the mean based on the actual anode consumption differs more with about 13% over.
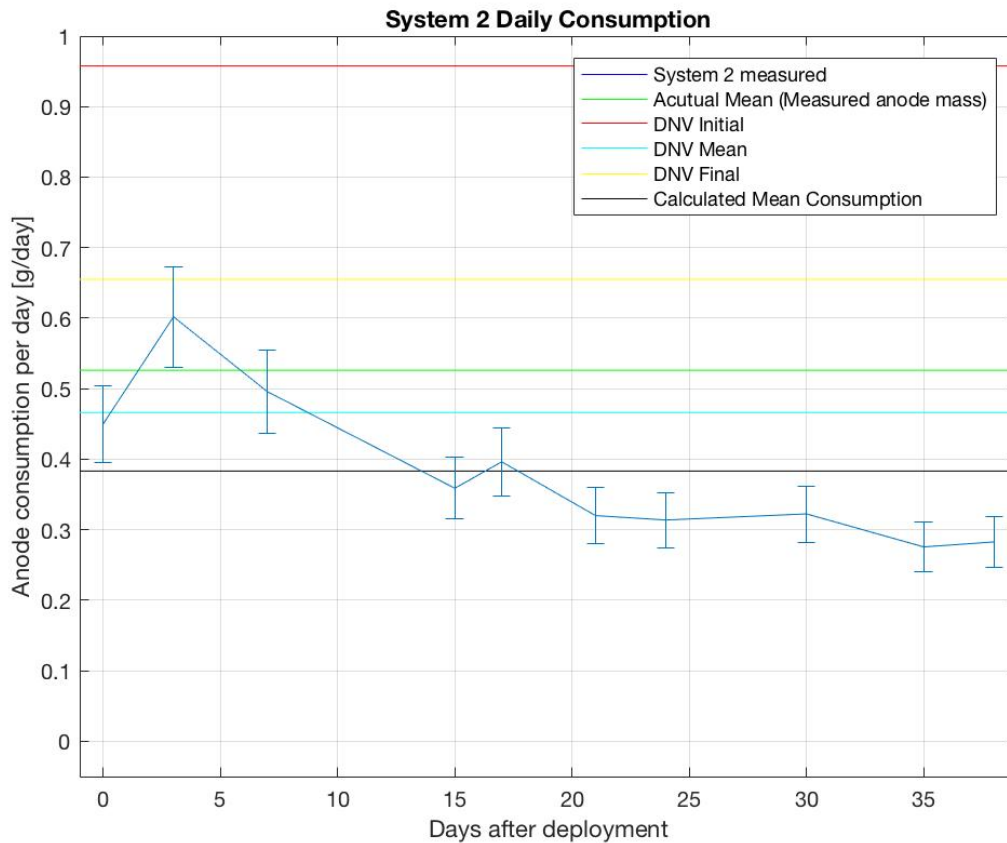

Figure 40 - System 2 Daily Anode Consumption

As for in system 1, the predicted mean consumption for system 2 based on DNV without including additional consumption due to utilization factor and anode current capacity have been plotted in Figure 41. Here, it is clear that the actual consumption based on the consumed anode weight, is a lot higher than the mean predicted by DNV and just slightly lower than the initial value.
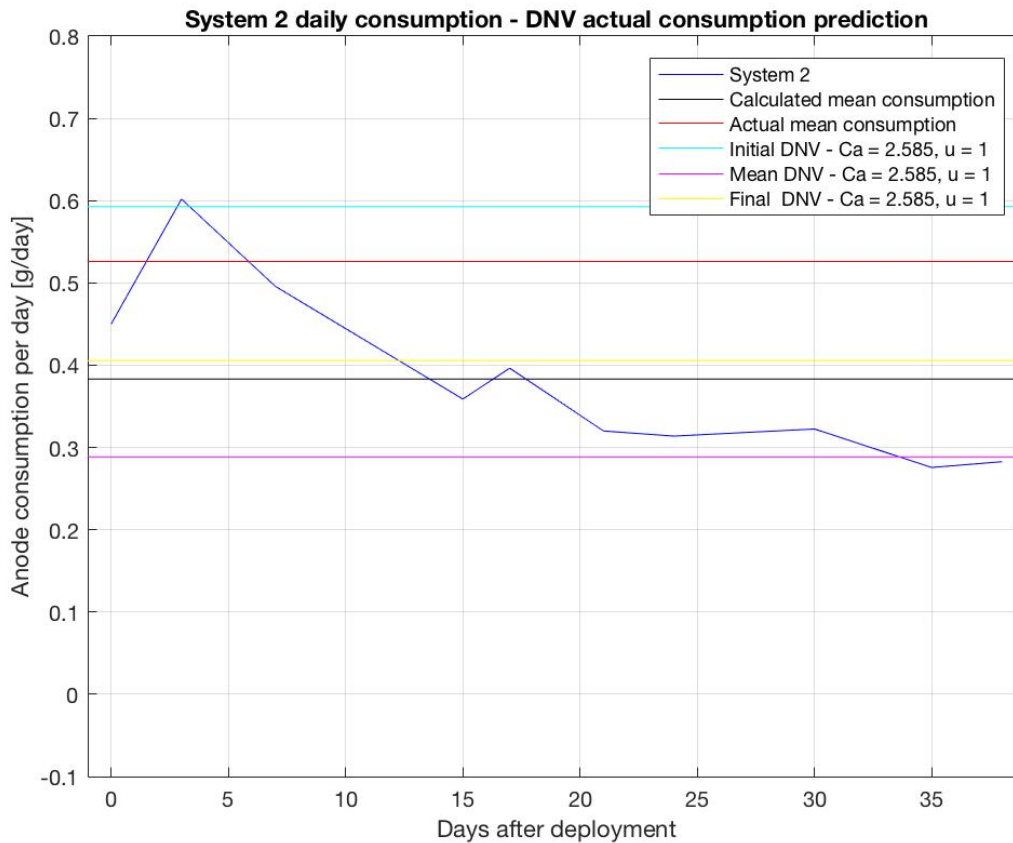
Figure 41 - System 2 daily consumption - DNV actual consumption prediction

In the last system, System 3, we can see (from Figure 42) that the consumption is generally lower than for the two other systems. This is also expected due to the larger area of aluminium compared to System 1 and 2.

The biggest difference between the measured means and the predicted means by DNV. The mean based on the electrical measurements are 10% under the predicted mean and the mean based upon the actual weight of the anodes are 33% over. However, if we compare the values to the initial mean predicted by DNV, we see that the DNV initial value is 41% and 71% respectively.
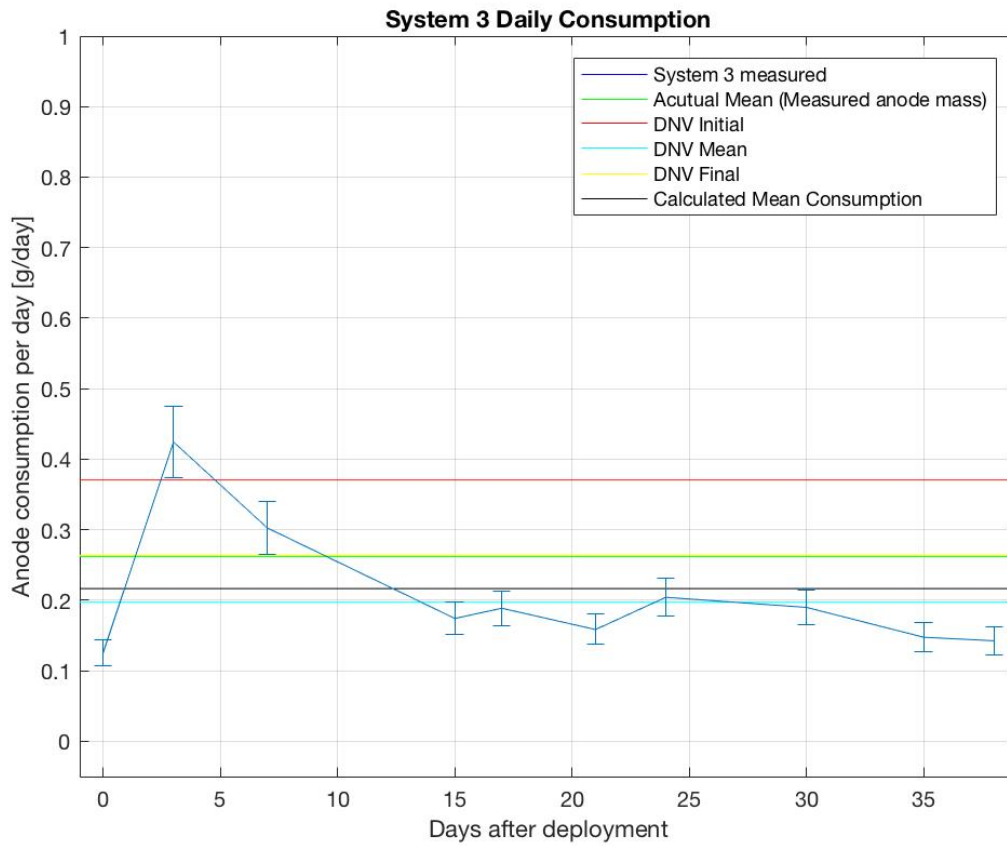
Figure 42 - System 3 Daily Anode Consumption

As for the two previous systems, the predicted mean consumption for system 3 based on DNV without including additional consumption due to utilization factor and anode current capacity have been plotted in Figure 43. Here, the actual anode consumption is even higher than the predicted initial value predicted by DNV.
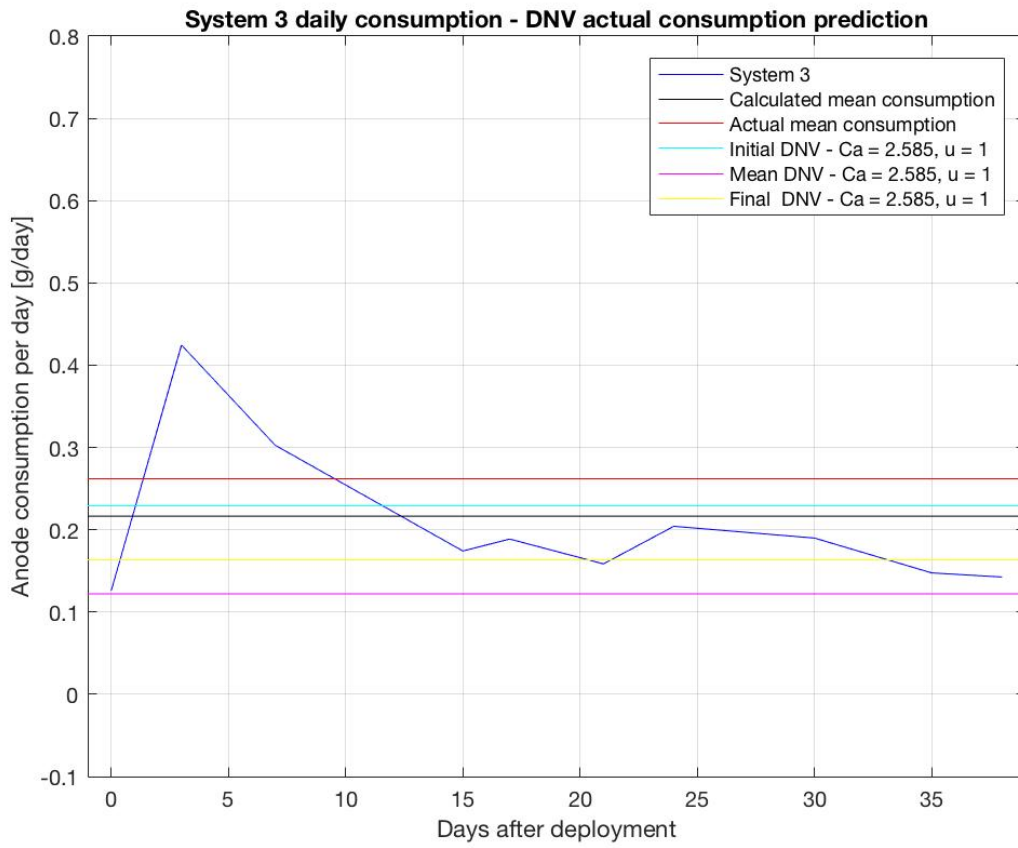
Figure 43 - System 3 daily consumption - DNV actual consumption prediction

6. Discussion

Current density

System 1

From Figure 44 (same as Figure 29 in the result chapter), we can see that in the beginning of the experiment, measurement at deployment, the aluminium plate acts like it were an anode. This could be due to impurities at the surface of either the cathode or the anode or simply be due to polarisation. Aluminium 6082 T6 has a potential of -750 mV, so it should not be due to a more negative galvanic potential. However, like most of the galvanic potential in (especially) seawater, factors like microbes, oxygen level, temperature and so on, will affect the potential and like for stainless steels they tend get more positive after some days.
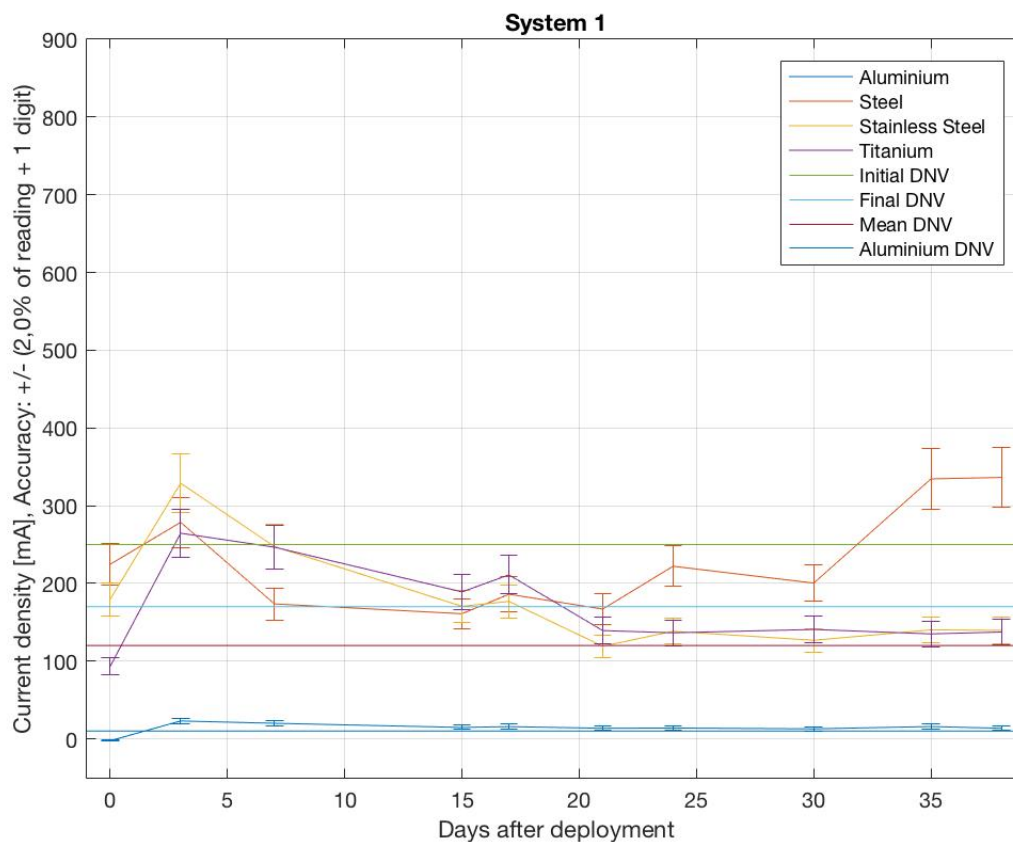
Figure 44 - System 1 Current Density

It was also observed a thin film of oil on the surface of where it was deployed, but this was most likely due to the floating elements that previously contained vegetable oil. However, at the next measurement, the aluminium plate worked as intended (cathode).

The other metals were measured to have a current density of between just under 100 mA/m^2 (titanium) to about 220 mA/m^2 for steel (with stainless steel on 180 mA/m^2). For the next measurement, at the 3rd day, the current densities had risen a lot. At this stage, the current densities are at the initial stage and hence drain the anodes at a high rate. It seems like the

current densities possibly were somewhat higher between deployment and the 3rd day, but it could just as well be that the 3rd day was the peek.

The rapid increase in current density that we can see from the 30th day to the 35th day, is most likely caused by an interruption of the cathodic protection between the measurements the 24th and the 30th day. On April 27th (24th day after deployment), it was raining heavily at the time of measurements, and hence the connection points in the top site junction box got wet. This led to some small, but visible corrosion in the box and this could explain why the cathode and the anode did not have electrical contact for some time. This was not discovered by the measurements since these was measured over the most likely point of problem. The corrosion can be seen in Figure 45.

Figure 45 - Corrosion on the steel cathode in system 1

Once the connection was fixed, we can clearly see that the polarization process has started all over again for this plate. Given a longer experiment, we would probably have seen that the current density had gone back down again (given that the rust does not effects it too much).

Compared to the predicted values given by DNV RP-B401, all the values (except for the first day for aluminium) were above the DNV mean that is used to calculate the anode mass, and that the average is closer to the DVN final value.

System 2
From Figure 46 (same as Figure 30 in the result chapter), we can see roughly the same trend for system 2 as we saw in Figure 29 - System 1 Current Density for system 1, the aluminium

plate worked as an anode in the beginning, but stabilised within 3 days and both the stainless steel and the titanium increased for the 3rd and 6th day. The biggest difference her is that the stainless steel increased a bit more in the beginning, that the steel seemed to have already been through the initial polarization during the first 3 days, and that the steel was protected the whole time.
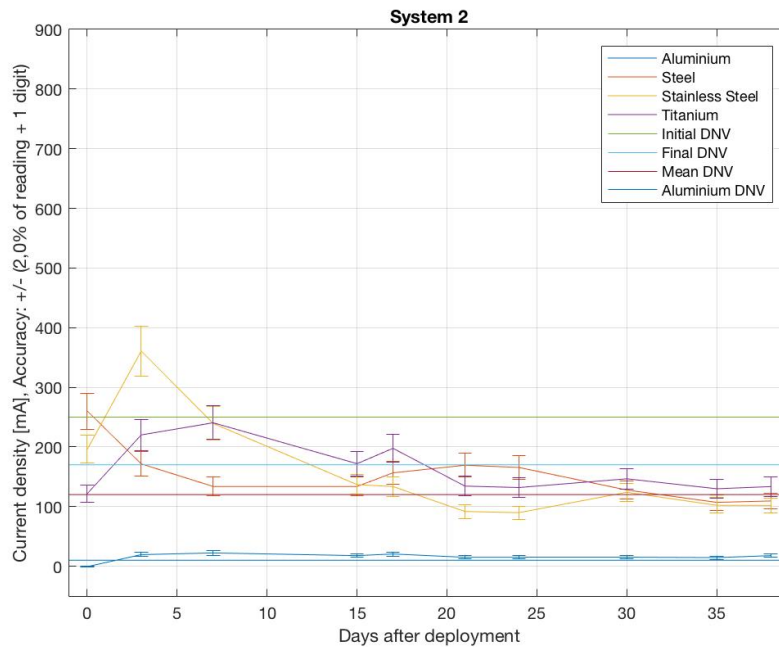

Figure 46 - System 2 Current Density

We can see that the values are closer to the mean value given by DNV in this system than in system 1, and that they seem to move around the mean after about 3 weeks.

System 3
In system 3 (Figure 47), we have huge deviations from the predicted DNV values. The only values that seem to be unaffected is the values for the aluminium plate. For both titanium and stainless steel, we have a current density the 3rd day of around 450 mA/m^2 which is close to double the value of DNV's prediction (250 A/m^2). For the steel plate the deviation is even greater. The 3rd day the current density reaches over 700 mA/m^2 and the 6th day it reaches 750 mA/m^2.
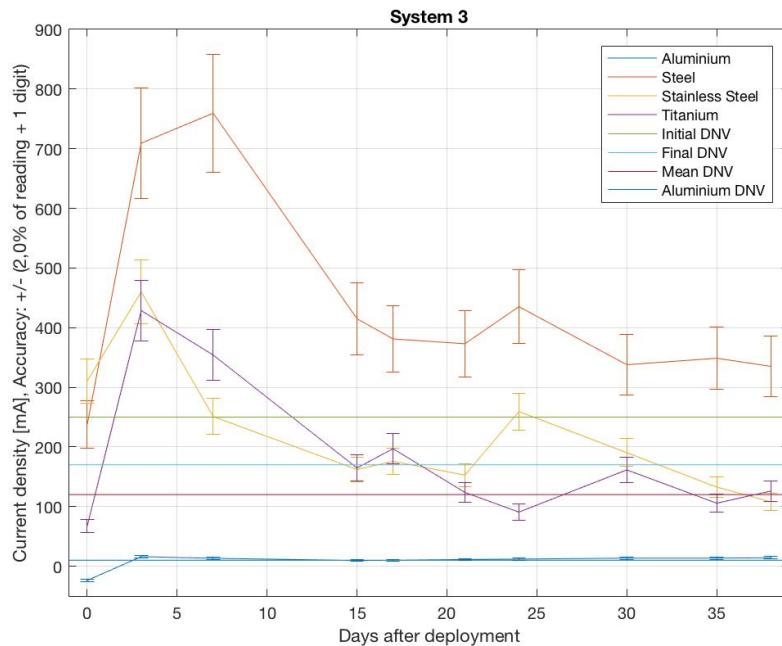
Figure 47 - System 3 Current Density

After two weeks, both the values for stainless steel and titanium seem to have stabilized at about the same values as they have for system 1 and 2, while the values for steel are still about twice as high.

One explanation of why the current density is so much higher than the predicted initial value by DNV is that the "Initial DNV"-value is a mean in the initial phase and needs to be seen in comparison with the duration of the initial phase.

The current density is the current divided by the surface area of the cathodes and hence it should not deviate. It should also be noted that the total surface area of all the anodes are the same as in system 1 and 2. However, we know that the ratio between the surface area of the cathodes and the anodes are important for the corrosion rate of the anodes.

It is worth noticing that the difference in current density for each metal between system 2 and 3 could be totally different if the relative surface area between the cathodes in system 3 was different. If say the surface area of titanium represented most of the surface area, the current density might be higher or lower.

Aluminium
When studying the current density for each metal against its own type, we can see that for aluminium we need to increase the y-axis to get a sense of how it acts in the various situations. The same graphs are plotted in both Figure 32 and Figure 33 (same as Figure 48 below) and we see that relative to the other metals, the variation is small. However, Figure 13 could indicate that the most important parameter in this experiment was the relative surface area ration between the different cathodes, but it should also be noted that this difference seems to diminish as the time goes by.
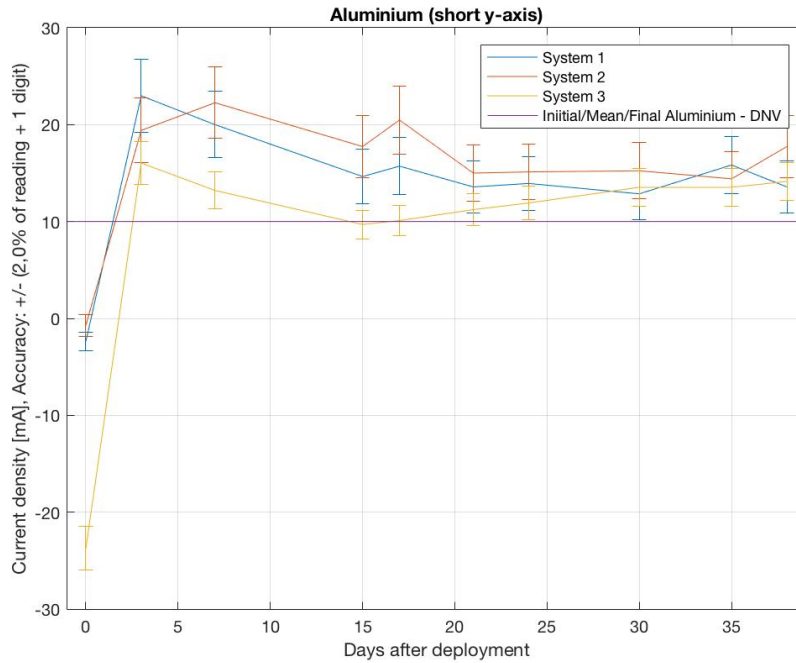
Figure 48 - Aluminium Current Density (short/adjusted y-axis)

All in all, there are not that significant differences between the different systems. Nonetheless, it is interesting that, except for the first measurement, as good as all values were above 10 mA/m^2. This value is stated by DNV as an average value for aluminium. It could be that this average would be reached after a longer test period, but this cannot be indicated by these data.

Steel
The biggest difference in predicted current density and the measured valued appears. As seen from Figure 49 (same as Figure 34), both the steel in system 1 and 2 looks to stay roughly within the DNV values while the steel in system 3 are more than two times as high. Still, it seems that the current density goes up and down at about the same time for the three metals (except for the last two weeks of system 2 where the connection failed). This should strengthen the argument that the external factors affect all systems equally in this experiment.
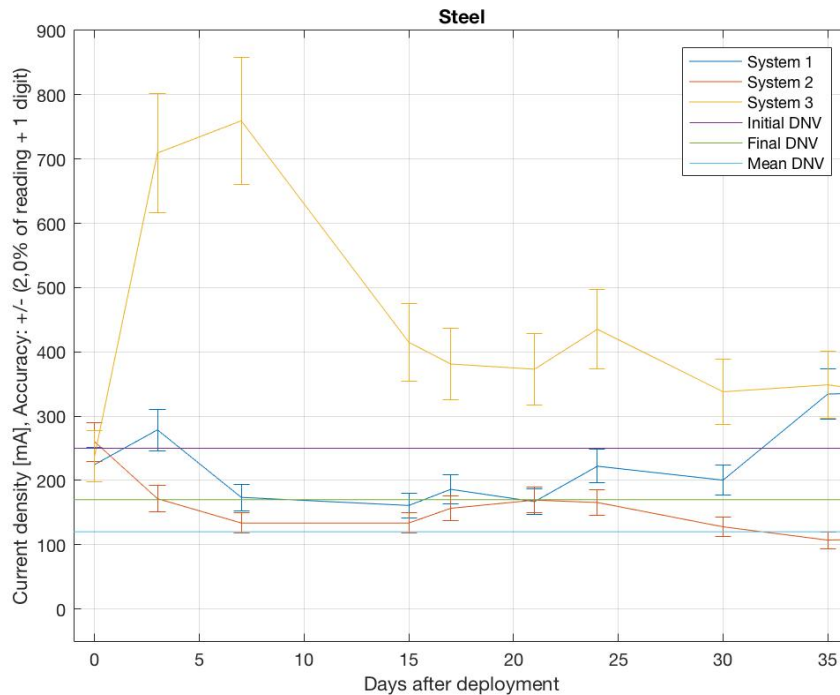
Figure 49 - Steel Current Density

The current density will due to the production of hydroide ions, which precipitate on the substrate surface, be reduced significantly over time. How much is will be reduced depends on several factors which is not easily separated, but will as a rule of thumb, go down to approximately one-fourth of the maximum initial value within a few months. [38]

Stainless Steel
The current density for stainless steel seems to be almost equal for system 1 and 2 and overlaps at several measurements (within the calculated uncertainty). This can also be said for system 3, but here it is clear that the initial value is somewhat higher, and at the point where the normal steel cathode failed the current density went up.

Compared to the DNV values, all values started a bit high, but they all seem to be heading for the mean DNV predicted value.

Titanium
For titanium, the initial current density for system 1 is higher than for the other two, but after two weeks this difference has diminished. The rest of the measurements gives values that for the most part correlate well.

Consumption
In terms of total current demand and the directly related anode consumption, the consumption is highest for system 1 lowest for system 3. This is not surprising since system 3 have a higher percentage aluminium. A more surprising difference, is the difference between system 1 and 2. These should be the same due to the exact same cathode size and materials.

When studying and comparing the consumption it is interesting to compare the actual anode consumption (measured by weight) to the predicted consumption by DNV. It should be noted

that in the formula for calculating the anode consumption by DNV, it is used a utilization factor of 0.8 and that the anode current capacity is conservatively chosen to be 2000 mAh and not 2585 mAh as the producer states. This means that if one dimension the anodes according to the DNV mean value, and the actual mean consumption follows this consumption rate, the anodes will be consumed before the design life is over. It should also be noted that there is an element of chance, several tries could possibly give a more similar result for system 1 and 2.

Figure 38, Figure 51 and Figure 52 (same as Figure 38, Figure 40 and Figure 42) shows the difference between the calculations based on the electrical measurements and those based actual weighing of the anodes. It seems like correlation is better in system 1 than the two others, but this is strange since one of the cathodes were not connected for some time. Still, the actual mean consumption is a bit higher for all systems, which is probably due to higher current density in between the measurements or that the anode capacity is underestimated in the calculations.
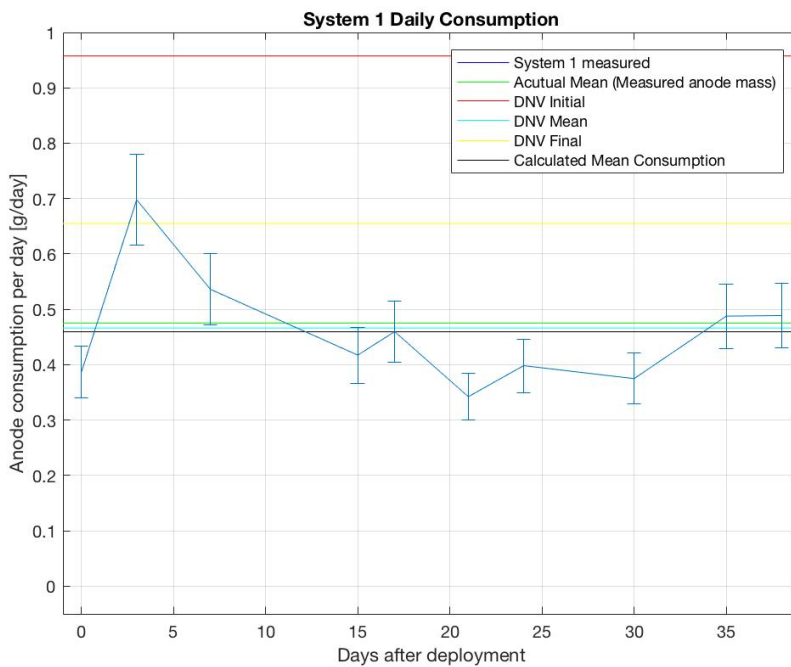
Figure 50 - System 1 Daily Anode Consumption
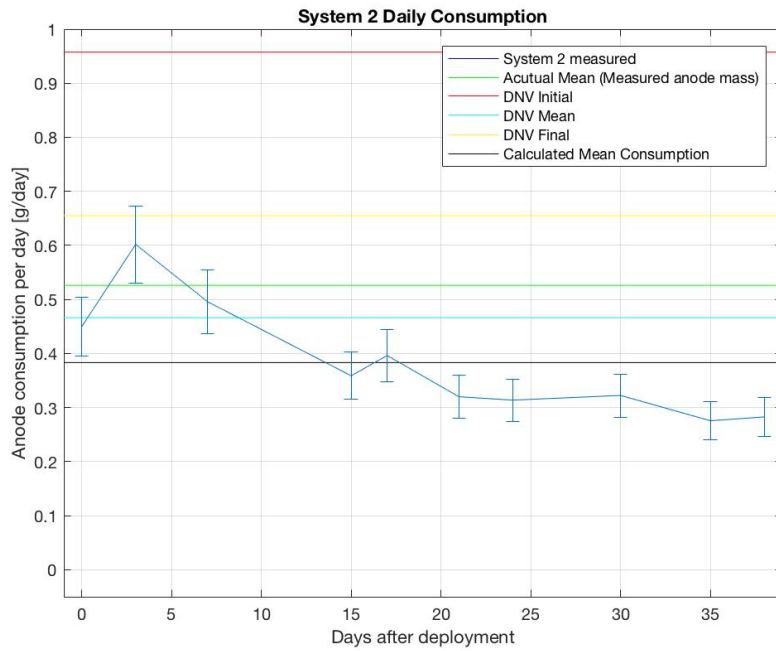
Figure 51 - System 2 Daily Anode Consumption
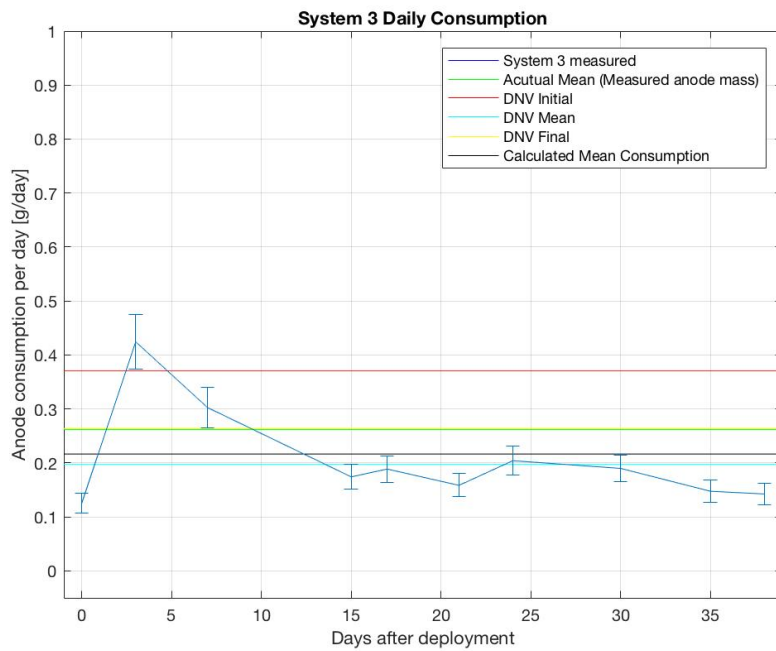
Figure 52 - System 3 Daily Anode Consumption

Figure 53, Figure 54 and Figure 55 (same as Figure 39, Figure 41 and Figure 43) uses a utilization factor of 1 and an anode current capacity of 2.585 Ah/kg to coincide with the means calculated from the experiment. A result of this is that the DNV values goes down and does not include the conservatism that we see in Figure 38, Figure 40 and Figure 42.
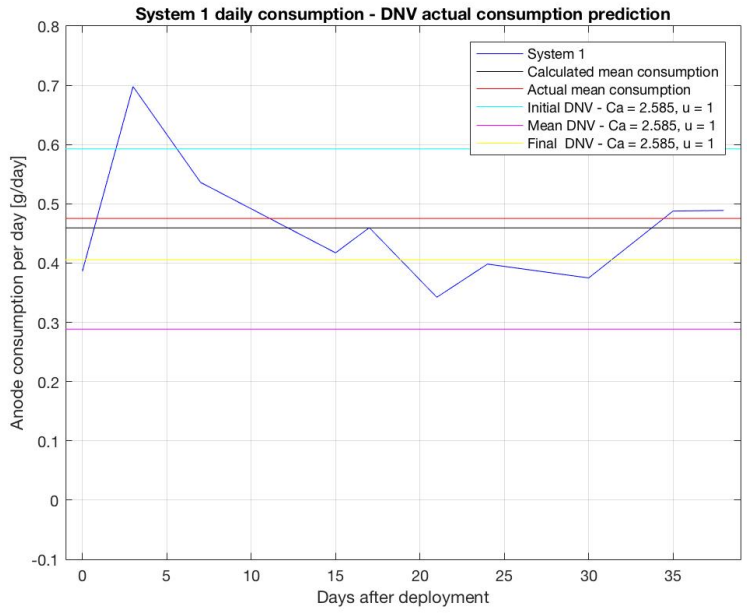
Figure 53 - System 1 daily consumption - DNV actual consumption prediction
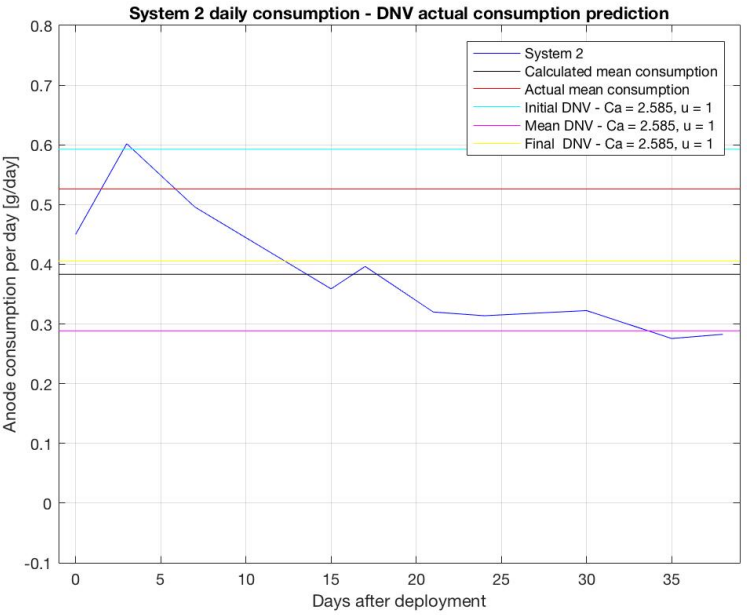
Figure 54 - System 2 daily consumption - DNV actual consumption prediction

Figure 55 - System 3 daily consumption - DNV actual consumption prediction

In system 1 the means from the experiment are higher than the initial and final values predicted by DNV. This means that, given 100% utilization of the anodes and that the anodes deliver the specified ampere hour, the anode mass calculated based on the DNV standard are not sufficient.

In system 2 the calculated mean consumption is below the DNV mean while the more accurate mean based on weighing the anodes are above. This means that calculating according to the DNV mean would not be sufficient for this short time period.

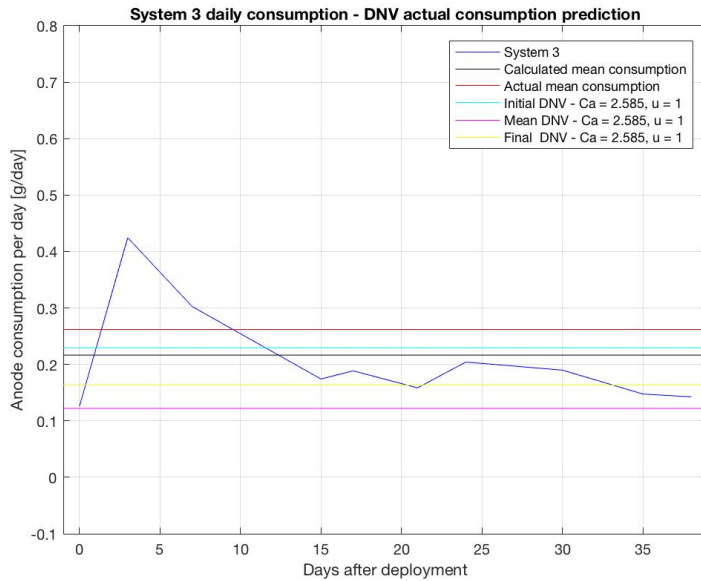In system 3 the calculated mean is just under the initial mean by DNV, while the actual mean is above. This indicates that within shorter periods of time, even calculating the mean after the initial value could be problematic. However, the trend is clear and is moving down towards the mean predicted by DNV or at least around the final mean.

DNV
The DNV RP-B401 standard is developed with the focus on long lasting structures subsea. It is typically used to calculate the anode mass consumption for steel pipelines, subsea equipment, ships, platform and rigs which is to be submersed completely or partially for several years. This ensures a relatively short time in the initial phase, while it for the most part is in the mean phase. For shorter design life, the standard might not be sufficient to ensure adequate protection.

For design purpose, the anode mean consumption based on both the electrical measurements and the weighing of the anodes, have been above the mean value predicted by DNV, but below the initial DNV mean (accept for system 3) and for this would indicate that the DNV initial value might be better for shorter periods.

The Merlin UCV are supposed to stay submersed for 3 months at the time and should, based on this experiment and the predictions by DNV, be designed for the initial phase all the time. It should also never be dimensioned for shorter design life than 3 months since the current density in this period can occasionally be even higher than the initial mean.

Due to the current development in resident ROV systems, the standard should be updated to include recommendations for shorter design life. A possible solution is to mount excessive amounts of anodes, but this will again add weight.

Comments to experiment
The experiment was somewhat limited by its small scale. It should ideally have been repeated, and performed with several of each setup to unsure better statistical certainty. On the other hand, all the results showed similar trends that should give it some validity.

A challenge with corrosion tests are that they should ideally be performed at the intended location of which is to replicate or at least in as close as possible to the intended environmental conditions. The experiment at Hundvåg was performed under roughly the same temperature as on the seabed of Snorre B, but factors like oxygen content and microbes are hard to replicate.

Among potential errors, the multimeter could give out false reading, but this seems somewhat unlikely given the consistency of the measurements, and the relative variation between the different metals.

As mentioned previously, other sources of error are everything from oxygen concentration, pH value, salinity, microbial growth, depth, temperature and so on. These are all errors that will affect the various types of corrosion, but for measurements of current density, they will most likely affect the results more or less equally.

In the beginning of the experiment, the potential between the anodes and cathodes was attempted to be measured, but this was abandoned due to the need for continually record the values over several days uninterrupted. The potential could also have been effected by the resistance in the wires, but this was so low that it is assumed to be neglectable.

Material combinations
In terms of metal combinations, the standard does not say a lot about the effects of combining several different materials together. The introduction of corrosion resistant materials has in some situations been used uncritically together with less noble metal and hence caused galvanic corrosion. In other situations, these metals have been isolated (to avoid galvanic corrosion) without the use of CP protection and caused crevice corrosion in the interface between the corrosive resistant metal and the isolating material.

For the Merlin UCV, most of the ROV are under CP protection and will hence be protected. For some of the metals that are under CP protection there is a possibility of HISC, but the metals susceptible like DUPLEX and SUPER DUPLEX are not under large stress or cyclic loads. Regarding the titanium, it is believed that for HISC to be a problem, the protective potential be lower than -700mV to "destroy the protective surface", the temperature should be over $\approx$ 77°C, and there must be a galvanic couple. Two of these conditions are present, but the temperature is about 70°C lower. It is however noted that for potentials lover than ~1000 mV, it could be a problem at ambient temperature (20°C). Since the potential is at around the potential where one starts to see problems, it should be regarded as a potential problem.

R. Francis et al. studied 7 years of CP protected DUPLEX. This was to find if the ferritic content of DUPLEX introduced a susceptibility to HISC, based on the fact that ferritic

stainless steels are susceptible to HISC, unlike austenitic stainless steels (austenitic stainless steels are believe to be immune to HISC below ~60ºC at high stress [39]). They performed tests on UNS S32550 and UNS S32760 found that UNS S32550 was weakened by hydrogen embrittlement, while UNS S32760 was not scientifically effected. They concluded that problems only occurred if the metal was under large stress, and most often due to thermal aging (which is unlikely for the Merlin UCV). [40] The article indicates that the risk of HISC will not be a huge risk for the DUPLEX parts on the MERLIN UCV since they are not excessively loaded.

Still on should design and dimension with HISC in mind and to reduce the risk of HISC, one could consider zinc anodes, due to their slightly lower potential (as suggested by D. K. Peacook). [41] However, this potential of -1.03V is barely more positive than the aluminium anodes of -1.09V and the operating conditions of the grade 2 titanium, it will most likely not cause any problems (in accordance with Ronald W. Schutz). [42]

Due to the otherwise inferior performance by aluminium anodes over zinc anodes, mitigation measures like coating of the titanium, strengthen it to reduce high stress concentrations, galvanic isolation or one could place the anodes on less noble metals that are in contact with the titanium. Under no circumstances shall the anodes be directly connected to titanium (or DUPLEX).

A possible solution, though somewhat extensive in work load, is to galvanic isolate noble parts from less noble parts by an isolator. This would ensure that galvanic corrosion is not a problem, but it will most likely increase the risk of crevice corrosion due to the tighter crevice between the metal and the isolator. Then, one could use aluminium anodes to protect the aluminium, and an anode with more positive potential to protect the noble material.

Uniform attack
The main effect of CP protection is to eliminate, or more correctly reduce, the degree of uniform attack. If visible uniform attack does occur, it is probably due to problems with the CP system. If parts of the ROV loses contact with the sacrificial anodes, it can result in uniform attack of steel or iron parts as shown by the experiment. This can be further intensified if the steel/iron parts become the least noble parts in connection.

Galvanic corrosion
The whole concept behind CP protection is to use the galvanic corrosion to our advantage. This works as long as the anodes are the least noble metal in the system, and that they do not pacifies. If less noble metals in contact with more noble metals, this could be steel in contact with stainless steel or titanium, the least noble metal will be scarified in the galvanic corrosion process.

To avoid galvanic corrosion, one can use metals with similar galvanic potential, isolate them from each other, use an isolating coating or make sure that every component is connected to a sacrificial anode.

One should avoid using aluminium in direct contact with metals more noble than steel. If connection between aluminium and steel is needed, one should use stainless steel washers, nuts and bolts which is in accordance with NORSOK STANDARD M-001. [43]

Aluminium should ideally not be in direct contact with titanium or DUPLEX-types of stainless steels. However, if this is the case, cathodic protection is crucial to shift the oxidation over from the aluminium parts to the sacrificial anodes.

Creviced and pitting corrosion
CP protection is generally considered to be an effective mitigation measure to avoid crevice corrosion, and since most of the Merlin UCV is galvanic connected to the CP anodes, the risk of crevice corrosion is low. However, the parts of the system that is not under protection, like the "electrical system", there is a possibility for this type of corrosion.

To reduce the risk of crevice corrosion, one can mount smaller anodes on the electrical system to ensure a negative protective potential. One can use elastic rather than plastic or hard materials for isolation or incorporate copper, molybdenum or palladium into the gasket. [41]

The risk of crevice corrosion is low for titanium as long as the temperature is below ~80°C and the pH is above 7. [44] The problem is greater for stainless steels like 316L, DUPLEX and SUPER DUPLEX. According to Robert N Gunn, the resistance to crevice corrosion in duplex steels can be related to its pitting corrosion resistance, as the critical crevice temperature are roughly proportional, although considerably lower. In general, Super Duplex performs better than Duplex, but they are still prone to crevice. [45] 316L is highly susceptible to crevice, and should, if possible, be anodized and checked for signs if crevice corrosion during maintenance.

Intergranular corrosion and selective leaching
Intergranular corrosion is regarded as not very likely at low temperature, or in the absence of welding in CRAs. On the Merlin UVC, there are very few welds, and the temperature is not believed to exceed 50°C.

Regarding selective leaching, it is possible for CRAs, but almost all problems with this type of corrosion has occurred in braze. There are no braze on Merlin UCV, and the probability is low in the other materials.

Flow Induced Corrosion
Flow induced corrosion is, as the name suggest, dependent on a flow over a susceptible metal. It occurs most often in metals that is protected by a layer of oxide film, and almost all the metals on the Merlin UCV have this. However, the flow in the location of the ROV small and should not cause problems relating to flow induced corrosion.

Stress-corrosion cracking
Stress corrosion cracking is not likely to be a problem on the ROV. This is mainly due to the low temperature of the surrounding seawater, but also partly because most of the ROV is under cathodic protection.

Microbial induced corrosion
It is not hard to estimate the effect of microbes on the corrosion potential and/or rate. This is because the microbes at the location is most likely not the same as those at the shallow location of the experiment. One could gather samples from the intended location, and tested them, but this is both uneconomical and time consuming. However, it is believed that most microbes lower the local pH level between itself and the metal it is holding on to. This will

probably be compensated by the cathodic protection, and hence not cause significant problems.

Stray Current Corrosion
The risk of stray current corrosion is dependent on stray current, and this is something that sensors can, and will detect before it results in problems. The problem is greatest when in the TN mode, but most likely will a grounding fault cause the fuse to shout down the power, and hence effectively stop the corrosion. Under IT mode (when divers are in the water), it is less vulnerable to grounding faults, but the fuses will in this mode break the current at a much lower current leak.

Anode consumption
The DNV RP-B401 standard was developed for "long term" cathodic protection and can't be used uncritically for shorter periods. Based on the results from the experiment, and the fact that we don't know how long the initial phase will last without testing it, the Merlin UCV should be equipped with anodes calculated based on the initial phase.

From the calculations, the anode consumption based on the initial phase is 3.87kg (versus 2,16 kg and 3,09 kg for the mean and final phase) which would suggest that 4kg is sufficient. However, the consumption in the experiment was 14,3% higher than predicted (initial), and even though it showed a clear trend towards polarization, it should be taken into account. Based on this potential scenario of 4.42kg, one should use 5 CORAL® A-12-1. This doesn't mean that it will consume 4.42kg, but rather 2.74kg if the experiment was 100% reprehensive. The remaining 1.68kg is due to the utilization factor, and the conservative anode capacity, C_a.

Mitigation measures and maintenance
To ensure sufficient protection against corrosion, one must make sure that there is electrical connection between the anodes and the cathodes it is intended to protect. If some parts don't have sufficient electrical contact, a solution can be to connect a wire directly from cathode to the anode according to DNV RP-B401.

For parts that are not under CP protection one might use coatings, but if metals with different potentials are connected together, one should not use coatings on the least noble parts. This is because the less noble metals will function as anode, and if it gets coated, there could be a violent corrosion concentration at defects or holydays in the coating.

When lifting the ROV up for maintenance, the anodes will most likely have to be changed and should be weighed to check how much of then that have been consumed. If they don't show signs of corrosion, one can assume that there is something wrong with the electrical connection.

7. Conclusion

Throughout this thesis, and in the experiment performed, the focus has been on studying different factors effecting the corrosion of ROVs that consists of multiple types of metals and that are to be submersed for longer periods than have been usual until now. The overall challenge is that some parts are only produced in one material that not necessarily works well together with the other materials in the system.

The results from the cathodic protection experiment shows that the current density in the initial phase was higher than predicted by DNV, but since the prediction is an average and not a fixed value, it should be seen in relation to the duration of the cathodic protection. The current density was close to the DVN values when connected to separate anodes, while it increased when joint together and when the relative size of the cathodes changed. The difference seems to diminish as the current density moves over to the mean phase. This is a strong indication that the need for dimensioning according to the initial phase is only applicable for the first few months (perhaps up to 6-12 months).

In terms anode consumption, that is theoretically direct related to the current density/demand, the experiment indicated that one should dimension the sacrificial anodes according to the initial phase given by DNV, rather than the mean phase that is suggested by DNV RP-B401. The results indicate that the joint anode system, and the relative surface area of the different metals, can further increase the anode consumption in the initial phase.

The Merlin UCV RROV should be equipped with 5 Coral A-12-1 anodes. However, based on the results from the experiment, but due to uncertainty in the length of the initial phase of the current density, 6 anodes will ensure the CP system will perform regardless of the length.

Regarding the different types of corrosion, cathodic protection will limit or almost completely stop all of them. However, for parts not connected to the CP system, especially crevice corrosion, pitting and galvanic corrosion is highly possible.

Possibly the most common mitigation measure of reducing the problems relating to bimetallic corrosion have been to isolate them by an isolator. This might not be a smart solution for systems that are to be submersed for longer periods due to the risk of crevice corrosion, unless the both sides of the isolated parts are cathodic protected by suitable negative potential that not cause other problems like HISC.

The risk of HISC is assumed to be low, but mitigations measures like trying to increase the protective potential of the more noble metals or make sure they are not under great stress should be considered. Research have been done to find anodes that have slightly more positive potential by altering the alloy elements, and by the introduction of diodes to reduce the excessive potential, but neither of them are regarded as reliable enough yet.

To reduce the problems relating to hydrogen production (and in turn the risk of HISC), one could use less noble materials. SS 316L could be a substitute for some of the DUPLEX and titanium parts since it has great strength, works well in combination with CP and is virtually immune to HISC.

Another possible solution is to use coatings on the nobler metals to reduce the effective surface area exposed to the seawater. This has however some possible negative side-effects, like the possibility of blister.

The DNV RP-B401 standard, is intended for permanently installed offshore structures associated with the production of oil and gas. It can be used for structures that operates for shorter periods, but then one should assume that the protected cathode is in the initial phase throughout its operation time.

In terms of maintenance, one should check that the CP system is working as intended each time the ROV is lifted for service. Signs of crevice corrosion, pitting or galvanic corrosion would be clear signs that something is not working as intended.

8. Recommendations for further work

The effect of cathodic protection on multi-metal systems is not fully understood, perhaps mostly because of its complexity. There are numerous types of metals and alloys that is used subsea, and there are several types of anodes, with varying potential. A more extensive experiment, where one tests the materials one are using subsea against anodes with different potential could give a better understanding of the anode consumption rate, the open-circuit potential, hydrogen production/embrittlement and the potential variation over a complex structure.

Since the current density varies the most in the beginning (almost independently of metal/alloy) before it stabilizes at a lower value, studies on the current density development in the initial phase of a cathodic protection system could help choosing the right type of anodes and the anode mass.

A more comprehensive study could look at how the potential drop over a multi-metal structure is increased further away from the anodes, and help placing the anodes and noble parts in relation to each other in order to reduce the risk of HISC. This could allow for higher stress on DUPLEX and titanium metals due to the possible increased relative anode potential.

Since not all parts of an ROV is suitable for CP protection, a study of crevice corrosion over time where one look at different subsea metals/alloys in contact with the same metal, other metals with roughly the same potential, and different isolators would give valuable information about corrosion risk and severity.

Information of how fast crevice corrosion is initiated and how fast it propagates once initiated for various CRAs and in combination with each other and various elastomers would help select the best metals for the intended use in a complex system.

To easier apply standards to short turn operations subsea, one should develop a timeframe of how the current density varies over time. In the simple experiment in this thesis, it is not possible to give a good estimate over the initial phase, but this should be possible to find out within a reasonable margin of error.

Further research on how the current density changes from the first time in the water to the next (and so on) will tell us if the corrosion rate is large at the first deployment and then stabilizes at a steady rate, or if the anode consumption rate profile is more or less the same for each time.

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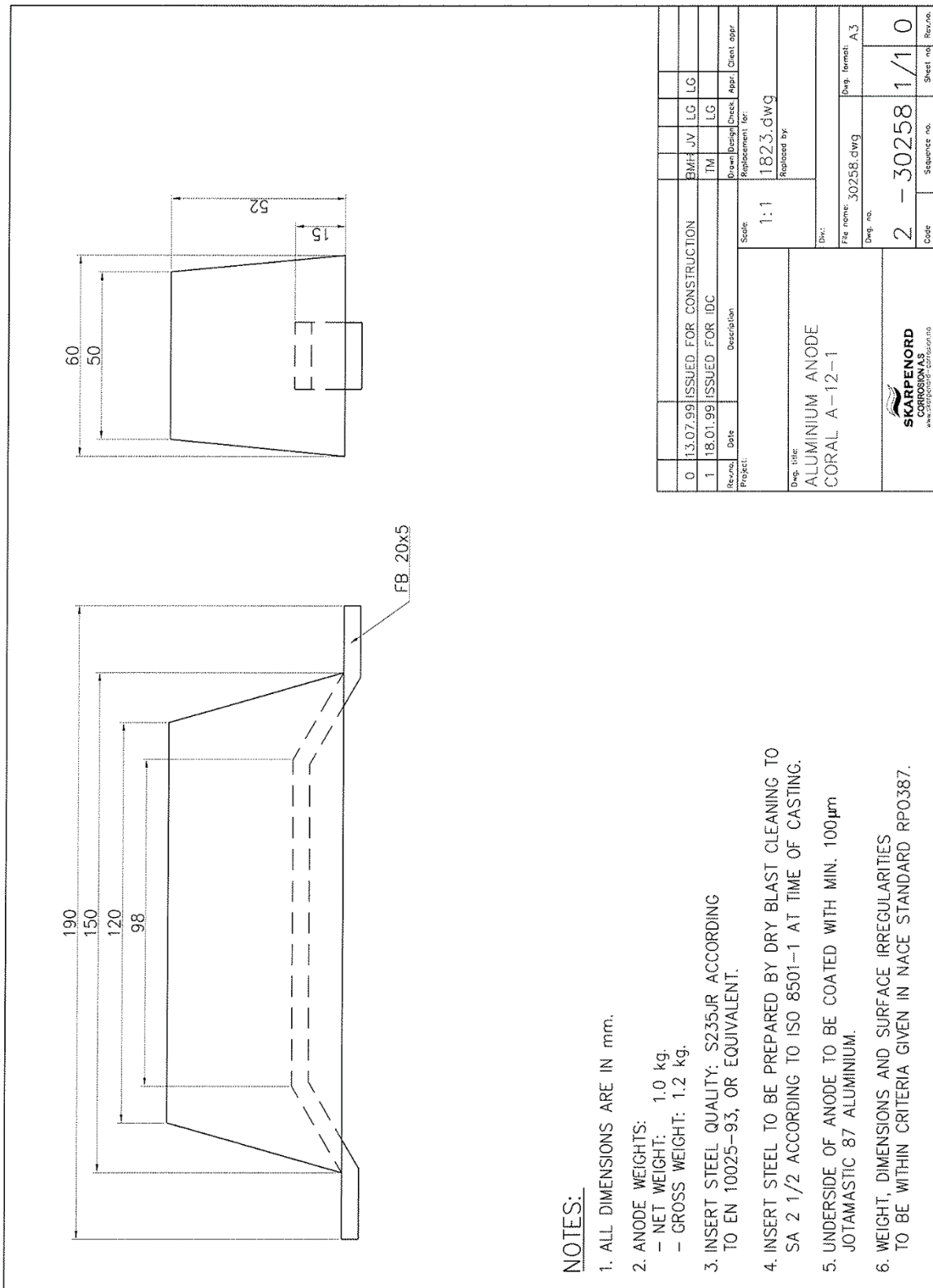
Appendix

8.1   Appendix A

Figure 56 - CORAL A High Grade Skarpenord

8.2   Appendix B

Table 12 - Raw Data Experiment [day], [C] and [A]

Day	0	3	7	15	17	21	24	30	35	38
Temperature [C]	5,1	5,4	7,9	7,9	6,8	7,4	7,4	6,6	8,2	9,3
S1 Aluminium	-0,20	1,93	1,68	1,23	1,32	1,14	1,17	1,08	1,33	1,14
S1 Steel	18,87	23,40	14,58	13,52	15,63	14,02	18,65	16,83	28,09	28,25
S1 Stainless Steel	15,11	27,62	20,78	14,32	14,85	10,01	11,62	10,65	11,78	11,72
S1 Titanium	7,85	22,22	20,71	15,88	17,72	11,70	11,46	11,82	11,34	11,54
S2 Aluminium	-0,06	1,63	1,87	1,49	1,72	1,26	1,27	1,28	1,21	1,49
S2 Steel	21,85	14,41	11,23	11,23	13,15	14,22	13,91	10,73	8,99	9,19
S2 Stainless Steel	16,46	30,30	20,11	11,49	11,22	7,71	7,54	10,41	8,58	8,56
S2 Titanium	10,22	18,49	20,20	14,44	16,60	11,28	11,08	12,31	10,91	11,21
S3 Aluminium	-5,88	3,97	3,27	2,40	2,50	2,78	2,95	3,35	3,35	3,50
S3 Steel	1,76	5,25	5,62	3,07	2,82	2,76	3,22	2,50	2,58	2,48
S3 Stainless Steel	15,52	22,99	12,54	8,10	8,79	7,63	12,96	9,51	6,63	5,40
S3 Titanium	2,13	13,51	11,16	5,19	6,21	3,90	2,86	5,09	3,33	3,97

8.3   Appendix C

Table 13 - Seawater Potential

Alloy	Potential in Seawater [mV]	Closed Circuit Potential (aluminium anode) [mV]
Aluminium 5052	-750 mV [46]	-259 mV
Aluminium 6082 T6	-750 mV [46]	-259 mV
Aluminium 6061	-720 mV [46]	-289 mV
S355J2Gr	-600 mV [5]	-409 mV
Titanium Gr. 2	-10 mV [47]	-999 mV
S165M	200 mV* [48] [49]	-1209 mV
DUPLEX	200 mV* [48]	-1209 mV
SUPER DUPLEX	200 mV* [48]	-1209 mV
Stainless Steel 316L	-100 - +300 mV* [50]	-909 mV – -1309 mV

*Initial potential is lower, but stabilises at roughly given value after a while