
Thesis

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Topic: Corrosion of mild steel and stainless steel in aqueous environment

The logo for The Hague University of Applied Sciences, featuring the text 'THE HAGUE' in a bold, sans-serif font, with 'HAGUE' in green and 'THE' in black. Below this, the word 'UNIVERSITY' is written in a smaller, green, sans-serif font, and at the bottom, 'OF APPLIED SCIENCES' is written in a very small, black, sans-serif font.

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Preface

Corrosion is a hot topic in material science and mechanical engineering. This internship allowed me to work on a project that incorporated both areas at the same time.

During the process of my work it was possible to build up international experience because the corrosion group at TU Delft consists of many international researchers. Thanks to this cooperation I had the chance to explore an international (academic) environment and acquire experience during this internship.

I must hereby thank dr. Umadevi Vadamadurai, dr. Y.Gonzalez-Garcia, dr.J.M.C Mol and ir.van der Meulen for making this internship possible and for the support. I also want to thank the members of the lab group for their support when it was necessary. Of course also all the people from the corrosion group for their support and assistance for the experiments performed.

Once again special thanks go to dr. Umadevi Vadamadurai, my mentor that supervised my work from the beginning until the end and helped me with measurements, interpretations and the writing process. Her method allowed me to work with a lot of own input, which has taught me to work independently. The whole corrosion group was at the same time very open when I had questions or wanted to discuss the results.

Last but not least: I also want to thank my parents giving me the opportunity to study and supporting me through my university years.

Abstract

Mild steel is the main material of alloys in use. Approximately 20% of corrosion damage of metals is induced by bio corrosion. The aim of this research was to study the corrosion performance of mild steel and stainless steel when immersed in natural seawater. In order to verify the effect of the microorganisms compared to the results with the ones obtained with artificial seawater and sodium chloride solution. The chloride ions in salty water are some of the most aggressive elements in seawater. The maximum oxygen concentration is reached at 3,5% of sodium chloride.

The samples are immersed in seawater, artificial seawater and 3,5 % NaCl solution. The surface area of the samples was 5cm^2 . Open circuit potential (OCP), potentiodynamic polarization and weight loss methods have been used to understand the corrosion behavior of the two alloys. Comparing the OCP of mild steel and stainless steel, it was clearly seen that the OCP of stainless steel is in the higher range approximately in the range of -200 mV while the mild steel is in the range of ~ -500 mV. The OCP of stainless steel in seawater is ~ 100 mV nobler than the OCP in artificial seawater and NaCl solution. The corrosion behavior of stainless steel in seawater showed ennoblement when exposed to seawater. The corrosion rate of mild steel in seawater was 0,097 mm/year, in artificial seawater was 0,109 mm/year and in NaCl solution was 0,088 mm/year. No significant difference in corrosion rate of mild steel in different solution is observed. The average corrosion rate of mild steel in natural seawater, artificial seawater and NaCl solution was 0,075, 0,089 and 0,082 mm/year respectively. There was no significant difference in corrosion rate of mild steel in natural seawater, artificial seawater and NaCl solution. It is observed that the corrosion rate from weight loss method and polarisation method are similar and have little variation. The average corrosion rate of stainless steel in seawater, artificial seawater and NaCl was 0,0016, 0,0042 and 0,0017 respectively. There was no significant difference in corrosion rate of stainless steel in different solutions. However it has to be noted that, the deviation of data between different measurements was high. This is because the polarisation of stainless steel results in small active region and large passive region afterwards with increase in potential. It is observed that the corrosion rate calculated from two different methods are comparable and not significantly different. The corrosion rate of stainless steel is very less approximately 10 times less compared to the mild steel.

Microscopy surface analysis showed, that there are different sort of corrosion products on the surface of the mild steel after immersing in the three salt solutions. The reason for this is the different combinations of Fe and O. The mild steel samples immersed in seawater and NaCl had the same green rust, this color is obtained from the Fe and O combination. After cleaning the mild steel in seawater and NaCl solution had all lot of little pits on the surface, mild steel in artificial seawater had less pits but the pits were bigger. The stainless steel samples immersed in all the three salt solutions had had pits on the surface. However the size of the pits on samples immersed in seawater and artificial seawater is large compared to the size of pits formed on the surface immersed in NaCl solution. For the future research more focus should be put on the effect of the biofilm in a corrosion process.

Keyword: mild steel, stainless steel, Polarization, Open Circuit Potential , seawater, artificial seawater, 3,5% NaCl, Weight loss, corrosion, Bio corrosion, corrosion rate.

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List of abbreviations an symbols

Abbreviations

CE	Counter electrode
OCP	Open circuit potential
POLZ	Polarization
PPM	Potentiodynamic polarization measurement
RE	Reference electrode
S	Steel
Ss	Stainless steel
WE	Working electrode
Wt.	Weight

Symbols

A	surface area
b_a	Anodic slope
b_c	Cathodic slope
CR	Corrosion rate
D	Density
E	Cell potential
E_{ocp}	Potential. Open Circuit Potential
E_{corr}	Corrosion potential
F	Faraday constant
I	Current
i_{corr}	Corrosion current density
M	Atomic weight
n	Number equivalent
T	Temperature
t	Time
V	Volts

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1. Introduction

1.1 Corrosion

Corrosion was defined in 1946, by The American Electrochemical Society as "the destruction of a metal by chemical or electrochemical reaction with its environment". (Chilingarian, Mourhatch, & Al Qahtani, 2013, p. 276). This definition is very overall and covers many types of corrosion. Rust or uniform corrosion is a familiar example of mild steel corrosion. Other examples are pitting corrosion specifically detected on aluminum and steel alloys. Also glass and polymers can suffer corrosion or degradation according to this definition. Corrosion, when mentioned in this thesis, refers to the electrochemical corrosion of metals (mild steel and stainless steel) that occurs in aqueous environment, according to a study of (Simillion, 2012). In several environments, corrosion is a natural phenomenon. Energy is needed to form metals from their minerals. The energy is kept inside the metal. This extra in energy is a driving potency for corrosion. The purest metals corrode in atmospheric conditions if there is no protection by their own passive layer.

Metallic corrosion in aqueous environment requires of four elements to occur:

- Anode
- cathode
- an electrolyte
- a metallic path

1.1.1 Different types of corrosion

Corrosion is an electrochemical process. In these reactions, the electrons are moved from one species to another indirectly through the electrodes positioned in the same or different medium. Electrochemical corrosion contains two half-cell reactions: a reduction reaction at the **cathode** and an oxidation reaction at the **anode**, According to a study of (Trethewey & Chamberlain, 2009). For iron corroding in water with a pH 7, these half-cell reactions can be showed as:

Anode reaction: $2\text{Fe} \Rightarrow 2\text{Fe}^{2+} + 4\text{e}^{-}$

Cathode reaction: $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^{-} \Rightarrow 4\text{OH}^{-}$

Different types of electrochemical corrosion:

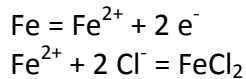
- (general) uniform corrosion
- Pitting corrosion
- Galvanic corrosion
- Soil corrosion
- Differential aeration corrosion
- Stress corrosion

1.2 Corrosion in salt environments

Chloride concentration

The chloride ions in salty water are some of the most aggressive elements in seawater. In seawater, the chloride concentration is regularly between 3.1 and 3.8 % per weight. The three factors why the chloride ions are so corrosive in seawater:

- Chloride ions can react with dissolved ferrous ions to form ferrous chloride giving the following reactions:



The ferrous chloride formed in this reaction can react with dissolved oxygen and produce ferric oxide (Fe_2O_3) and ferric chloride (FeCl_3), which is a well-known oxidizer that can enhance the uniform corrosion rate and pitting corrosion.

- In pitting corrosion the chloride ions can initiate the pit formation. The ions can penetrate the passive layer and further increase pit initiation risk. Also, chlorides can increase the pit growth through an autocatalytic process. Pitting corrosion is unlikely to happen in places where water flows.
- Dissolved oxygen is also an important aspect that can stimulus the corrosively of natural seawater. The chlorides concentration can influence the oxygen solubility's in seawater. From **figure 1** can be obtained that, increasing Cl concentration the corrosion rate will increase. At certain point is the corrosion rate limited and decrease, since the metal is attacked by the Cl, the metal cannot progress in corrosion since the oxygen concentration for the reduction process is limited. Chloride decreases the solubility. The maximum concentration of oxygen can be reached at 3.5 weight percent sodium chloride, as shown in the **figure 1**:

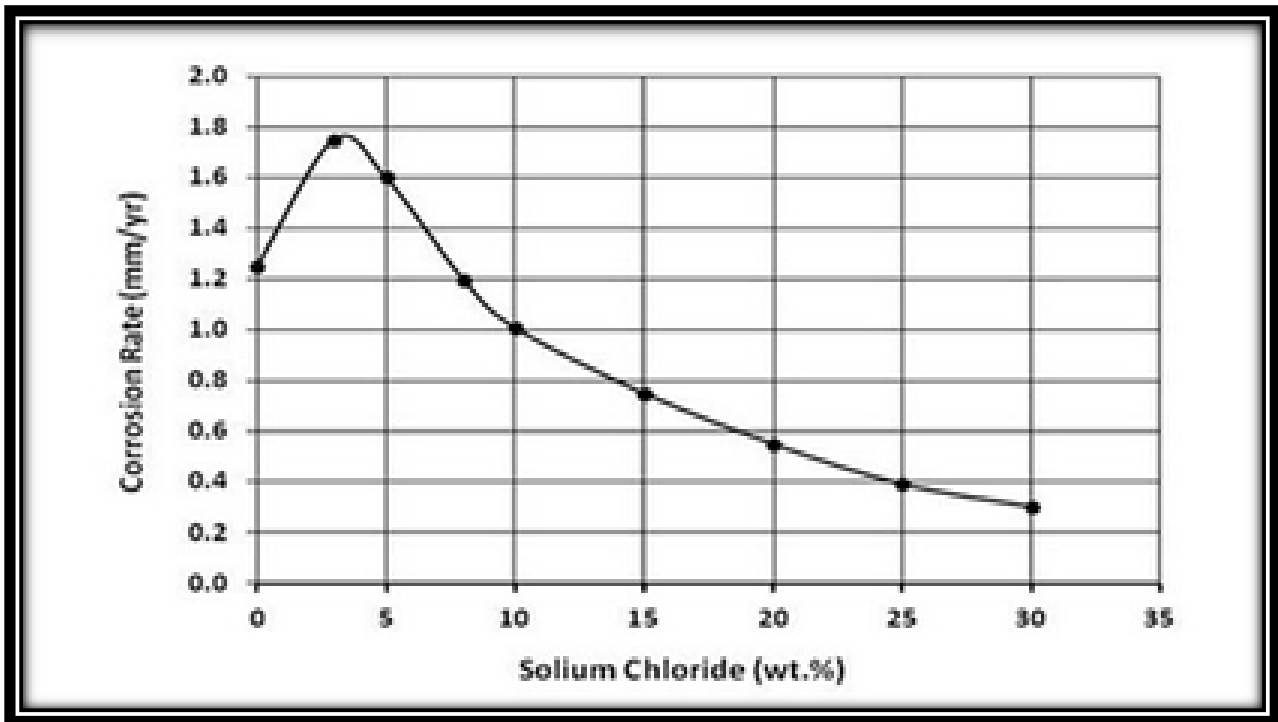


Figure 1: Influence of concentration of chloride ions in the corrosion rate.

Oxygen

The pH of seawater is between 7.5 to 8.5, the oxygen reduction reaction is the main cathodic reaction in competition with the hydrogen reaction. Dissolved oxygen can have an important influence on the corrosion rate in seawater since the cathodic reaction limits the anodic process. Oxygen solubility is limited by chloride concentration. The maximum oxygen concentration is reached at 3.5% of sodium chloride (**Figure 1**).

Temperature

Temperature is an aspect that can affect the activation polarization and concentration polarization, which increase the corrosivity in most types of corrosion. The corrosion of steel in water will rise from 2 to 4% per 1.5°F (1°C) increasing of temperature. Seawater corrosion in tropical regions is higher than in arctic regions, according to a study of [*Yari, 2015*](#).

1.3 Steel

Corrosion of metals costs the U.S. economy almost \$300 billion per year at current prices. Approximately one-third of these costs could be reduced by broader application of corrosion-resistant materials and the application of best corrosion-related technical practices. These estimates result from a recent update of findings of study *Economic Effects of Metallic Corrosion in the United States. (Bennett, Kruger & Parker, 1978)*

1.3.1 Mild steel

In general

The material which is used the most in the world is mild steel. The corrosion resistance of mild steel is quite limited. In large sizes in marine applications, fossil fuel power and nuclear power plants, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment is mild steel used. Mild steel is the main material of alloys in use, both in terms of size and total price. the corrosion of mild steels is an enormous problem. This is the reason for the entire industries to protect mild steel against corrosion.

Properties

The researches (Quraishi & Jamal, 2000) defines mild steel as follows: Steel is considered to be mild steel when no minimum content is specified or required for chromium, cobalt, columbium [niobium], molybdenum, nickel, titanium, tungsten, vanadium or zirconium, or any other element to be added to obtain a desired alloying effect. The compositions of mild steel are shown in **Table 1:**

General properties mild steel		Composition of Mild steel	
		Element	Percentage
Corrosion	Mild steel corrodes fast, when it is not protected	Copper	0.14%
Density:	7800 – 7900 kgm ⁻³	Manganese	0.35%
Modules of elasticity	200 – 250 GPa	Silicon	0.17%
Yield strength	250 – 395 MPa	Sulphur	0.025%
Price:	0,4692 – 0,5247 euro per kg	Phosphorus	0.03%
		Iron	remainder

Table 1: Properties and compositions of mild steel.

1.3.2 Stainless steel 304

In general

Stainless steels are iron-based alloys, stainless steel have at least around 10.5% Chromium. The Chromium in the steel makes a protective self-healing oxide-layer. The reason that stainless steel is corrosion resistance is because of the oxide layer. The self-healing of the oxide layer means that the corrosion resistance stays intact irrespectively of fabrication techniques. even though if the stainless steel surface is scratch or damaged, the oxide layer will selfheal and corrosion resistance will be recovered. Normal mild steels must be painted or have other coatings to be protected for corrosion. Any scratch of damage on the paint or coating will corrode the underlying mild steel. See **table 2** and **annex 1: specification stainless steel 304**, for the specification and the composition of stainless steel 304 that is used for this study.

Stainless steels have a wide range of properties, compared with mild steel:

- more corrosion resistance
- more cryogenic toughness
- higher work hardening rate
- higher hot strength
- higher strength and hardness
- lower maintenance

General properties stainless steel		Composition of Stainless steel	
		Element	Percentage
Corrosion	Quite corrosion resistance	Copper	0.30% max.
Density:	7480 - 8000 kgm ⁻³	Manganese	2.00% max.
Modules of elasticity	196,5 GPa	Nickel	19.00% max.
Yield strength	205 – 515 MPa	Sulfur	0.030% max.
Price:	2,3295 – 2,6829 euro per kg	Phosphorus	0.045% max.
		Silicon	0,75% max.
		Iron	remainder

Table 2: Properties and composition of stainless steel 304.

1.4 Why this study

For over 50 years corrosion connected with microorganisms has been recognized. However for researches bio corrosion is still not completely understood. Bio corrosion, also known as microbiologically influenced corrosion, has to do with the effect of micro-organisms on the kinetics of corrosion developments of metals. A film formed by the micro-organisms on the metal-solution interfaces is the cause of bio corrosion. This film is known as the biofilm, **see figure 2**. Bio corrosion is an old branch of corrosion, it fits into the part of micro-organisms in the corrosion processes. It called bio corrosion because of the existence of living micro-organisms. The corrosion reactions may be changed by microbial influence, particularly when the micro-organism adheres to metal surface forming biofilm. Parts of their metabolic movements such as enzymes, exopolymers, organic and inorganic acids, and compounds, for example, ammonia or hydrogen sulfide can affect cathodic and / or anodic reactions, this will cause the change in electrochemistry of the biofilm / substrate interface. The role of biofilm on the surface of the metal may result in deterioration of the metal.

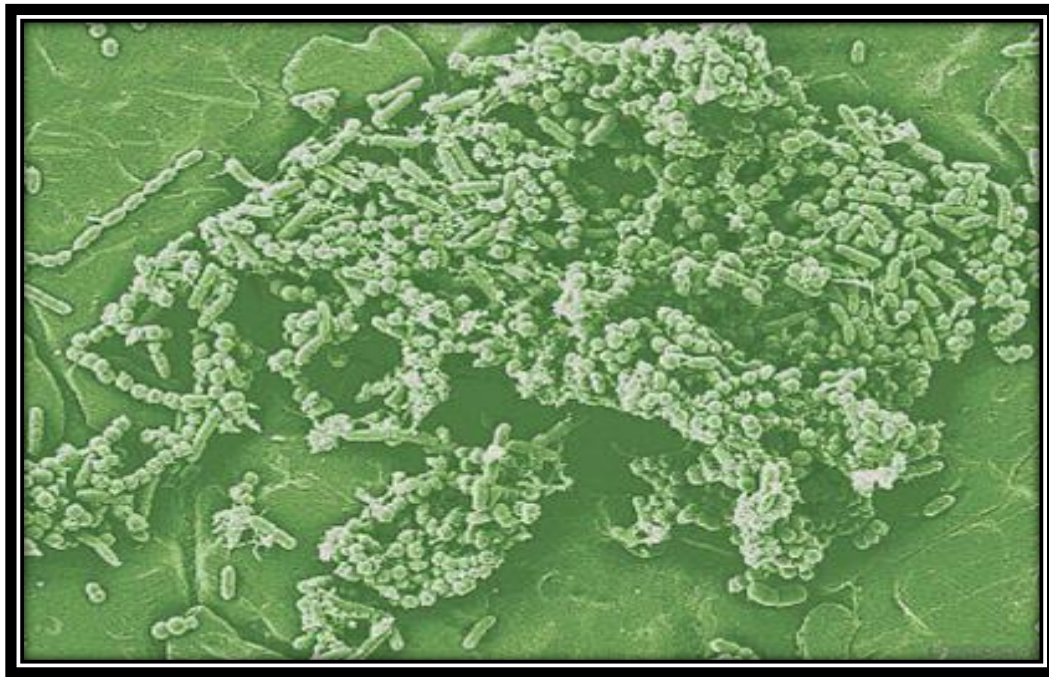


Figure 2: Photomicrograph of a multi-species biofilm on a stainless steel surface

The aim of this research

the aim of this research is to study the corrosion performance of mild steel and stainless steel when immersed in natural seawater. in order to verify the effect of the microorganisms compared to the results with the ones obtained with artificial seawater (microorganism-free) and sodium chloride solution (NaCl).

Effects of bio corrosion:

- that approximately 20% of all corrosion damage of metals is induced by bio corrosion (Flemming, 1996)
- Brennenstuhl et al. (1992) reported that bio corrosion caused a damage of approximately \$ 55 million in stainless steel exchangers within 8 years
- reduced speed of marine vehicles due to increased weight of bio fouling
- cost to burn extra fuel
- environment impact related to increased fuel usage
- accelerated corrosion of metals and alloys resulting in safety issues
- A biofilm of 1 mm thickness can increase the ship hull friction by 80% weight which results in 15 % reduction in speed
- 5% increase in greenhouse gases CO₂, NO_x and SO₂ emissions

The most susceptible parts of a typical ship to bio corrosion are indicated in **Figure 3**. Common hard shelled barnacles generally found on ship hulls are shown also in the **figure 3** :

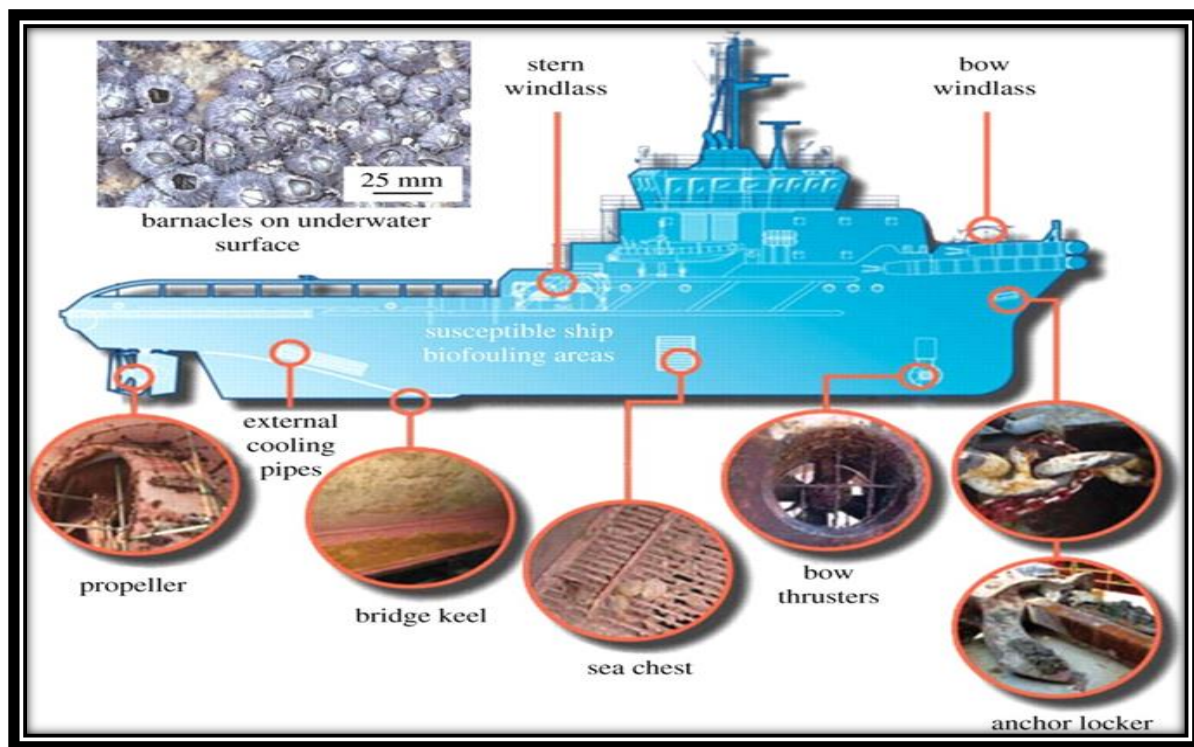


Figure 3: Parts of the ship that are more susceptible to bio corrosion (or bio fouling)

2. Materials and methods

This chapter will discuss which materials, solutions, experimental setups and methods are used for the research study.

2.1 Sample preparation

The surface area of the mild steel and stainless steel was around $25 \times 25 \times 4$ mm. For OCP and Polarization experiments, the samples were embedded in the epoxy mold, exposing only the surface of the sample. The mild steel and stainless steel samples were polished with sandpaper using 80, 160, 320, 800, 1200 roughness. After that the polished mild steel and stainless steel samples were rinsed with Ethanol, washed using distilled water, dried and stored in the lab. After the sample preparation, the mild steel and stainless steel samples were weighted.

2.2 Different salt solutions

2.2.1 Sodium Chloride (NaCl)

To get a clear idea how much influence only salt water has on the corrosion of steel, in relation to seawater. The chloride ions in salty water are some of the greatest aggressive elements in seawater. Seawater contains approximately 3,5 weight percent sodium chloride solution. See, **annex 2: specification NaCl**.

2.2.2 Artificial seawater

Artificial seawater does not contain bacteria, further artificial seawater has all the chemical species that also contained in seawater. The Artificial seawater formula contains mineral salts, some anhydrous salts that can be weighed out, and some hydrous salts that should be added to the artificial seawater as a solution.. In **table 3** the components of artificial seawater are showed, and see **annex 3: specification artificial seawater** for more in information.

Component	valence	Concentration (mol/kg)
H ₂ O	--	53.6
Cl	-1	0.546
Na	+1	0.469
SO	-2	0.528
Mg	+2	0.0282
Ca	+2	0.0103
K	+1	0.0102
C _T	-1	0.00206
B	-1	0.000844
B _T	-3	0.000416
Sr	+2	0.000091
F	-1	0.000068

Table 3: Properties and composition of artificial seawater.

2.2.3 Seawater

Seawater covers 71% of the surface of the world. This electrolyte approximates a 3,5 weight percent sodium chloride solution but it is much more complex, containing almost all naturally occurring elements, (Shifler, Tsuru, Natishhan & Ito, 2005). In different places in the world, seawater can differ in chemical structure, content of salt, the content of oxygen, and pH. Seawater pH differs from 7,5 to 8,5. **Table 4** shows the component and concentration in seawater . Seawater as corrosive media has been taken from Kijkduinen, **see figure 4**.

Component	valence	Concentration (mol/kg)	Part of salinity %	Molecular weight	Concentration ppm, mg/kg
Cl	-1	0.546	55.03	35.453	19345
Na	+1	0.468	30.59	22.990	10752
SO	-2	0.0281	7.68	96.062	2701
Mg	+2	0.533	3.68	24.305	1295
Ca	+2	0.0104	1.18	40.078	416
K	+1	0.00997	1.11	39.098	390
C _T	-1	0.00234	0.41	61.016	145
B	-1	0.00083	0.19	79.904	66
B _T	-3	0.00046	0.08	58.808	27
Sr	+2	0.000091	0.04	87.620	13
F	-1	0.000068	0.003	18.998	1

Table 4: Properties and composition of artificial seawater.



Figure 4: Seawater is taken from this spot in Kijkduinen (the red arrow).

2.3 Methods

2.3.1 Weight loss

Before immersion the mild steel samples in the three different solutions, the samples were polished and cleaned. The samples were polished till the surface was smooth and mirror-like. After the polishing the samples were cleaned in an ultrasonic bath filled with ethanol for 5 minutes. The next step is to measure the weight of the mild steel samples with a balance METTLER AE50 Libra, This balance measured the weight with high precision (till 0,0000 gram), see **annex 5: specification METTLER AE50 Libra** for more details . The samples are immersed in seawater, artificial seawater an 3,5 % NaCl solution for 1 week (168 hours). The salt solutions were sealed and kept at room temperature to avoid evaporation. After one week the samples were removed from the salt solutions. The samples are immersed in the ultrasonic bath filled with ethanol for 5 min to clean them. The samples are weighed again. From the difference of weight of the samples the corrosion rate can be calculated.

Using the weight loss method results the corrosion rate can be calculate with the following formula:

CR= corrosion rate [mm/year]

D= density [g/cm³]

t= immersion time [h]

W= weight loss [g]

A= surface [cm²]

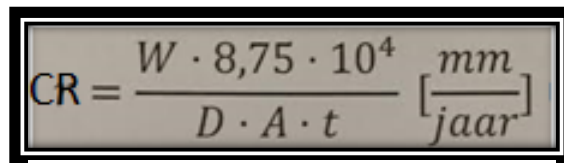

$$CR = \frac{W \cdot 8,75 \cdot 10^4}{D \cdot A \cdot t} \left[\frac{mm}{jaar} \right]$$

Figure 5: Formula corrosion rate by weight loss.

2.3.2 Electrochemical setup

The process of corrosion is an electrochemical process. Electrochemical process consisted of oxidation and reduction reactions. The released electrons from the metal (oxidation) are added by the components (reduction) in the corroding solution. The electron (current) in the corrosion reaction is a flow, the flow can be measured electronically. Thus, controlled electrochemical experimental method is a method to know the properties of corrosion of metal components in combination with different electrolyte solutions. For each metal in a solution the corrosion characteristics are unique.

The experimental setup of a polarization measurement consists of an electrochemical cell. This is constituted by the electrolyte solution, a counter electrode(s), a reference electrode and a working electrode that is the metal sample, see **annex 4: electrochemical cell setup**. The potentiostat is the electronic instrument to measure and/or apply current and/or potential. The electrodes are connected to this. The reference, working a counter electrode are immersed in the electrolyte solution, see **figure 6**. An electrochemical potential (voltage) is generated between the different electrodes in the solution. From the potentiostat the corrosion potential (E_{CORR}) is measured, by the difference in energy between the reference electrode and the working electrode. Electrochemical corrosion tests measure the potential and current of the oxidation or reduction reactions, see **figure 7**. By input of a constant potential in a specific time period on the working electrode imposes the potentiostatic. The current is plotted vs. $\log I$ (Amps/cm²).

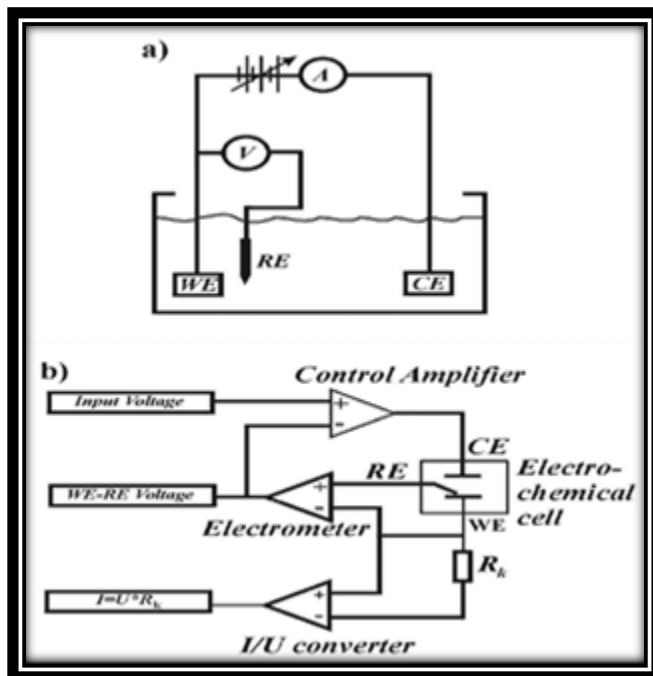


Figure 7: Electric circuit of potentiostat.

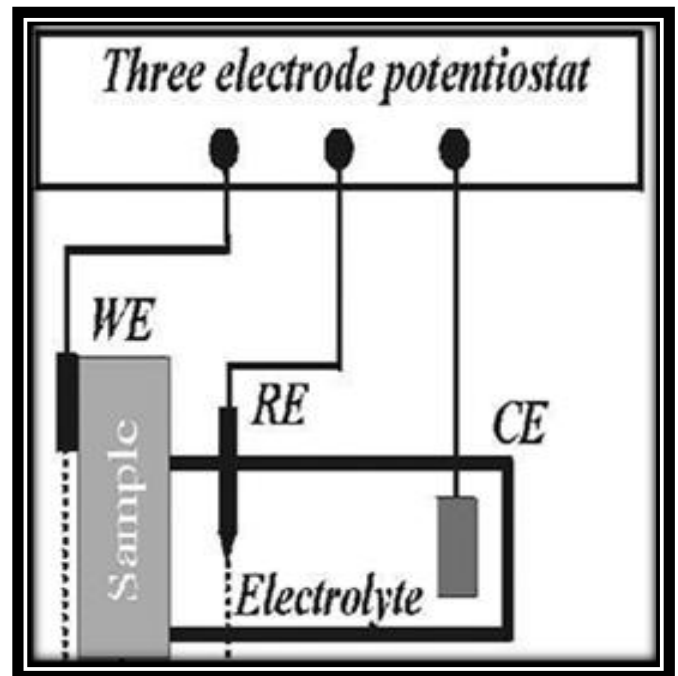


Figure 6: Three electrode potentiostat.

2.3.3 OCP (open circuit potential)

What is OCP?

A metal which is immersed in a solution, there will be an electrochemical reactions of the metal-solution crossing point at the surface of the metal, ensures that the metal will corrode. These reactions create an electrochemical potential, this test called the open circuit potential. The open circuit is measured in Volts (V).

Experimental details

The OCP measurements were carried out on mild steel and stainless steel samples in seawater, artificial seawater and 3,5 % NaCl solution for 1 hour (3600 sec). For the OCP measurements is used the following equipment: Solartron SI- 1287 Electrochemical Interface and Solartron 1218 multiplexer. The 3,5 % NaCl solution and artificial seawater are prepared in room temperature. Seawater as corrosive media has been taken from Kijkduinen. The fixed rate method is used. The OCP curve (E (V) vs. Time (sec)) is plotted. For obtaining the measurement, the software ZView is used.

2.3.4 Polarization

What is POLARIZATION method?

A method for polarizing an electrode, where the time for each potential is constant called Potentiodynamic polarization. To changing the potential to the next step the current is allowed to become stable (*R. Rosliza, H.B. Senin and W.B. Wan Nik, 2008.*). The potential increase small, this method resembles a potentiodynamic curve. The potentiodynamic measurement is presented by the plot E (V) vs. log I (Amps/cm²).

Experiment details:

The potentiodynamic polarization measurements were carried out on mild and stainless steel samples immersed in seawater, artificial seawater and 3,5 % NaCl solution for 1 hour (3600 sec). The 3,5 % NaCl solution and artificial seawater are prepared in room temperature. Seawater as corrosive media has been taken from Kijkduinen, **see figure 2**. For all experiments a volume of 500ml of solution was used. The exposing area of the samples was around 5 cm². This is used as working electrode. For the counter electrode is made use of a platinum mesh and for the reference electrode is made use of silver/silver chloride(Ag/AgCl). The initial potential of the scan was -0,2V and the final potential was 0,5V. Anodic and cathodic polarization curves were recorded. For the potentiodynamic polarization measurements is used the Solartron SI- 1287 Electrochemical Interface and Solartron 1218 multiplexer. For obtaining the measurement is the software ZView used.

Obtained values:

In addition to the polarization curve, other important data are obtained like the tafel slopes b_a and b_c , E_{corr} and the i_{corr} . From these values the corrosion rate of the tested samples can be calculated. The corrosion rate depends on the cathodic (reduction) and anodic (oxidation) reactions. there is a linear relationship between the corrosion rate, CR, and the corrosion current i_{corr} , according to the Faraday's law. The formula for the calculation of the corrosion rate is:

The corrosion rate was determine using the formula **see figure 8**. The corrosion current density i_{corr} was calculated using the tafel plot.

CR = Corrosion rate [m / s]

a = atomic mass [g / mol]

i = current density [A / m²]

n = Number of electrons exchanged in reaction

F = Faraday's constant (96500 C / mol)

D = Density [g / m³]

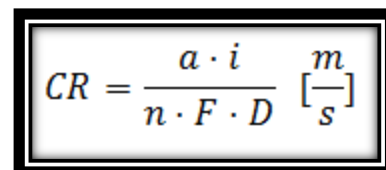

$$CR = \frac{a \cdot i}{n \cdot F \cdot D} \left[\frac{m}{s} \right]$$

Figure 8: Formula for corrosion rate by polarization

Surface study by microscopy

The corrosion on the mild steel and stainless steel surface after OCP and Polarization tests in seawater, artificial seawater and 3, 5 % NaCl solution was observed using optical microscope.

After the electrochemical study the mild steel samples were cleaned for corrosion products by immersing in samples in concentrated Hydrochloric acid that contains 50 g / L SnCl_2 and 20 g / L SbCl_3 in Ice bath, until the surface is clean. The samples were then carefully washed with distilled water, cleaned with an ultrasonic sound bath for 5 minutes in ethanol and dried.

The stainless steel samples were washed only with distilled water, cleaned with an ultrasonic sound bath for 5 minutes in ethanol and dried. The sample surface were observed using the Olympus-BX 60M computer controlled microscope, see **annex 6: specification Olympus-BX 60M microscope** for more information about the microscope. Observation was carried at different magnifications (5 x, 10x, 20x, 50x, 100x) and images were recorded.

3. Results and discussion

3.1 Corrosion rate by weight loss

Corrosion rate of mild steel was studied using the weight loss experiment. The weight loss of mild steel immersed in NaCl, artificial seawater and seawater after 1 week (168 h) duration is shown in **table 5**. From the weight loss, rate of corrosion of mild steel was calculated using the formula mention in Section 2.3.1. The corrosion rate obtained was converted in to the unit mm/year. The results are shown in the **table 5**.

Mild steel	Weight before	Weight after	Weight loss	Corrosion rate (mm/year)
Seawater	18,8839 g	18,8584 g	0,0246 g	0,097
Artificial seawater	18,3644 g	18,3370 g	0,0274 g	0,109
NaCl solution	18,2232 g	18,2016 g	0,0216 g	0,088

Table 5: Weight loss and corrosion rate of mild steel immersed in solutions for duration of 168 hours

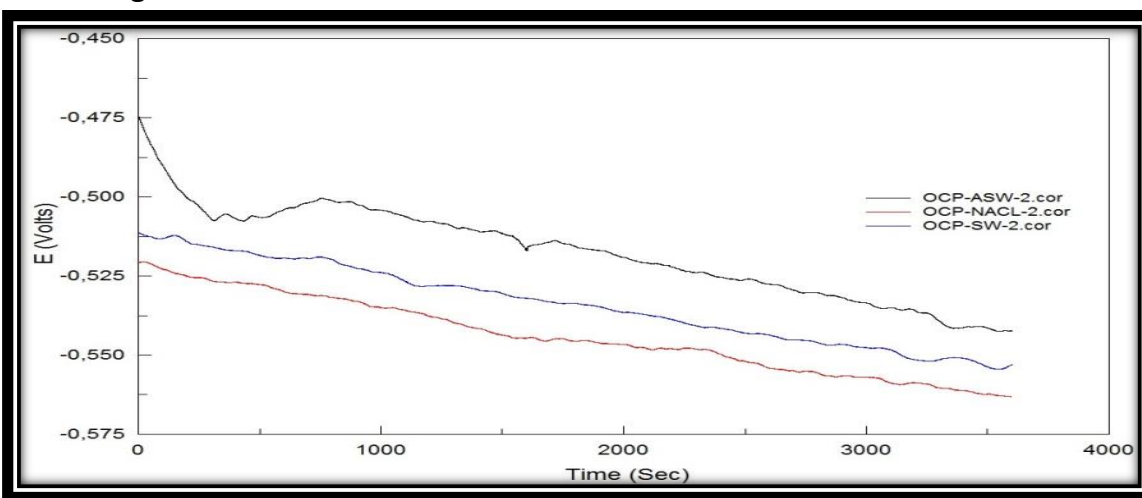
The corrosion rate of mild steel in seawater is 0,097 mm/year, in artificial seawater is 0,109 mm/year and in NaCl solution is 0,088 mm/year. No significant difference in corrosion rate of mild steel in different solution is observed.

3.2 Open circuit Potential

All the electrochemical measurements were done in replicates and confirmed that the measurements are reproducible and consistent. The most representative plot from each measurement is shown in the results below and the replicate measurements are attached as annexure, see **annex 6 and 7: OCP plots mild steel and stainless steel**.

Mild Steel

The OCP of mild steel in the three different aqueous solutions measure for a period of 1 hour is shown in **figure 9**



It is

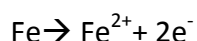
Figure 9: OCP of mild steel in the three aqueous solutions

observed that OCP of mild steel varies very little with respect to the different solutions. The starting and final potential of the above OCP measurements is shown in **table 6**. The OCP of mild steel in all the three solutions was moving towards the more negative potential with time and in the range of -550 to -475 mV.

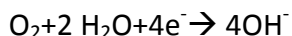
Mild steel	Initial potential (mV)	Final potential (mV)
seawater	-512 V	-554 V
artificial seawater	- 475 V	-543 V
NaCl solution	-521 V	-562 V

Table 6: OCP values mild steel in three aqueous solutions

It shows that, upon exposure to the solutions the Fe from the mild steel is dissolving in to solution as



And the cathodic reaction takes place as



However the reaction is not vigorous, hence only very small change in equilibrium potential occurs with time.

304 Stainless Steel

The OCP of stainless steel in the three solutions are shown in **figure 10**. The OCP of stainless steel in all the three solutions is observed to be steady with time compared to the OCP of mild steel. It is because there was not much activation on the surface of the samples. The initial and final potential values of the measurements are shown in **table 7**. The OCP of stainless steel in seawater is ~100 mV nobler than the OCP in artificial seawater and NaCl solution.

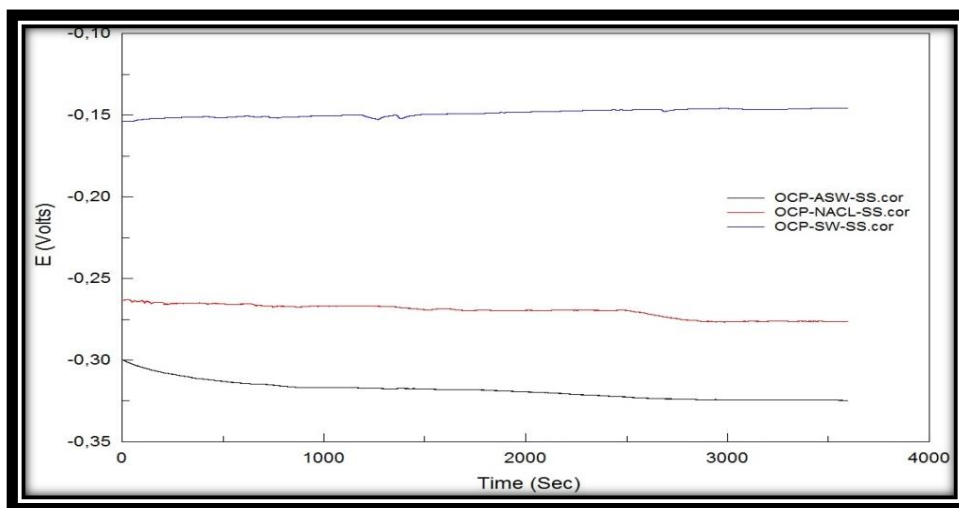


Figure 10: OCP of stainless steel in three aqueous solutions

Stainless steel	Initial potential (mV)	Final potential (mV)
seawater	-160 V	-150 V
artificial seawater	- 300 V	-325 V
NaCl solution	-265 V	-270 V

Table 7: OCP values stainless steel in three aqueous solutions

The increase in equilibrium potential of stainless steel in seawater is called ennoblement according to the study by (K.K. Turekian, 1968). When stainless steel or other metals such as platinum or titanium that have oxide layer on surface are exposed to seawater the free corrosion potential is increased. It is due to the micro-organisms present in the seawater which forms the bio-film on the surface. The microbial activity of the micro-organisms seems to increase the equilibrium potential of stainless steel.

Comparing the OCP of mild steel and stainless steel, it is clearly seen that the OCP of stainless steel is in the higher range approximately in the range of -200 mV while the mild steel is in the range of ~ -500 mV. It demonstrates the nobility of stainless steel compared to the mild steel. The resistance for corrosion is higher in stainless steel compared to the mild steel. The stainless steel has higher corrosion resistance because it has a passive chromium oxide layer on the top which prevents dissolution of Fe from the steel in the solution and further electrochemical reactions.

3.3 Potentiodynamic polarization measurements

Polarization of mild steel and stainless samples in the anodic and cathodic direction is plotted as potential(volts) in x-axis Vs. current density in the y-axis (A/cm^2). Such plot is called as Tafel plot. The x-axis is represented in logarithmic scale in order to accommodate large range of current values that occur during polarization.

Mild steel

The polarization of mild steel in the three aqueous solutions are given in **figure 11**. The corrosion behavior of mild steel in artificial seawater and natural seawater is similar while in NaCl solution more noble corrosion behavior was observed compared to the seawater and artificial seawater. In **annex 8: POLZ plots mild steel in three aqueous solutions** is shown all the polarization plots

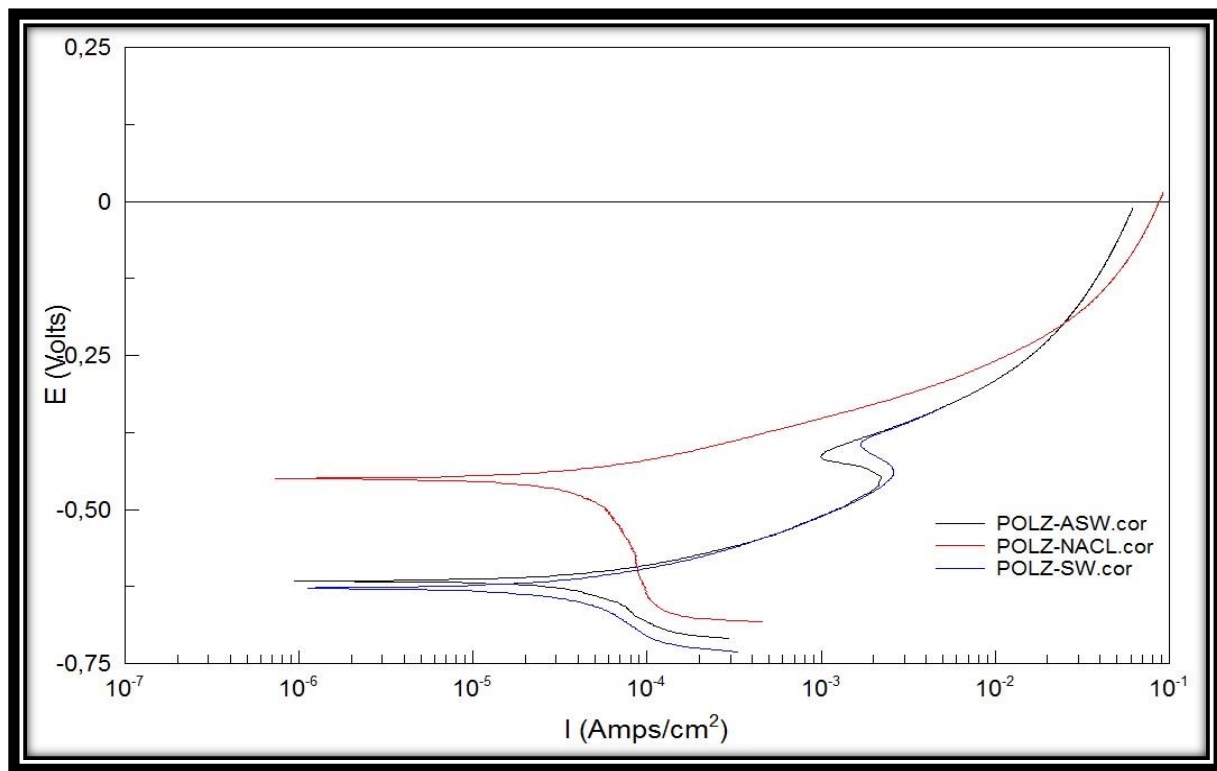


Figure 11: POLZ mild steel in three aqueous solutions

The E_{corr} and I_{corr} values are tabulated in **table 8**.

Steel	E_{corr} (mV)	I_{corr} (A/cm^2)
seawater	-633,75	6,42E-06
Artificial seawater	-620,48	6,41E-06
3,5 % NaCl	- 453,48	8,01E-06

Table 8: Mild steel values obtained from POLZ curves

The anodic polarization of mild steel in seawater and artificial seawater showed active corrosion with little reduction in current density at $\sim -500\text{mV}$, which might be due to the formation of temporary passive layer, however with increase in potential, the corrosion current is increased. In NaCl solution, the anodic polarization showed only active corrosion. It might be due to the influence of other salts present in the artificial and natural seawater. The cathodic polarization from the OCP corresponds to the reduction of oxygen and water in solution.

304 Stainless Steel

The polarisation curves of stainless steel in the three aqueous solutions are shown in **figure 12**. The polarisation behaviour of stainless steel is more noble in seawater than compared to the artificial seawater and NaCl solution. The E_{corr} and I_{corr} of the polarisation curves are given in **table 9**. In **annex 9: POLZ plots stainless steel in three aqueous solutions** is shown all the polarization plots

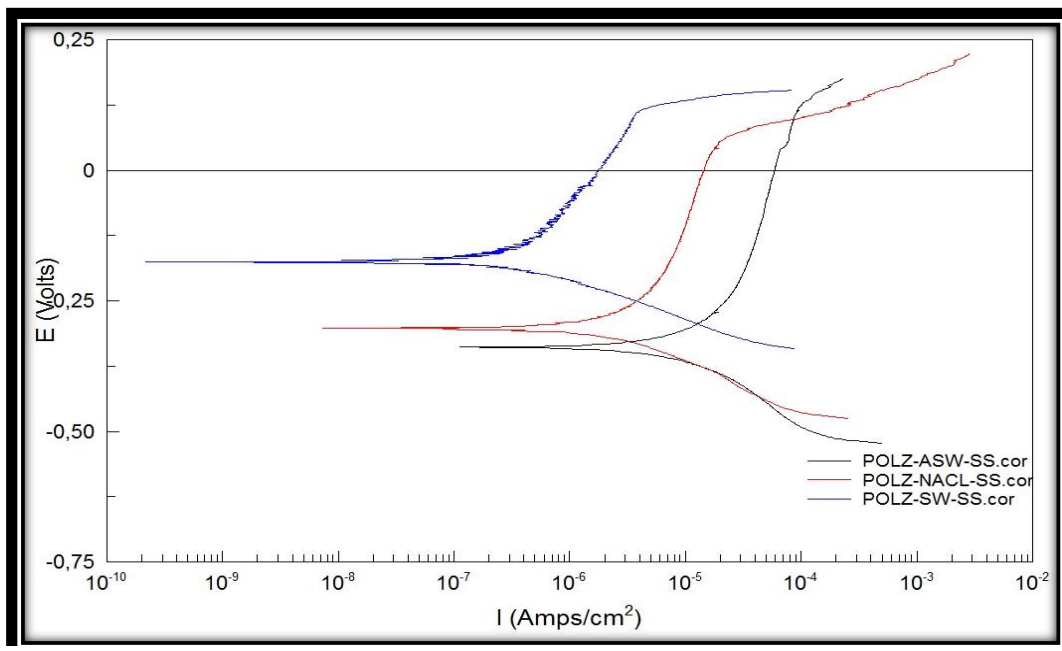


Figure 12: POLZ stainless steel in three aqueous solutions

The noble corrosion behavior of stainless steel in seawater is due to the ennoblement of the alloy as discussed in the **section 3.2**. Polarisation in the anodic direction resulted in the passive layer formation in all the three solutions. However with increase in potential the passive layer is broken and rapid increase in corrosion current was observed resulting in active corrosion.

Stainless Steel	E_{corr} (mV)	I_{corr} (A/cm ²)
seawater	-178,53	5,43E-08
Artificial seawater	-343,94	6,33E-07
3,5 % NaCl	- 288,56	1,85E-07

Table 9: Stainless steel values obtained from POLZ curves

3.4 Determination of corrosion rate from Tafel plot

The corrosion rate was determined using the formula, **see figure 8**. The corrosion current density i_{corr} was estimated from the experimental polarization curves. The i_{corr} was estimated from the Tafel slopes by intersecting the anodic and cathodic curves. An example of drawing the slopes on the curves and finding the i_{corr} is shown in **figure 13**.

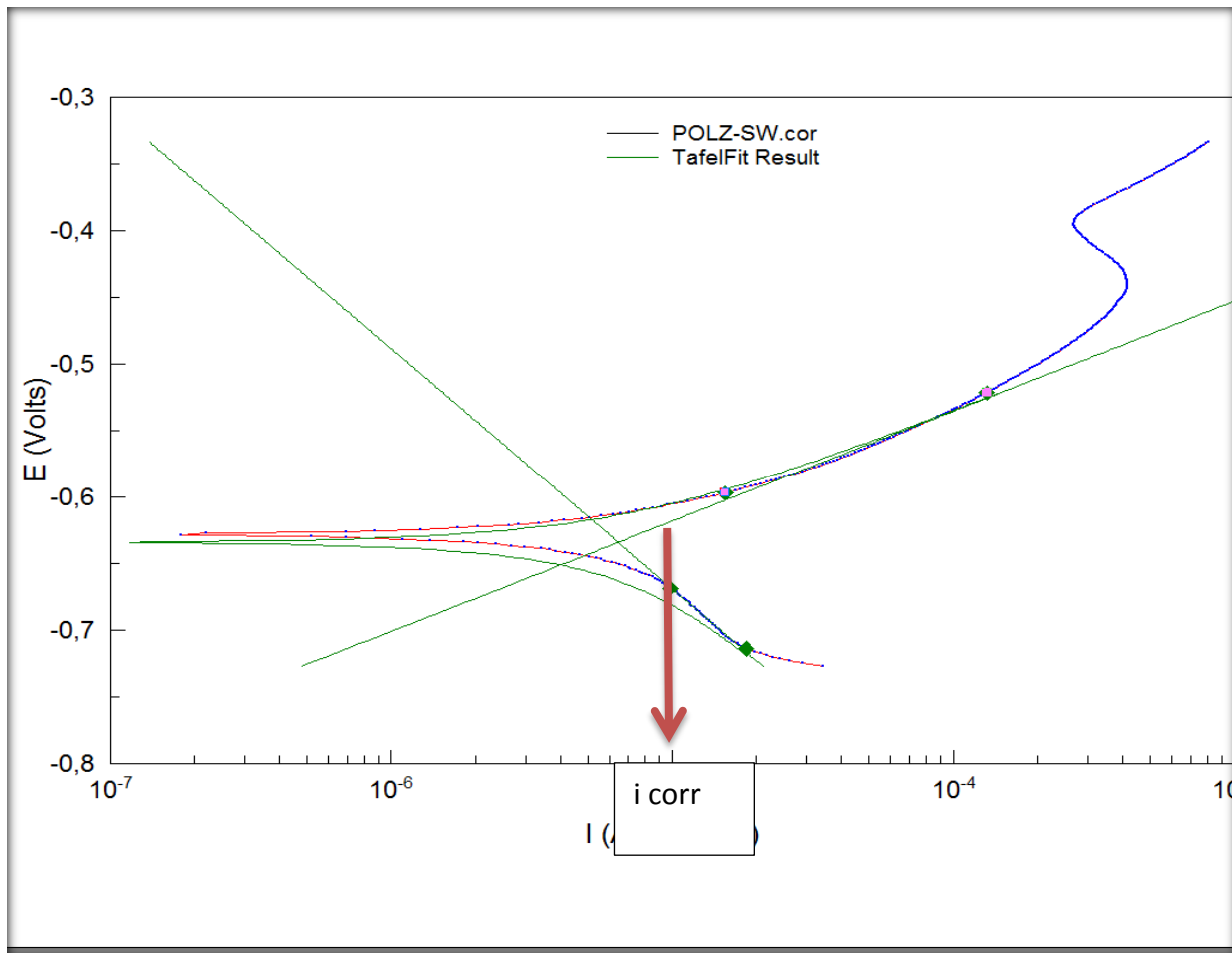


Figure 13: POLZ curves stainless steel in aqueous solutions

Mild Steel

The corrosion rate of mild steel in the three solutions calculated from the all the measurements are shown in the **table 10**. The average corrosion rate of mild steel in natural seawater, artificial seawater and NaCl solution is 0,075, 0,089 and 0,082 mm/year respectively. There is no significant difference in corrosion rate of mild steel in natural seawater, artificial seawater and NaCl solution. It is observed that the corrosion rate from weight loss method and polarisation method are similar and have little variation.

<u>Mild steel</u>	i_{corr} (A/Cm2)	CR (mm/year)	Average CR (mm/year)	STD (mm/year)	Mild Steel-Weight loss
SW	6,42E-06	0,0732	0,0754	0,02604	0,097
	4,43E-06	0,0506			
	8,99E-06	0,1025			
ASW	6,41E-06	0,0731	0,0883	0,013965	0,109
	8,81E-06	0,1005			
	8,00E-06	0,0913			
NaCl	8,01E-06	0,0914	0,0824	0,00811	0,088
	7,02E-06	0,0801			
	6,63E-06	0,0756			

Table 10: Corrosion rate mild steel in three aqueous solutions

304 Stainless Steel

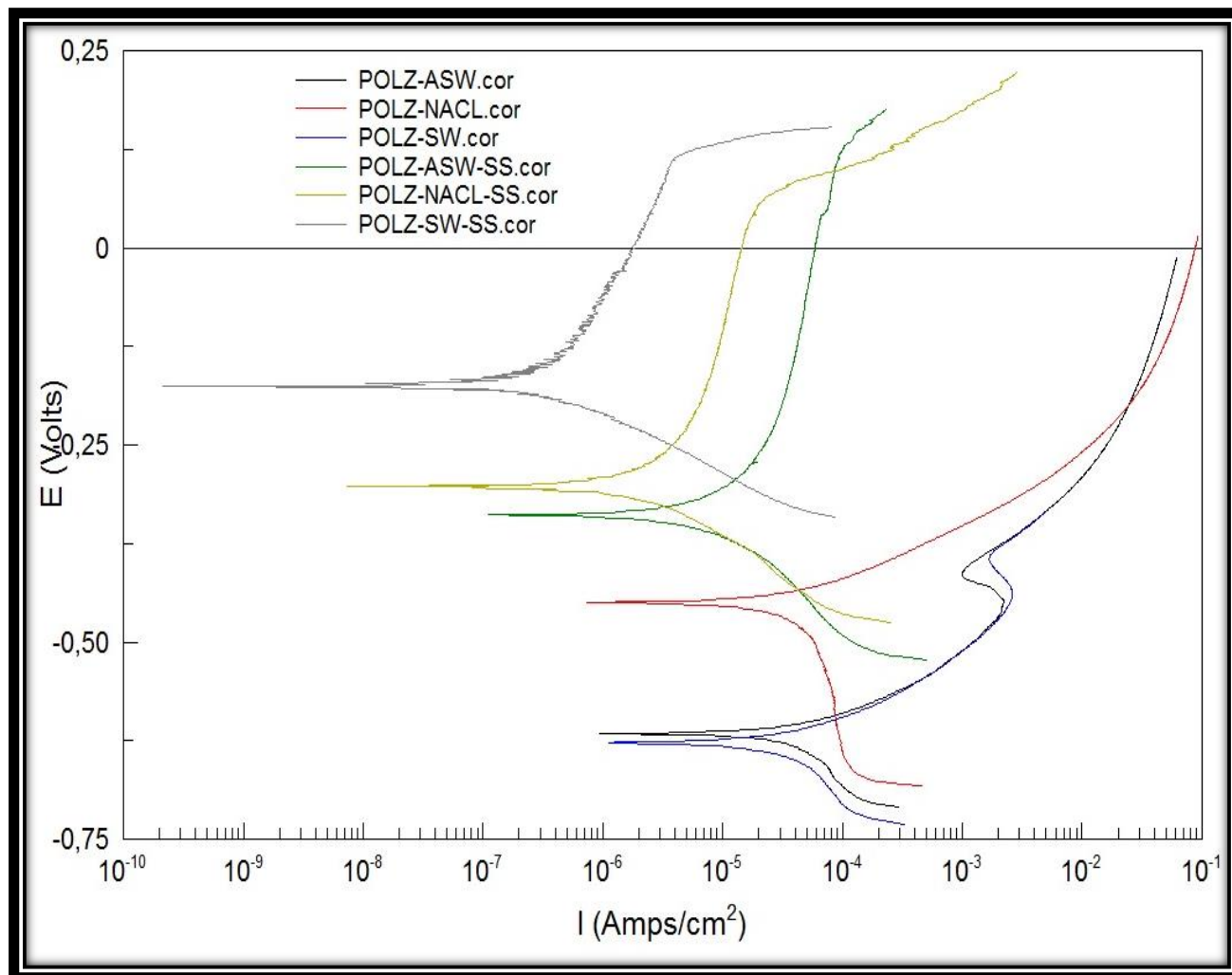
The corrosion current density i_{corr} and corrosion rate of stainless steel in the three solutions is given in **table 11**. The average corrosion rate of stainless steel in seawater, artificial seawater and NaCl is 0,0016; 0,0042 and 0,0017 respectively. There is no significant difference in corrosion rate of stainless steel in different solutions. However it has to be noted that, the deviation of data between different measurements is high. This is because the polarisation of stainless steel result in small active region and large passive region afterwards with increase in potential. The extrapolation of tafel plot in the active region becomes narrow and results in deviation of i_{corr} values.

Stainless Steel 304	i_{corr} (A/Cm2)	CR (mm/year)	Average CR (mm/year)	Standard deviation
SW	5,43E-08	6,27E-04	0,0016	0,0012
	2,55E-07	2,94E-03		
	9,76E-08	1,13E-03		
ASW	6,33E-07	7,32E-03	0,0042	0,0031
	9,18E-08	1,06E-03		
	3,54E-07	4,09E-03		
NaCl	1,85E-07	2,13E-03	0,0017	0,0008
	6,28E-08	7,26E-04		
	1,92E-07	2,22E-03		

Table 11: Corrosion rates stainless steel in three aqueous solutions

Comparison between Mild Steel and 304 Stainless Steel

The polarization plots of mild steel and stainless steel in the three solutions are shown in **Figure 14**. The curves of stainless steel are located at more positive potential. In general they showed lower current densities when compared to mild steel results. It indicates that stainless showed less corrosion or higher corrosion resistance compared to the mild steel. The curves of stainless showed a passive region during anodic polarization, which indicates the formation of passive layer, while mild steel showed active without any formation of strong passive layer. It is also clearly observed from the corrosion rate calculated for the mild steel and stainless steel.



The Figure 14: POLZ curves mild steel and stainless steel together

Corrosion rates of mild steel and stainless steel

Corrosion rates of mild steel and stainless steel are shown graphically in **figure 15** for comparison. The corrosion rate of mild steel calculated from the two different methods, weight loss and polarization experiments are shown in the **figure 15**. It is observed that the corrosion rate calculated from two different methods are comparable and not significantly different. The corrosion rate of stainless steel is very less approximately 10 times less compared to the mild steel.

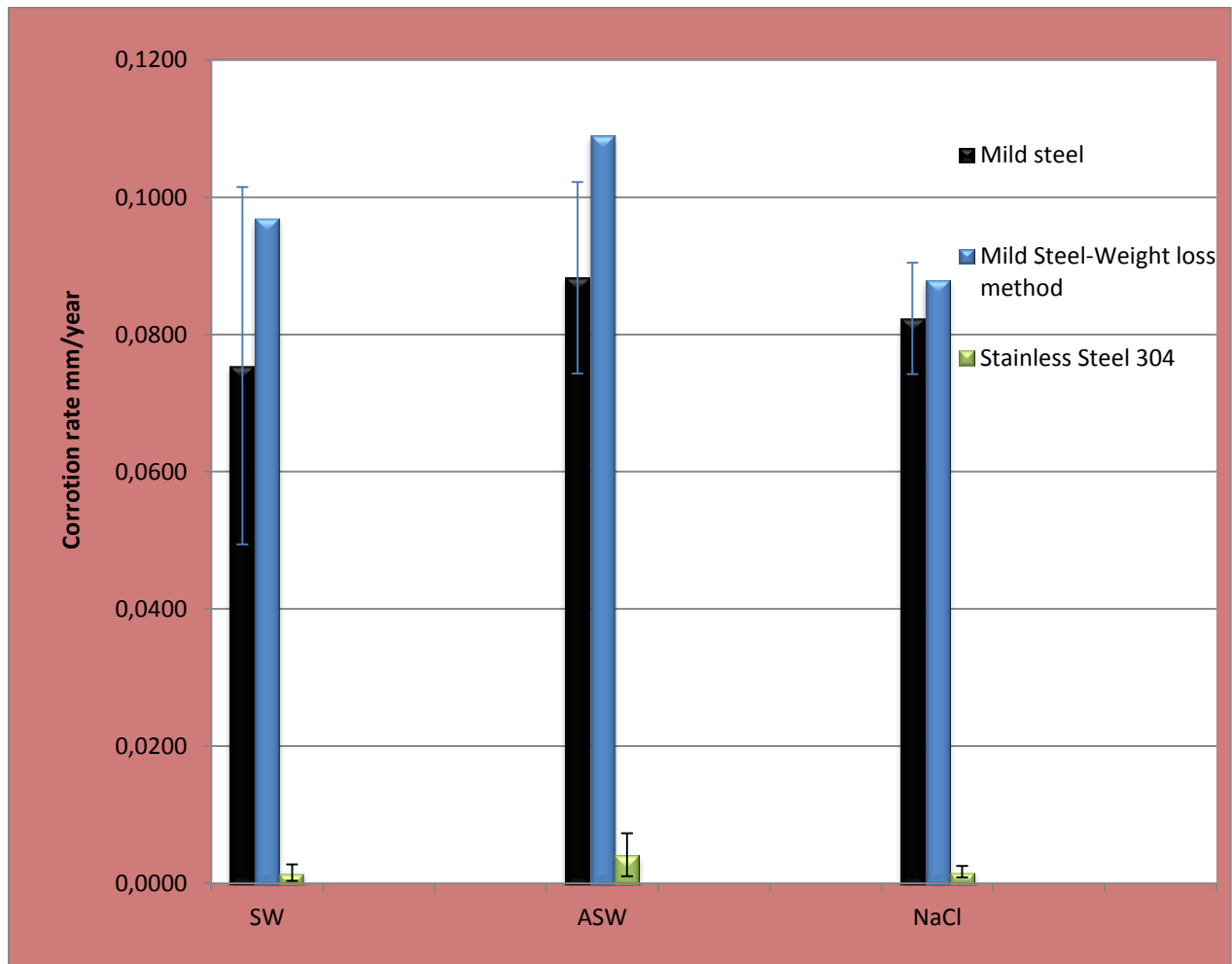


Figure 15: Beam graph corrosion rate mild steel and stainless steel

3.5 Surface study by optical microscope

The images of mild steel and stainless steel samples observed in optical microscope after polarization measurements are shown in **table 12**. The mild steel showed more uniform corrosion compared to the stainless steel where pitting corrosion has occurred. The mild steel samples immersed in seawater and 3,5% NaCl had the green/blue rust, this color is obtained from the Fe and O combination to form the oxide, $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$. Mild steel immersed in artificial seawater had a red-brown color, this rust color is obtained from the Fe and O combination to form the oxide, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. All the samples were almost 100 % covered with rust on the surface. See **annex 10: all the micrographs of the mild steel samples** for more micrographs of the samples.

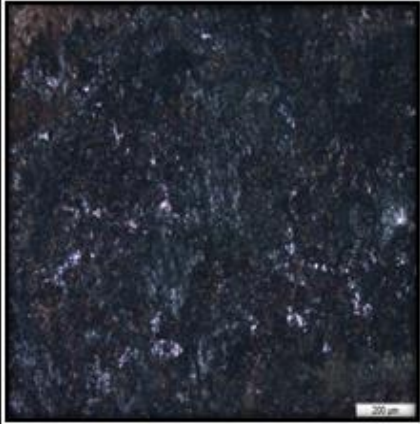
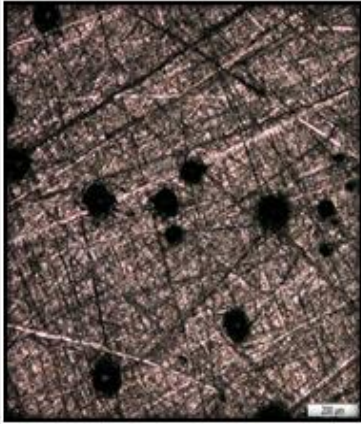

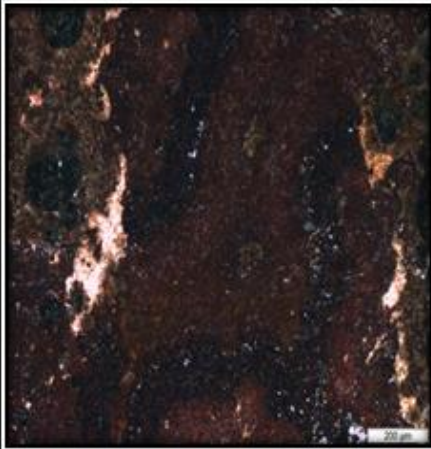
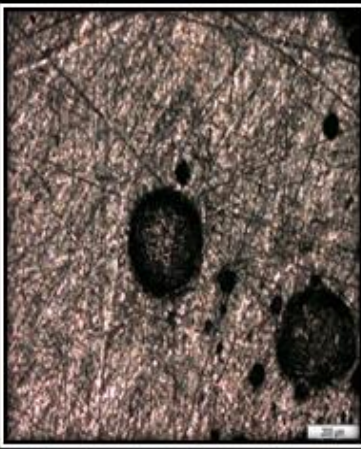

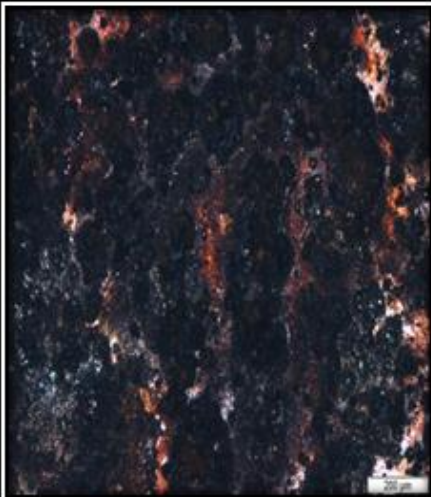
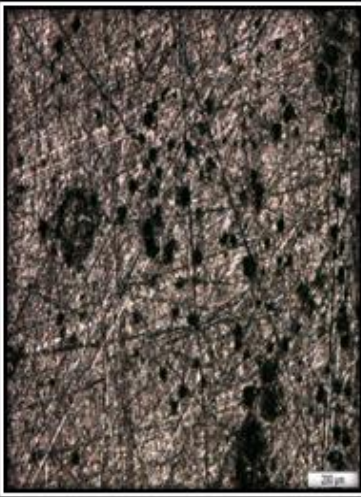

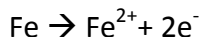
Micrograph, 5x(200 μm)	Mild Steel		304 Stainless Steel
	Before cleaning	After cleaning	
NSW			
ASW			
<u>NaCl</u>			

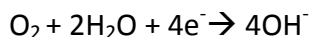
Table 12: Micrograph mild steel and stainless steel immersed in three aqueous solutions

The corrosion products are formed on the surface through following reactions:

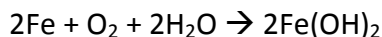
When mild steel is immersed in the salt solution



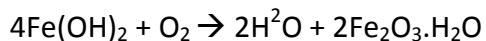
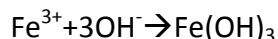
The electrons are consumed by the hydrogen ions from water and dissolved oxygen in the water



The hydroxide ions combine with Fe^{2+} ions to produce iron hydroxides



The Fe^{2+} ions further react with hydrogen ions and oxygen to produce Fe^{3+} ions. The Fe^{3+} ions react with hydroxide ions to produce hydrated iron oxides



$\text{Fe}(\text{OH})_3$ is a loose porous rust and transform into crystalline form as $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. When oxygen is limited Fe_3O_4 is formed, according to (Nimmo & Hinds, 2003).

After cleaning the mild steel in seawater and 3,5% NaCl solution, had all lot of little pits on the surface, mild steel in artificial seawater had less pits but the pits were bigger. The pits were spread on the surface of all the samples, but there were more pits on the edges of the samples.

The before cleaning pictures of stainless steel is not shown as stainless steel samples were cleaned only to remove the residual NaCl on the surface with water and ethanol. The stainless steel samples which are immersed in seawater and artificial seawater had almost the same kind of pits. There were pits spread all over the surface of the sample. For the stainless steel samples which are immersed in 3,5% NaCl solution the pits were small in size compared to the stainless steel immersed in seawater and artificial seawater. It might be due to the fact that there are more chloride ions in NaCl solution whereas in seawater and artificial seawater there are combinations of other ions such as Br^{-} , SO_4^{-} etc. See **annex 11: all the micrographs of the stainless steel samples** for all the micrographs of the stainless steel samples.

4. Conclusion

- The OCP of the mild steel in the three salt solutions shifted towards more negative values, indicating the activation of the surface. The OCP of 304 stainless steel is not shifted much in negative direction because there was not much activation on the surface of the samples. It is due to the formation of chromium oxide passive layer in stainless steel that prevents corrosion.
- The potentiodynamic polarization measurements correlate to the results from the OCP. The potentiodynamic polarization results of mild steel showed that in NaCl solution the corrosion behaviour was $\sim 200\text{mV}$ more noble compared to the artificial and natural seawater. However in all the three solutions active corrosion was observed during anodic polarisation.
- The potentiodynamic polarization results of 304 stainless steel showed in natural seawater the corrosion potential was noble compared to the artificial seawater and NaCl solution. The noble corrosion potential of stainless steel in natural seawater is due to the process of ennoblement that occurs due to the activity of the micro-organism present in the seawater. The polarisation behaviour of stainless steel in artificial seawater and NaCl is similar.
- The weight loss experiment showed also almost the similar corrosion rates for the mild steel in different salt solutions. Corrosion rate of mild steel determined by the polarisation method and weight loss method is similar and not significantly indifferent.
- There is significant difference in the corrosion rate between mild steel and stainless steel. The corrosion rate of mild steel is 10 times higher than the stainless steel.
- Microscopy surface analysis showed, that there are different sort of corrosion products on the surface of the mild steel after immersing in the three salt solutions. The reason for this is the different combinations of Fe and O. The mild steel samples immersed in seawater and 3,5% NaCl had the same green/blue rust, this color is obtained from the Fe and O combination : $\text{Fe}_3\text{O}_4 \cdot \text{H}_2\text{O}$. Mild steel immersed in artificial seawater had a red-brown colour, this rust colour is obtained from the Fe and O combination: $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. All the samples were almost 100 % covered with rust on the surface.
- After cleaning the mild steel in seawater and 3,5% NaCl solution had all lot of little pits on the surface, mild steel in artificial seawater had less pits but the pits were bigger.
- The stainless steel samples immersed in all the three salt solutions had had pits on the surface. However the size of the pits on samples immersed in seawater and artificial seawater is large compared to the size of pits formed on the surface immersed in NaCl solution.

5. Remarks and recommendations

The focus on this research was to study the corrosion behavior of mild steel and stainless steel immersed in three different salt solutions. The biofilm plays a role in the in the corrosion process. For the future research more focus should be put on the effect of the biofilm in a corrosion process. When the optimal concentration of the biofilm has been discovered, this can be used to see what the effect is of a biofilm layer on the steel and stainless steel samples. The microorganisms can also add to the NaCl solution and artificial seawater. After measuring the values of the samples in the solutions with the added microorganisms, is it possible to see what the correlation is between the samples with microorganism. Further is it possible to increase the microorganism to see how it effect on the corrosion process of the samples. In a future study could also be considered how certain coatings behave against bio corrosion. As mild steel is used a lot into the sea for example pipelines, platforms and much more industries.

6. References

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7. Annexes

Annex 1: specification stainless steel 304

P R O D U C T D A T A S H E E T

304/304L

STAINLESS STEEL

UNS S30400/UNS S30403



AK Steel

AK Steel Type 304 is a variation of the basic 18-8 grade, Type 302, with a higher chromium and lower carbon content. Lower carbon minimizes chromium carbide precipitation due to welding and its susceptibility to intergranular corrosion. In many instances, it can be used in the "as-welded" condition, while Type 302 must be annealed in order to retain adequate corrosion resistance.

Type 304L is an extra low-carbon variation of Type 304 with a 0.03% maximum carbon content that eliminates carbide precipitation due to welding. As a result, this alloy can be used in the "as-welded" condition, even in severe corrosive conditions. It often eliminates the necessity of annealing weldments except for applications specifying stress relief. It has slightly lower mechanical properties than Type 304.

Typical uses include architectural moldings and trim, kitchen equipment, welded components of chemical, textile, paper, pharmaceutical and chemical industry processing equipment.

AVAILABLE FORMS

AK Steel produces Type 304 Stainless Steel in thicknesses from 0.01" to 0.25" (0.025 to 6.35 mm) max. and widths up to 48" (1219 mm). For other thicknesses and widths, inquire.

COMPOSITION

	Type 304 %	Type 304L %
Carbon	0.08 max.	0.03 max.
Manganese	2.00 max.	2.00 max.
Phosphorus	0.045 max.	0.045 max.
Sulfur	0.030 max.	0.030 max.
Silicon	0.75 max.	0.75 max.
Chromium	18.00-20.00	18.0-20.0
Nickel	8.00-12.00	8.0-12.0
Nitrogen	0.10 max.	0.10 max.
Iron	Balance	Balance

SPECIFICATIONS

AK Steel Types 304 and 304L Stainless Steels are covered by the following specifications:

Type 304	Type 304L
AMS 5513	AMS 5511
ASTM A 240	ASTM A 240
ASTM A 666	ASTM A 666

MECHANICAL PROPERTIES

Typical Room Temperature Mechanical Properties

	UTS ksi (MPa)	0.2% YS ksi (MPa)	Elongation % in 2" (50.8 mm)	Hardness Rockwell
Type 304L	85 (586)	35 (241)	55	B80
Type 304	90 (621)	42 (290)	55	B82

PHYSICAL PROPERTIES

Density, 0.29 lbs/in³
8.03 g/cm³

Electrical Resistivity, microhm-in
(microhm-cm)

68°F (20°C) – 28.4 (72)

1200°F (659°C) – 45.8 (116)

Specific Heat, BTU/lb/°F (kJ/kg•K)

32 - 212°F (0 - 100°C) – 0.12 (0.50)

Thermal Conductivity, BTU/hr/ft²/ft/°F
(W/m•K)

at 212°F (100°C) – 9.4 (16.2)

at 932°F (500°C) – 12.4 (21.4)

Mean Coefficient of Thermal Expansion,
in/in/°F (µm/m•K)

32 - 212°F (0 - 100°C) – 9.4×10^{-6} (16.9)

32 - 600°F (0 - 315°C) – 9.6×10^{-6} (17.3)

32 - 1000°F (0 - 538°C) – 10.2×10^{-6} (18.4)

32 - 1200°F (0 - 649°C) – 10.4×10^{-6} (18.7)

Magnetic Permeability, H = 200

Oersteds, Annealed - 1.02 max.

Modulus of Elasticity, ksi (MPa)

28.0×10^3 (193×10^3) in tension

11.2×10^3 (78×10^3) in torsion

Melting Range, °F (°C) – 2550 - 2650

(1399 - 1454)

CORROSION RESISTANCE

These steels exhibit excellent resistance to a wide range of atmospheric, chemical, textile, petroleum and food industry exposures.

OXIDATION RESISTANCE

The maximum temperature to which Types 304 and 304L can be exposed continuously without appreciable scaling is about 1650°F (899°C). For intermittent exposure, the maximum exposure temperature is about 1500°F (816°C).

HEAT TREATMENTS

Type 304 is non-hardenable by heat treatment. Annealing: Heat to 1900 - 2050°F (1038 - 1121°C), then cool rapidly. Thin strip sections may be air cooled, but heavy sections should be water quenched to minimize exposure in the carbide precipitation region.

Stress Relief Annealing: Cold worked parts should be stress relieved at 750°F (399°C) for 1/2 to 2 hours.

FORMABILITY

Types 304 and 304L have very good drawability. Their combination of low yield strength and high elongation permits successful forming of complex shapes. However, these grades work harden rapidly. To relieve stresses produced in severe forming or spinning, parts should be full annealed or stress-relief annealed as soon as possible after forming.

WELDABILITY

The austenitic class of stainless steels is generally considered to be weldable by the common fusion and resistance

techniques. Special consideration is required to avoid weld "hot cracking" by assuring formation of ferrite in the weld deposit. Types 304 and 304L are generally considered to be the most common alloys of this stainless class. When a weld filler is needed, AWS E/ER 308, 308L or 347 are most often specified. Types 304 and 304L Stainless Steels are well known in reference literature and more information can be obtained in this way.

METRIC CONVERSION

Data in this publication are presented in U.S. customary units. Approximate metric equivalents may be obtained by performing the following calculations:

Length (inches to millimeters) –

Multiply by 25.4

Strength (ksi to megapascals or meganewtons per square meter) –

Multiply by 6.8948

Temperature (Fahrenheit to Celsius) –

(°Fahrenheit - 32) Multiply by 0.5556

Density (pounds per cubic inch to kilograms per cubic meter) –

Multiply by 27,670

The information and data in this product data sheet are accurate to the best of our knowledge and belief, but are intended for general information only. Applications suggested for the materials are described only to help readers make their own evaluations and decisions, and are neither guarantees nor to be construed as express or implied warranties of suitability for these or other applications.

Data referring to mechanical properties and chemical analyses are the result of tests performed on specimens obtained from specific locations with prescribed sampling procedures; any warranty thereof is limited to the values obtained at such locations and by such procedures. There is no warranty with respect to values of the materials at other locations.

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Annex 2: Specification NaCl

SIGMA-ALDRICH®

sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: www.sigmaaldrich.com

Email USA: techserv@sial.com

Outside USA: eurtechserv@sial.com

Product Specification

Product Name:
Sodium chloride - ReagentPlus®, ≥99%

Product Number:	S9625	NaCl
CAS Number:	7647-14-5	
MDL:	MFCD00003477	
Formula:	ClNa	
Formula Weight:	58.44 g/mol	

TEST	Specification
Appearance (Color)	White
Appearance (Form)	Powder or Crystals
Solubility (Color)	Colorless
Solubility (Turbidity)	Clear
100 mg/mL, H ₂ O	
Titration with AgNO ₃	99.0 - 101.5 %
Recommended Retest Period	-----
6 years	

Specification: PRD.3.ZQ5.10000021771

Annex 3: Specification artificial seawater

SIGMA-ALDRICH®

sigma-aldrich.com

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: www.sigmaaldrich.com

Email USA: techserv@sial.com

Outside USA: eurtechserv@sial.com

Product Specification

Product Name:

Sea salts

Product Number:

S9883

TEST

Specification

Appearance (Color)	White
Appearance (Form)	Powder
Solubility (Color)	Colorless
Solubility (Turbidity)	Clear
38 mg/ml, Water	
Chloride (Cl)	Conforms
19290 mg/L	
Sodium	Conforms
10780 mg/L	
Sulfate	Conforms
2660 mg/L	
Potassium	Conforms
420 mg/L	
Calcium	Conforms
400 mg/L	
Carbonate	Conforms
(Bicarbonate)	
200 mg/L	
Strontium	Conforms
8.8 mg/L	
Boron	Conforms
5.6 mg/L	
Bromide	Conforms
56 mg/L	

3050 Spruce Street, Saint Louis, MO 63103, USA

Website: www.sigmaaldrich.comEmail USA: techserv@sial.comOutside USA: eurtechserv@sial.com

Product Specification

Product Name:

Sea salts

Product Number:

S9883

TEST**Specification**

Iodide	Conforms
0.24 mg/L	
Lithium	Conforms
0.3 mg/L	
Fluoride	Conforms
1.0 mg/L	
Magnesium (Mg)	Conforms
1320 mg/L	
Note	Conforms
Typical Ion Concentration of sea water. Also contains < 0.5 mg/L other trace elements.	

Specification: PRD.0.ZQ5.10000031869

Annex 4: Electrochemical cell setup



Autolab Application Note EC08

Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup

Keywords

Potentiostat, galvanostat, PGSTAT, electrochemical cell, reference electrode, counter electrode, working electrode

Summary

A basic overview of the working principle of a potentiostat/galvanostat is presented. Depending on the application, the connections of the instrument to the electrochemical cell can be (or must be) set up in different ways. Below, the three commonly used electrochemical cell setups are discussed together with the role of the electrodes used in electrochemical measurements.

Basic principle of a potentiostat/galvanostat (PGSTAT)

A basic diagram of a PGSTAT is presented in Figure 1.

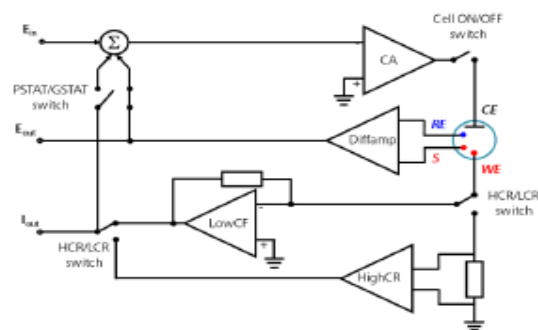


Figure 1 – Basic diagram of a potentiostat/galvanostat

In *potentiostatic mode*, a potentiostat/galvanostat (PGSTAT) will accurately control the potential of the *Counter Electrode* (CE) against the *Working Electrode* (WE) so that the potential difference between the working electrode (WE) and the *Reference Electrode* (RE) is well defined, and correspond to the value specified by the user. In *galvanostatic mode*, the current flow between the WE and the CE is controlled. The potential difference between the RE and WE and the current flowing between the CE and WE are continuously monitored. By using a PGSTAT, the

value specified by the user (i.e. applied potential or current) is accurately controlled, anytime during the measurement by using a negative feedback mechanism.

As can be seen from the diagram, the CE is connected to the output of an electronic block which is called *Control Amplifier* (CA). The control amplifier forces current to flow through the cell. The value of the current is measured using a *Current Follower* (LowCF) or a *Shunt* (HighCR), for low and high currents, respectively. The potential difference is measured always between the RE and S with a *Differential Amplifier* (Diffamp). Depending on the mode the instrument is used (potentiostatic or galvanostatic) the PSTAT/GSTAT switch is set accordingly.

The signal is then fed into the *Summation Point* (Σ) which, together with the waveform set by the digital-to-analog converter (E_{in}) will be used as an input for the control amplifier.

The cell cables of the Autolab PGSTAT (figure 2) have a total of five connectors: WE, CE, RE, S and ground. The potential is always measured between the RE (blue) and the S (red) and the current is always measured between the WE (red) and CE (black). The ground connector (green) can be used to connect external devices to the same ground of the PGSTAT.

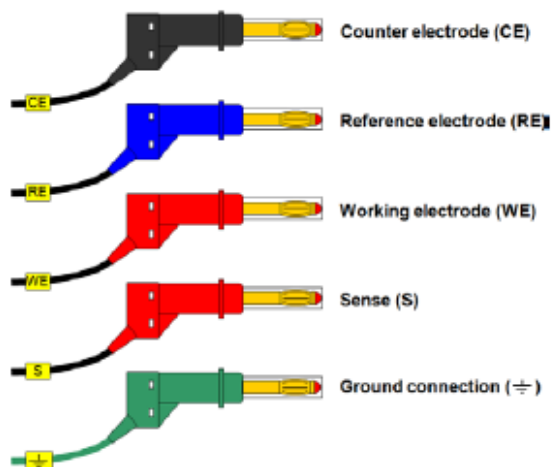


Figure 2 - The connections available on the cell cables of the Autolab PGSTAT and the color code used

Note: some Autolab instruments are not fitted with the S connector (like the μ Autolab type III). In these instruments, the potential difference is measured between the RE and the WE.

Electrodes used in Electrochemistry

The counter electrode (also known as auxiliary electrode), is an electrode which is used to close the current circuit in the electrochemical cell. It is usually made of an inert material (e.g. Pt, Au, graphite, glassy carbon) and usually it does not participate in the electrochemical reaction. Because the current is flowing between the WE and the CE, the total surface area of the CE (source/sink of electrons) must be higher than the area of the WE so that it will not be a limiting factor in the kinetics of the electrochemical process under investigation.

The reference electrode is an electrode which has a stable and well-known electrode potential and it is used as a point of reference in the electrochemical cell for the potential control and measurement. The high stability of the reference electrode potential is usually reached by employing a redox system with constant (buffered or saturated) concentrations of each participants of the redox reaction. Moreover, the current flow through the reference electrode is kept close to zero (ideally, zero) which is achieved by using the CE to close the current circuit in the cell together with a very high input impedance on the electrometer ($> 100 \text{ G}\Omega$).

Autolab Application Note EC08

Basic overview of the working principle of a potentiostat/galvanostat (PGSTAT) – Electrochemical cell setup

Figure 3 provides an overview of some commonly used reference electrodes.

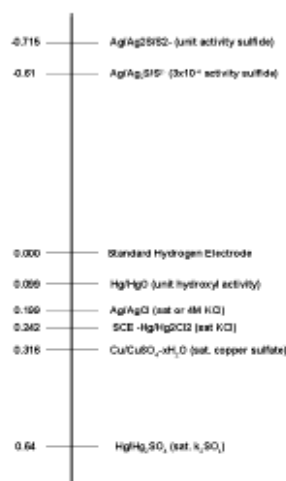


Figure 3 – Potential scale of commonly used reference electrodes (at 25 °C, liquid junction potentials are not considered)

The working electrode is the electrode in an electrochemical system on which the reaction of interest is occurring. Common working electrodes can be made of inert materials such as Au, Ag, Pt, glassy carbon (GC) and Hg drop and film electrodes etc. For corrosion applications, the material of the working electrode is the material under investigation (which is actually corroding). The size and shape of the working electrode also varies and it depends on the application.

Electrochemical cell setups with Autolab PGSTATS

Two electrode setup

In a two-electrode cell setup (see Figure 4), CE and RE are shorted on one of the electrodes while the WE and S are shorted on the opposite electrode. The potential across the complete cell is measured. This includes contributions from the CE/electrolyte interface and the electrolyte itself. The two-electrode configuration can therefore be used whenever precise control of the interfacial potential across the WE electrochemical interface is not critical and the behavior of the whole cell is under investigation. This setup is typically used with energy storage or conversion devices like batteries, fuel cells, photovoltaic panels etc... It is also used in measurements of ultrafast dynamics of electrode processes or electrochemical impedance measurements at high frequencies ($> 100 \text{ kHz}$).

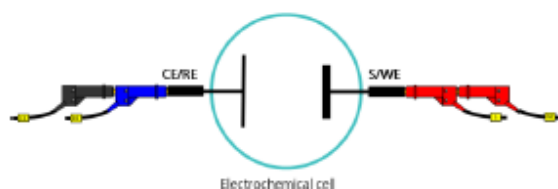


Figure 4 – Schematic view of the 2 electrode setup

Note: to avoid ohmic losses in high current applications, it is recommended to connect the S and RE leads directly to the cell, as indicated in Figure 4.

Three electrode setup

The three-electrode cell setup is the most common electrochemical cell setup used in electrochemistry (see Figure 5). In this case, the current flows between the CE and the WE. The potential difference is controlled between the WE and the CE and measured between the RE (kept at close proximity of the WE) and S. Because the WE is connected with S and WE is kept at pseudo-ground (fixed, stable potential), by controlling the polarization of the CE, the potential difference between RE and WE is controlled all the time. The potential between the WE and CE usually is not measured. This is the voltage applied by the control amplifier and it is limited by the compliance voltage of the instrument. It is adjusted so that the potential difference between the WE and RE will be equal to the potential difference specified by the user. This configuration allows the potential across the electrochemical interface at the WE to be controlled with respect to the RE.

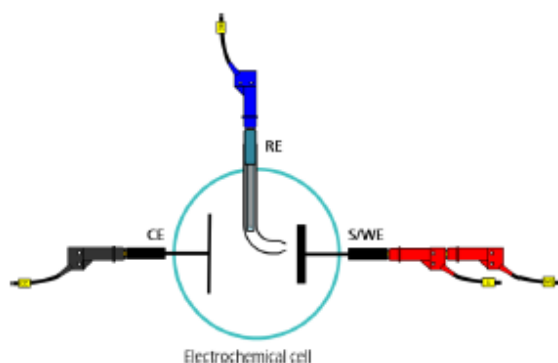


Figure 5 – Schematic view of the 3 electrode setup

To decrease the ohmic losses due to the existence of residual solution between the RE and WE (called the *Uncompensated resistance*), a so-called Luggin-Haber (or

just Luggin) capillary can be used to bring the RE extremity as close as possible to the surface of the WE (see Figure 5). Since almost no current flows into the reference electrode (typically, the leakage current is a few pA at most), there is little or no voltage drop across the capillary, ensuring that the extremity of the capillary is at a potential very close to the potential of the RE.

Four electrode setup

The four-electrode cell setup (see Figure 6) is used for applications where the potential difference (between RE and S) which occurs as a result of a passage of a current across a well defined interface (between WE and CE) needs to be measured. This type of experimental setup is not very common in electrochemistry and usually it is used for measurements of junction potentials between two non miscible phases or across a membrane, giving the possibility to calculate the resistance of the interface or the membrane conductivity.

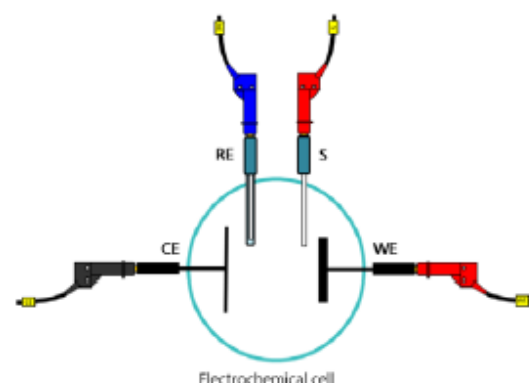


Figure 6 – Schematic view of the 4 electrode setup

References

- A. Bard, L. Faulkner, *Electrochemical Methods – Fundamental and Applications*, 2nd Edition, John Wiley and sons

Date

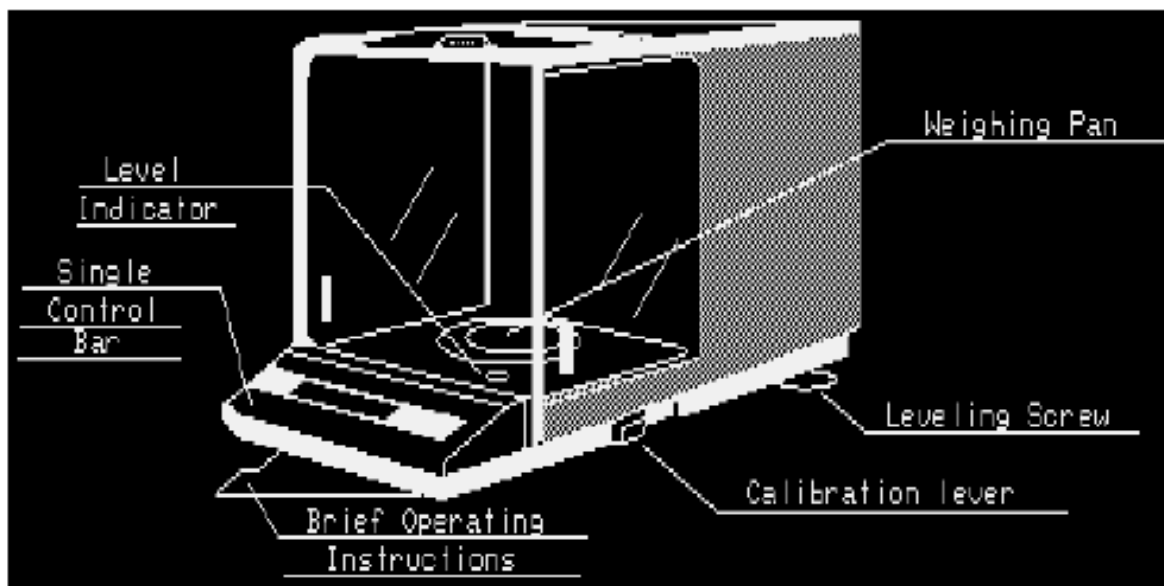
20 December 2011

Annex 5: Specification METTLER AE50 Libra

MODELS AE 50/100 and/or AE 160/200

The single pan electronic balance works off of the theory of a double pan mechanical balance, but is a much faster and unencumbered process. The procedure, basically, consists of establishing a calibrated zero point, placing an object on the pan, and reading the mass presented on the digital display.

First, you will be familiarized with the balance controls. Discussion of the calibration and measuring cycle will then be explained. Finally, the actual massing process will be determined.



START-UP

First, inspect the balance for scattered chemicals on or nearby the balance. Use the small artist's brush to clean the pan and inside the balance chamber. Do not blow air through the chamber!

If chemical is underneath the pan, you may remove the pan by lifting it, in a vertical fashion, off of its pedestal. Clean the chamber with the artist's brush and then replace the pan upon the pedestal.

Check the bubble inside the chamber to see if the balance is level. If not, adjust the leveling screw(s) until adequate. At this point, all balance doors should be closed.

Lightly press the control bar DOWN and then release. You will feel a faint 'click' when this function is performed properly. Immediately the digital mass display will show the following for a few seconds.

8.8.8.8.8.8.8.8. g

This display will then be automatically followed by:

- - - - g

massing or taring) after the stability detector lamp goes out. If selection 3 (ASd off) is made, the digital display can be read at any time. The stability detector lamp will remain off at all times while in this mode. Since this is the case, fluctuations in the mass readings are normal and the operator must decide which mass readings to accept.

TARING/MASSING

When massing chemical reagents that require a container, it is faster and much more convenient to zero the balance with the container on the balance pan. In this way, the digital mass displayed will reflect only the mass of the chemical.

To tare out the container's mass, simply place the container on the pan.

Close all balance doors.

Press the control bar down once and release.

The digital mass display will then read 0.0000.

At this point, whatever is placed inside the container will be massed directly.

To obtain the mass of a reagent, simply open the balance door(s), add the required amount of chemical to the container and then close the balance door(s).

Wait for the stability detector lamp to go dark and then read the digital mass display.

If the stability detector was switched off, then the display may be read at anytime.

i.e.



stability detector

CARE AND MAINTENANCE

The balance pan and housing may be cleaned with a soft cloth containing soapy water.

DO NOT USE ANY STRONG SOLVENTS!

The small artist's brush may be used to remove residues from the massing chamber.

REPLACING THE MICROFUSE

If a microfuse becomes defective (indicated by a total power loss to the balance), then proceed as follows.

1. Disconnect the power cable.
2. Locate the fuse holder (directly above the 3-prong power socket).
3. With a small screwdriver and from the bottom of the fuse holder, pry the fuse holder out by turning the tool in the bottom notch.
4. Replace with the proper fuse(s).
5. Replace the fuse holder to the balance.
6. Plug the power cable in the balance.

Annex 6: specification Olympus-BX 60M microscope

// **SPECIFICATIONS**

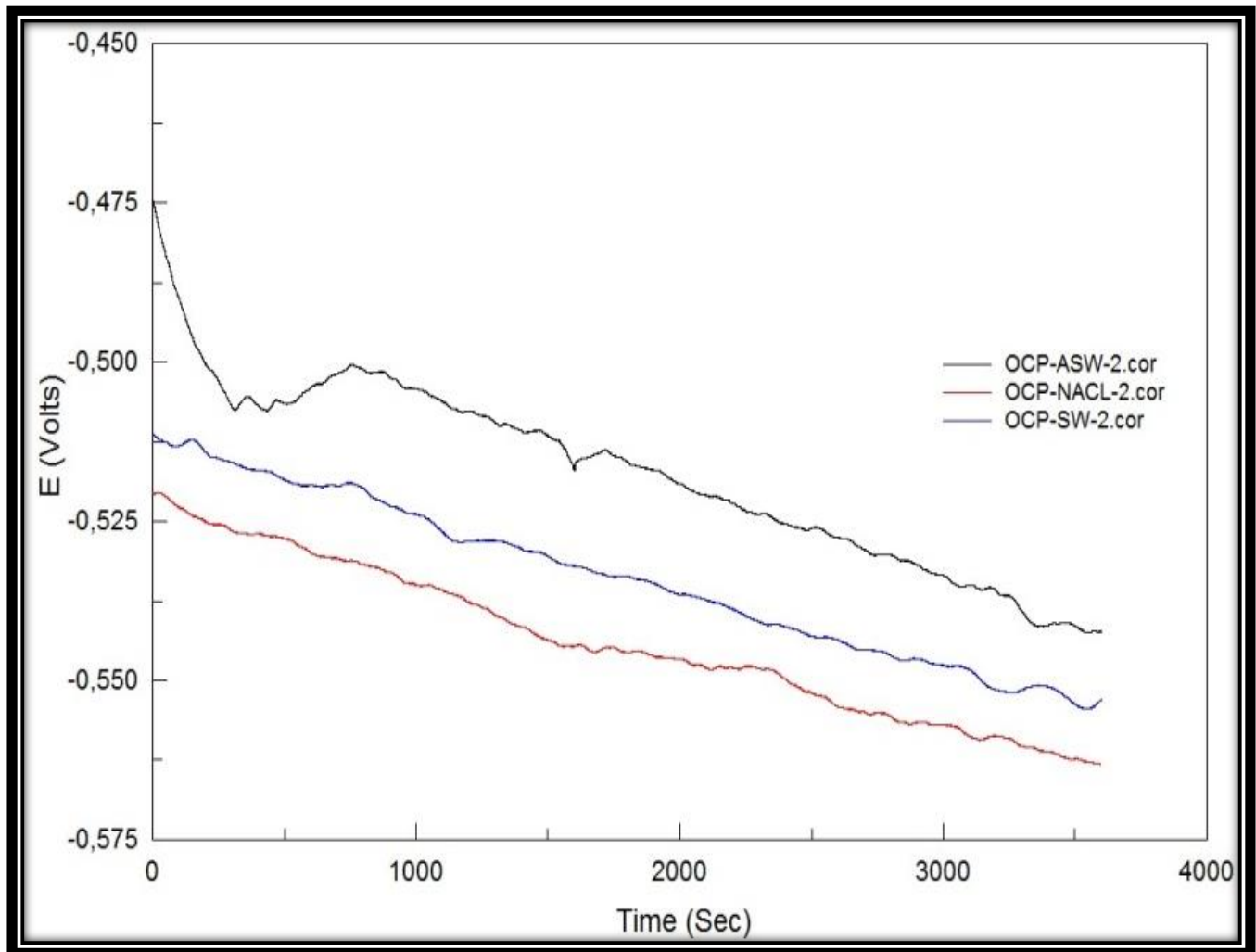
Item	Specification				
(1) Optical system	UIS (Universal Infinity System) optical system				
(2) Transmitted light illumination	Built-in transmitted Koehler illumination (Super widefield applicable: Field number 26.5)				
(3) Reflected light illumination	Brightfield/darkfield mirror cube housing/ collector lens unit		Universal cube housing/ collector lens unit		
	Observation tube magnification: 1X; (Super widefield applicable: Field number 26.5)				
	Observation mode selection: Slide system BF ↔ DF		Observation mode selection: Turret system (max. four cubes)		
	Possible observation modes: • Reflected light brightfield • Reflected light darkfield • Reflected light Nomarski differential interference contrast • Reflected light simple polarized • Transmitted light		Possible observation modes: • Reflected light fluorescence • Reflected light fluorescence/ transmitted light Nomarski differential interference contrast • Reflected light fluorescence/ transmitted light phase contrast • Reflected light brightfield • Reflected light darkfield • Reflected light Nomarski differential interference contrast • Reflected light simple polarized • Transmitted light		
(4) Electrical system (transmitted light/ reflected light)	12V 100W Halogen bulb (pre-centered) 12V 100W HAL-L (PHILIPS 7724) Light intensity DC 1.0V-12.0V (continuous) Light preset switch (setting range 1.0V-12.0V) Rated current 100-120/220-240V-2.8/1.8A 50/60 Hz Fuse  T5A(H) 250V (LITTELFUSE 215005) Transmitted light/reflected light selector switch				
(5) Focusing	Stage movement by roller guide (Rack & Pinion) Stroke per rotation: 0.1 mm (fine), 15 mm (coarse) Full range stroke: 25 mm Upper limit stopper Torque adjustment on coarse focus knob				
(6) Revolving nosepiece	Type	U-6RE Sextuple	U-5BDRE Quintuple	U-D5BDRE Universal reversed quintuple	U-D6RE Universal reversed sextuple
	Attachment	None		DIC prism for transmitted light	
(7) Observation tube	Type	U-BI30 Widefield binocular		U-TR30 Widefield trinocular	U-SWTR Super widefield trinocular
	Field No.	22			26.5
	Tube inclination	30°			
	Interpupillary distance adjustment	50 mm - 76 mm			
	Light path selector	None		3 steps: ① Bi 100% ② Bi 20%, photo 80% ③ Photo, video 100%	

Item		Specification		
(8) Stage	Type	U-SVRD (B) Common axis with low positioned co-axial knobs on the right side (rectangular ceramic coated stage)	U-SVLD (B) Common axis with low positioned co-axial knobs on the left side (rectangular ceramic coated stage)	U-SIC4L (R) Large mechanical stage with left-hand (right-hand) low drive control knobs
	Size	135 mm (D) X 180 mm (W)		169 mm (D) X 216 mm (W)
	Movement mechanism	Adjustable vertical and horizontal knob tension Movement range: 52 mm vertically, 76 mm horizontally		Movement range: 100 mm vertically, 105 mm horizontally
	Specimen holder	Double slide holder*		Adjustable
(9) Condenser	Type	U-AC Abbe condenser	U-SC Swing-out condenser	U-AAC Achromat aplanat condenser
	N.A.	1.25	0.9 - 0.16	1.40
	Aperture iris diaphragm	With numerical aperture scale		
	Applicable objectives	4X to 100X (for wide-field observations) 10X-100X (for super wide-field observations)	2X to 100X (for wide to super widefield observations)	10X to 100X (for wide to super widefield observations)

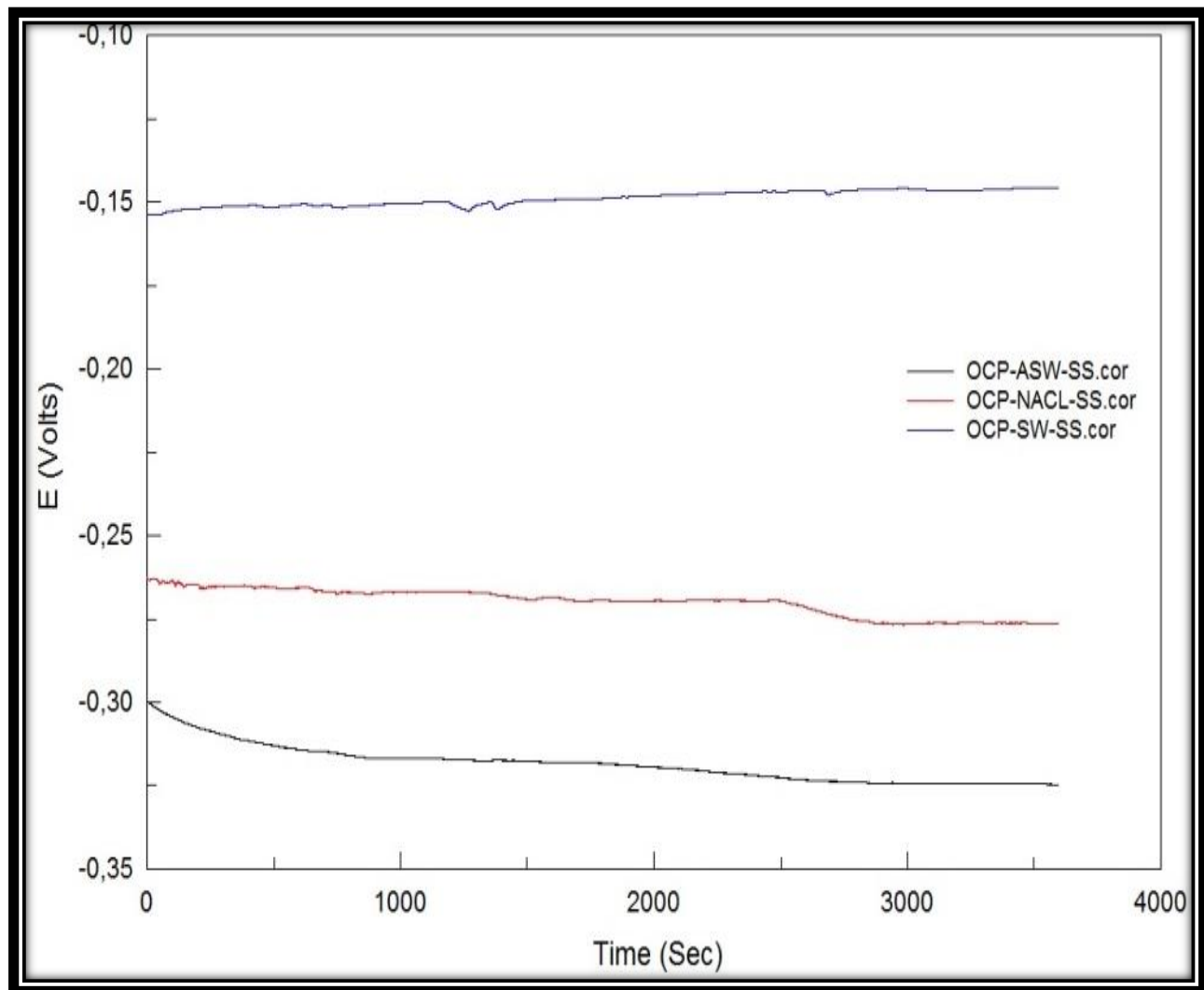
*One-hand operation slide holder

Operating environment	<ul style="list-style-type: none"> Indoor use Altitude up to 2000 m Temperature: 5° to 40°C (41° to 104°F) Maximum relative humidity 80% for temperatures up to 31°C (88°F) decreasing linearly to 50% relative humidity at 40°C (104°F) Main supply voltage fluctuations not to exceed $\pm 10\%$ of the nominal voltage Installation/Overvoltage Category II (in accordance with IEC664) Pollution Degree 2 (in accordance with IEC664)
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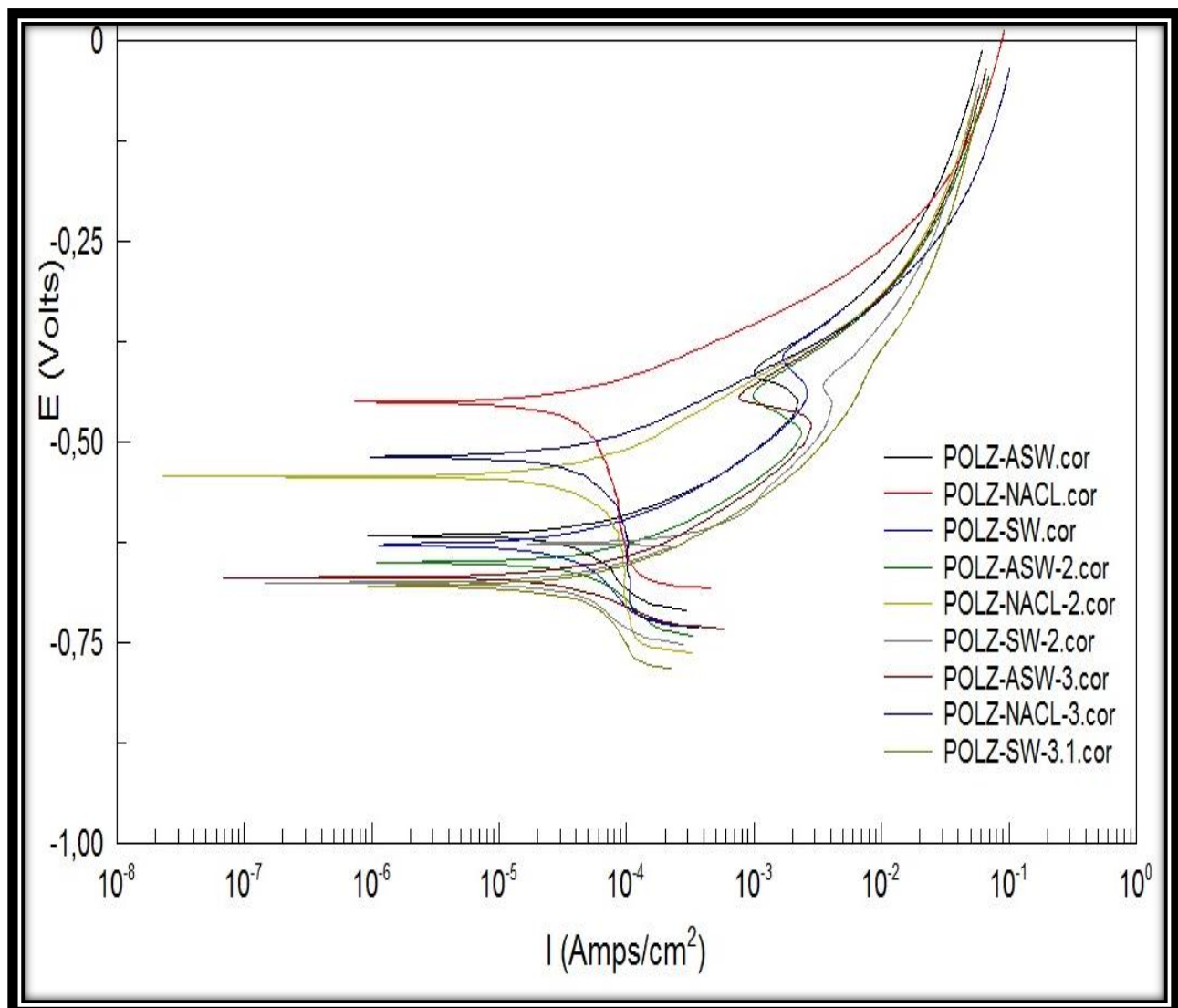
Annex 7: OCP plots mild steel in three aqueous solutions



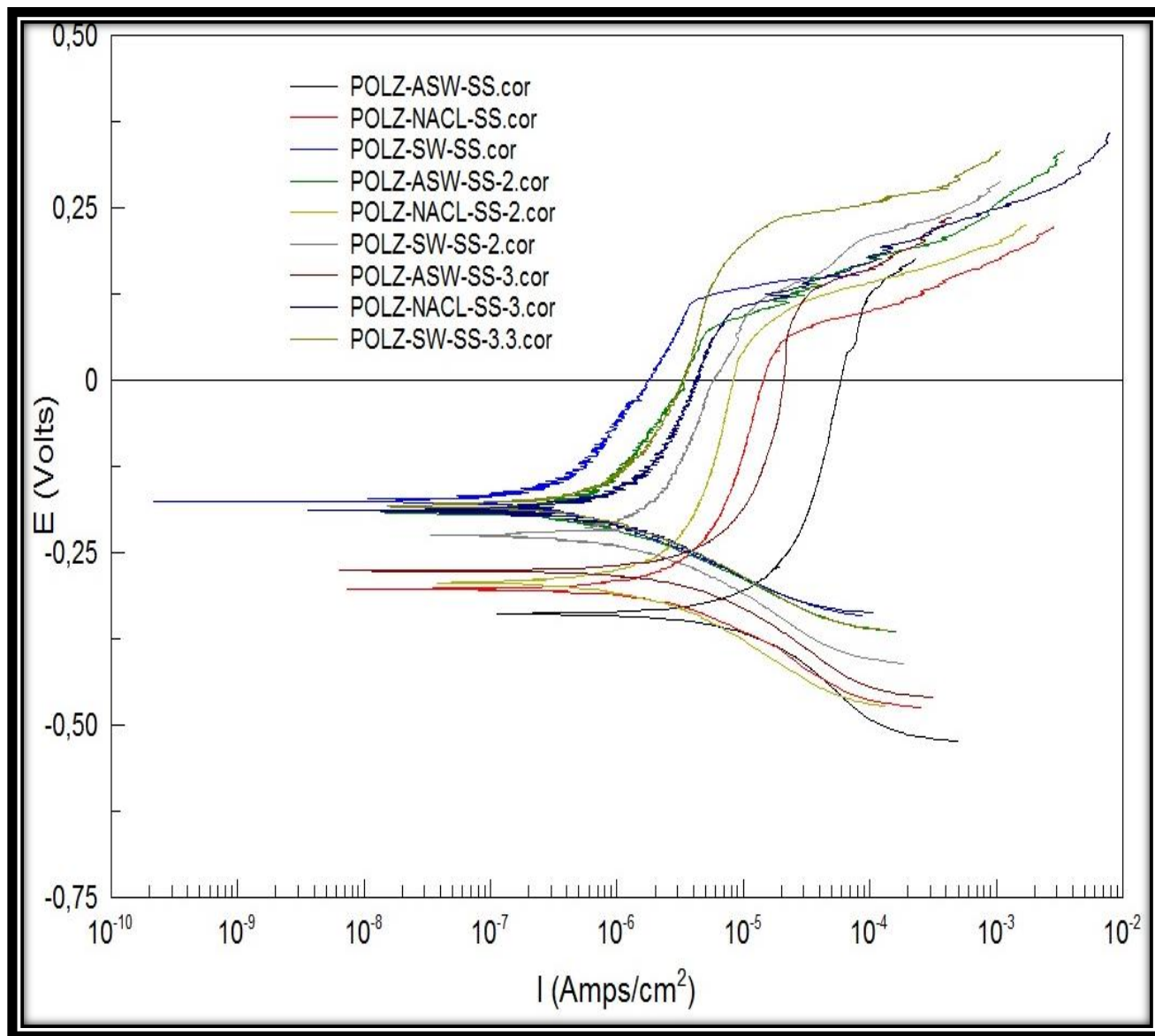
Annex 7: OCP plots stainless steel in three aqueous solutions



Annex 8: POLZ plots mild steel in three aqueous solutions



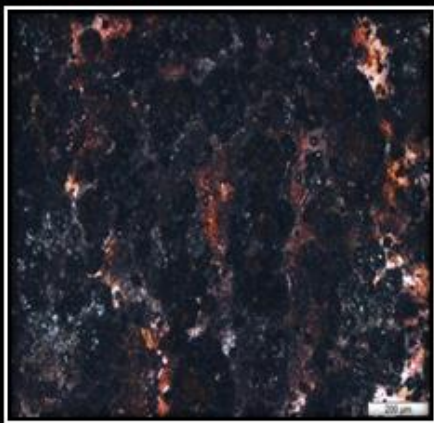
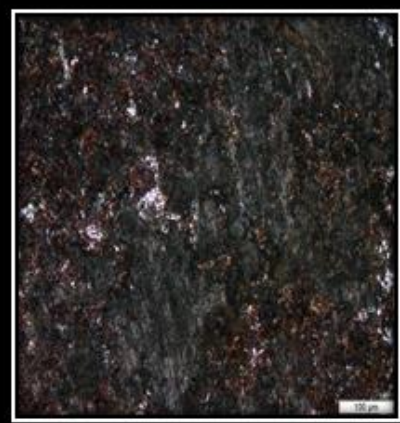
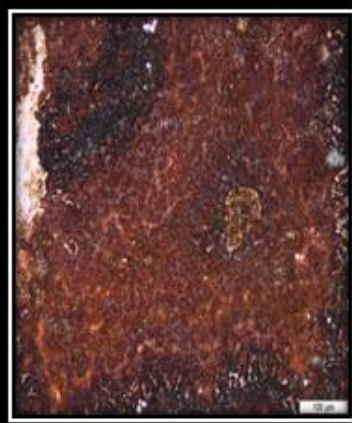
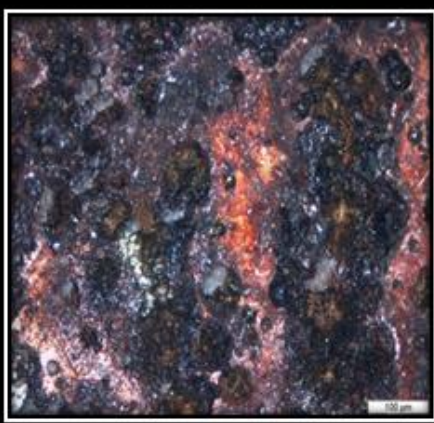
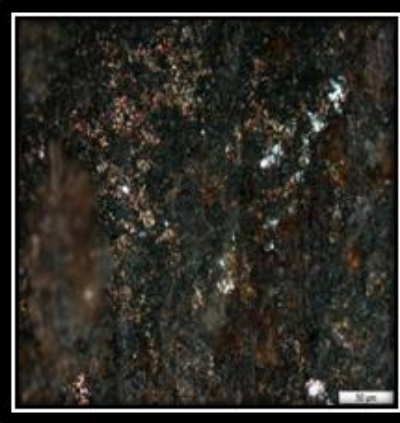

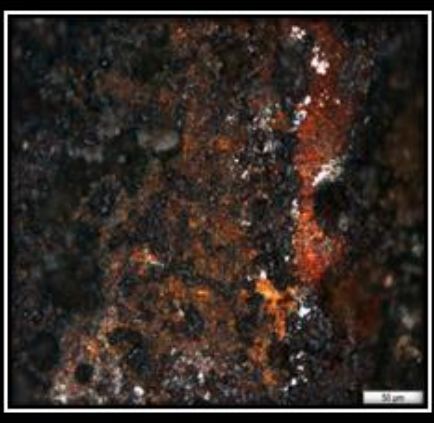


Annex 9: POLZ plots stainless steel in three aqueous solutions

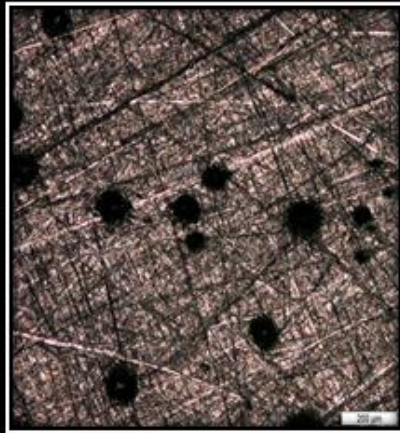
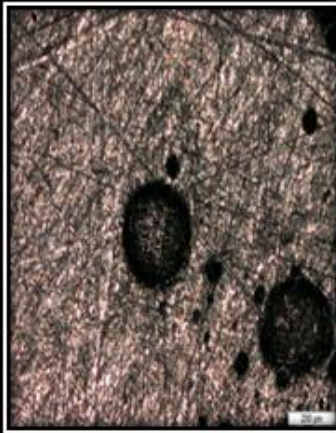
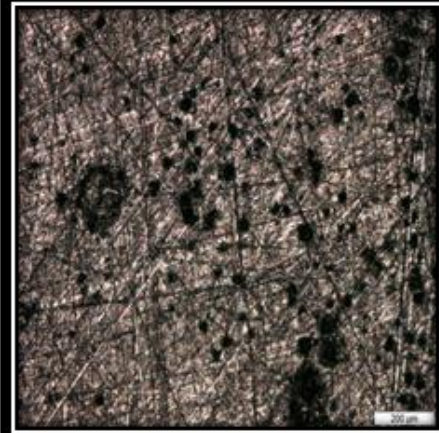
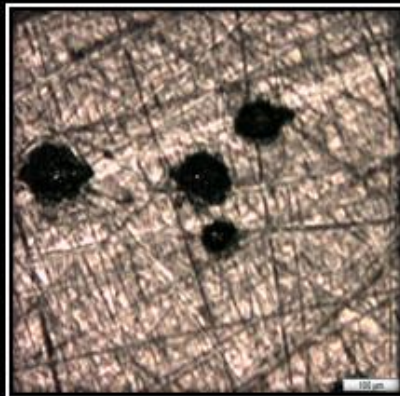
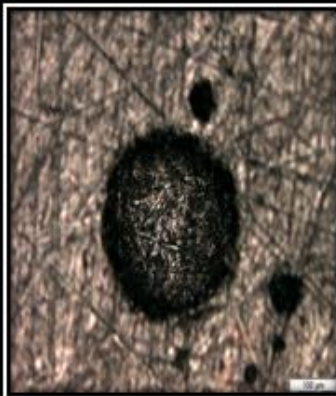
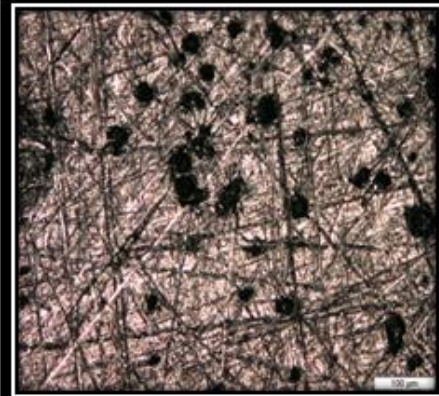
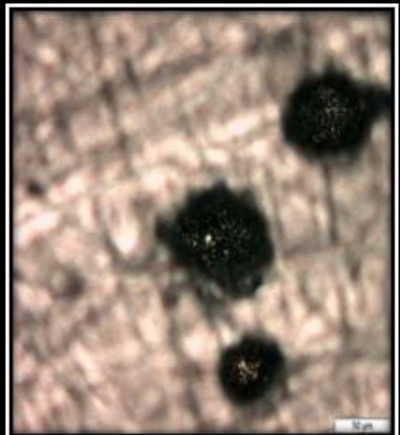

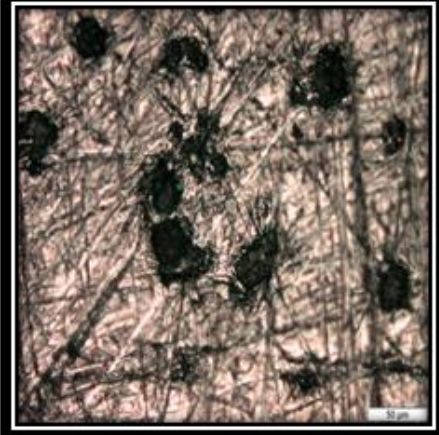


Annex 10: All the micrographs mild steel samples



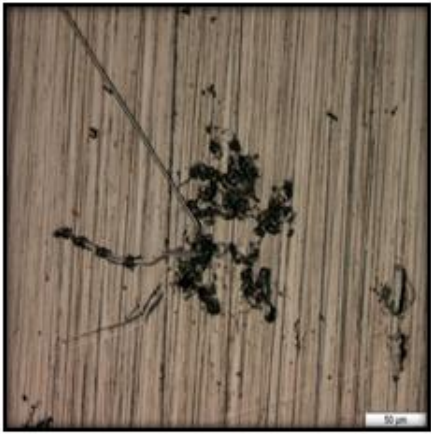



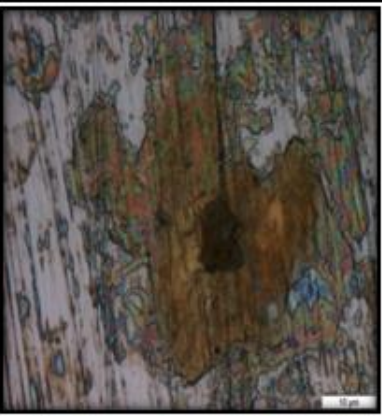

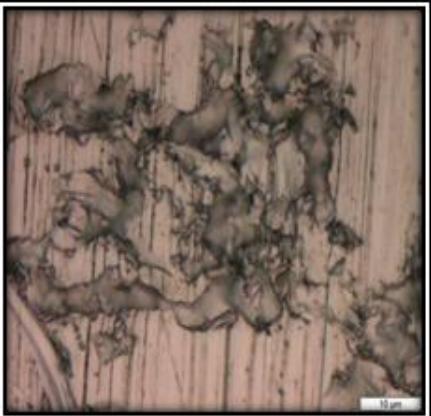
Before cleaning

Zoomed: A(5x), B(10x),C(20x)		
Seawater	Artificial seawater	3,5% NaCl
		
A	A	A
		
B	B	B
		
C	C	C

After cleaning:

Zoomed: A(5x), B(10x),C(20x)		
Seawater	Artificial seawater	3,5% NaCl
		
A	A	A
		
B	B	B
		
C	C	C

Annex 11: All the micrographs stainless steel samples

Zoomed: A(5x), B(10x),C(20x)		
Seawater	Artificial seawater	3,5% NaCl
 A	 A	 A
 B	 B	 B
 C	 C	 C