ELECTROCHEMICAL TESTING FOR PEDEFERRI DIAGRAMS OF STAINLESS STEEL IN CHLORIDE CONTAINING ENVIRONMENT

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ABSTRACT ITALIANO

Gli acciai inossidabili sono ampiamente utilizzati in ambienti aggressivi grazie alla loro resistenza alla corrosione, dovuta alla presenza di uno strato superficiale composto da ossidi misti, chiamati film passivo. Nel caso specifico degli acciai inossidabili il comportamento passivo è concesso dalla presenza di cromo, almeno il 10,5% definito dallo standard, e dalla presenza di una frazione minore di altri elementi per migliorarne le qualità, quali nickel, manganese, molibdeno. Tuttavia questo tipo di acciai può soffrire di attacchi di corrosione localizzati, nello specifico attacchi di vaiolatura e di corrosione in fessura, e sono necessari strumenti pratici per selezionare materiali per specifici ambienti corrosivi in funzione dei contenuti di cloruri, della temperatura e di altri parametri.

Cruciale è la valutazione del potenziale di rottura del film, chiamato \( E_{pit} \) o \( E_{loc} \), e potenziale di ri-passivazione, \( E_{prot} \) o \( E_{rep} \), variando i parametri dell’esperimento. Ciò può essere ottenuto usando un test di polarizzazione potenzio-dinamica (per valutare entrambi i potenziali in funzione del contenuto di cloruri) sia le prove di polarizzazione potenzio-statica (per valutare il contenuto di cloruri critici rispetto al potenziale di polarizzazione).

I dati raccolti sono stati utilizzati per costruire una mappa di corrosione con Potenziale (vs Ag/AgCl/KCl sat) rispetto al contenuto di cloruri. Questa mappa è stata proposta da Pietro Pedeferrì per l’applicazione di protezione o prevenzione catodica nei calcestruzzi armati in presenza di cloruri.

L’importanza del diagramma Pedeferrì sta nella sua capacità di prevedere le zone di protezione in caso di presenza di corrosione e di ri-passivazione per un certo potenziale e per determinati parametri ambientali. La deviazione standard dei potenziali di interesse è stata studiata in funzione di diversi parametri ambientali (contenuto di cloruri), di set-up (velocità di scansione del potenziale) e geometrici (diversa area superficiale).

La tesi è strutturata in sei capitoli:

- Introduzione
- Metodi elettrochimici
- Materiali e strumentazione
- Risultati
Questa tesi è il proseguito di una tesi precedente, i cui risultati sono utilizzati sono utilizzati nel Capitolo 5: Discussione.
ABSTRACT

Stainless steels are widely adopted in corrosive environments and their resistance to corrosion due to the presence of a superficial layer composed by mixed oxides, called passive film. In the case of passive film the passive behaviour is granted by the presence of chromium, at least 10.5% defined by the standard, and the presence of smaller fraction of other elements to enhance this behaviour. Nonetheless, they may suffer of localized corrosion attack, i.e. as pitting and crevice, and practical tools are needed to select materials for specific corrosive environments as a function of chlorides contents, temperature and other parameters.

Crucial is the evaluation of the breakdown potential, $E_{\text{loc}}$, and repassivation potential, $E_{\text{rep}}$, by varying the chlorides content of the solution. This can be achieved using potentiodynamic polarization test (to evaluate both potential respect a chloride content) and potentiostatic polarization tests (to evaluate the critical chloride content respect to the polarization potential).

The data collected have been used to build a corrosion map with Potential (vs SSC) vs Chloride. This map have been proposed by Pietro Pedeferri for the application of cathodic protection or prevention in a concrete in presence of chloride.

The importance of Pedeferri diagram stays in its capability of predict pitting and protection potentials ranges where pitting corrosion and repassivation occur for a certain potential and for certain environmental parameters. The data deviation of $E_{\text{loc}}$ and $E_{\text{rep}}$ was studied, along with that of corrosion potential, $E_{\text{corr}}$.

In line with the theoretical explanation, the results showed that the mean values and the data deviation of the three mentioned potentials was decreasing with increasing chloride contents.
Chapter 1

INTRODUCTION

1.1  BASICS OF CORROSION: THE ELECTROCHEMICAL MECHANISM

A generic corrosion reaction for a metal (Me) can be schematized as follows

\[ \text{Eq 1.1} \quad \text{Me} + \text{environment} \rightarrow \text{Me corrosion products} \]

When the environment is an electrolyte solution, the overall corrosion reaction involves a metal oxidation process and the reduction of the oxygen dissolved in the solution or in the case of acid solutions the reduction of hydrogen occurs; in the case of iron:

\[ \text{Eq 1.2} \quad \text{Iron} + \text{oxygen} + \text{water} \rightarrow \text{corrosion products (rust)} \]
\[ \text{Eq 1.3} \quad \text{Iron} + \text{acid solution} \rightarrow \text{iron ions} + \text{hydrogen} \]

These two reaction (Eq 1.2 and Eq 1.3) proceed according to an electrochemical mechanism involving the electrons of the metallic material. The reaction is the sum of two complementary electrode processes: an anodic process involving the oxidation of the metallic material, which makes electron available in the metallic phase, and a cathodic process which consumes the electrons that are made available in the anodic process through a reduction reaction of molecular oxygen, hydrogen ions or both.

The generic anodic process of a metal can be represented by the oxidation reaction of a metal to its ion which passes into solution (Eq 1.4) or, in some cases, the metallic material tends to form hydroxides (Eq 1.5).

\[ \text{Eq 1.4} \quad \text{Me} \rightarrow \text{Me}^{z+} + ze^- \]
\[ \text{Eq 1.5} \quad \text{Me} + z\text{H}_2\text{O} \rightarrow \text{Me(OH)}_z + z\text{H}^+ + ze^- \]

Where Me is a generic metal, Me\textsuperscript{z+} is the metal ion that passes in the solution, z is the valence of
the metal, e\(^{-}\) indicates the electron and H\(^{+}\) indicates the hydrogen ions.

By contrast, the cathodic process that are of practical interest in corrosion are limited. In case of corrosion in acidic solution, the cathodic process is the reduction of hydrogen ion and the production of molecular hydrogen, according to reaction Eq 1.6. In natural environments, the predominant reaction is the oxygen reduction, which can be distinguished in two different reactions depending if it is a neutral or basic environment (Eq 1.7) or in acidic environment (Eq 1.8).

\[
\text{Eq 1.6} \quad 2\text{H}^{+} + 2e^{-} \rightarrow \text{H}_2 \\
\text{Eq 1.7} \quad \text{O}_2 + 2\text{H}_2\text{O} + 4e^{-} \rightarrow 4\text{OH}^{-} \\
\text{Eq 1.8} \quad \text{O}_2 + 4\text{H}^{+} + 4e^{-} \rightarrow 2\text{H}_2\text{O}
\]

The oxygen which appears as a reagent is a molecular oxygen dissolved in water, whose concentration ranges from 0 to 12 ppm.

Since the electroneutrality must be maintained, the two reactions must occur simultaneously and with the same velocity (Fig 1.1) [1].

![Figure 1.1](image-url) – Schematic of the current circulation during a corrosion process, with the expression of the electroneutrality

1.2 THERMODYNAMIC AND KINETICS OF CORROSION

The fundamental questions that must be answered in corrosion is if the metal can be corroded in such a solution and, if the answer is yes, how fast the corrosion rate is.

To answer the first question, it is to point out that corrosion reaction for a metallic material occurs
if it is thermodynamically favoured: in other words if the variation of the free energy $\Delta G$ associated to it is negative. If it is considered a corrosion reaction of two complementary anodic and cathodic reaction, for example Eq 1.4 and Eq 1.7, the general thermodynamic condition outlined can be applied to the reactions. Since these are electrochemical reactions, the variations of Gibbs free energy can be expressed as the variation of the electro-motive force associated with the reaction (Eq 1.9):

$$\text{Eq 1.9} \quad \Delta G = -zF\Delta E$$

Where $\Delta E$ is the electromotive force of the reaction considered, $z$ is the valence of the metal and $F$ is the Faraday constant. For sake of simplicity, $\Delta E$ can be thought as the difference of the cathodic reaction potential and the anodic reaction potential. So, if the Gibbs free energy have to negative, $\Delta E$ have to be positive for the spontaneity of the reaction: this means that the cathodic reaction have to be nobler than the anodic reaction.

In 1946 Marcel Pourbaix introduced a potential-pH diagram which plot the equilibrium potentials as the pH varies for metal in contact with electrolytes. In this diagram (Fig 1.2) the two possible cathodic reactions, i.e hydrogen release and oxygen reduction, are represented by two parallel lines with an angular coefficient of -0.059 and a distance of 1.23 V, which are obtained by the corresponding Nernst equations, with the line a) being the hydrogen evolution and line b) being the oxygen reduction. In the interval between the two lines the water stability is defined, while below the hydrogen release there is the stability region of the molecular hydrogen an above the oxygen reduction, the molecular there is the molecular oxygen stability region. The metal dissolution is represented in this diagram with horizontal lines, depending on its ions concentration in the solution. It is to point out that while the cathodic reactions are pH dependant, the anodic ones are pH independent. Each horizontal line divides the plane in two regions: the upper part corresponds to the corrosion regions, while the lower part is the thermodynamic stability region, also known as the immunity zone.
In the simplest case, if dissolution reaction of the metal leads to the formation of hydroxides, which occurs especially in the neutral or basic environment, can be derived that the equilibrium condition varies with the pH (Eq 1.10)

\[
E_{eq}^{M/M(OH)_z} = E_0^{M/M(OH)_z} - 0.059pH
\]

The Pourbaix diagrams, which are constructed on the bases of thermodynamic equilibrium data for electrochemical reactions involving the metal as pH varies, show the stability zones of the chemical species involved: immunity zone of the metal, the stability zone for oxides, which may lead to passivation phenomena, the stability zones of the metal ions. So it can be used to determine the thermodynamic condition of the system, but cannot give the information on the kinetics of the processes.

The availability of driving force represents a necessary, but not sufficient, condition or the corrosion reactions to take place: the reactions resistances condition the corrosion rate may delay or stop the corrosion.

To describe a corrosion system it is opportune to use Evans diagram, proposed by U.R. Evans in 1945. In this diagram the two axis represents the potential (E) and the current density, in logarithm scale (log j or log i). As shown in Fig 1.1, the current circulating in the cell must be conserved: so the current of the anodic reaction have to be equal to the current of the cathodic one. This diagram show the characteristic curves of the anodic and cathodic reactions obtained experimentally (Fig 1.3) starting from the reaction’s equilibrium potential (\(E_{eq,a}\), \(E_{eq,c}\)). As the current increases, the
reaction potential shifts: for anodic reaction the shift is positive, for the cathodic one is negative. Eventually the two curves, if plotted in the same diagram, will meet and the corrosion potential \( E_{\text{corr}} \) and the corrosion rate \( \log i_{\text{corr}} \) are then calculated (Fig 1.3) [2].

![Evans diagram for a generic corrosion process: anodic (blue) and cathodic (red) processes](image)

**Figure 1.3** – Evans diagram for a generic corrosion process: anodic (blue) and cathodic (red) processes [2]

As said before in the Pourbaix diagram, if an oxide or hydroxides is present, so the metal in in the stability zone of that state, passivation phenomena can occur.

When iron, as also carbon and low alloy, are in natural (soils and water) or acid solutions, it is in the so-called active condition (Fig 1.3). In these cases the anodic process cannot contribute in the reducing of corrosion rate. Numerous metals, and their alloys, with an high affinity for oxygen have the characteristics of covering themselves with a protective layer of oxides, which prevents their corrosion in a corrosive environment. This condition is called passivity and unable the metal to behaves as a nobler metal. The anodic curves of these metals has a characteristic shape, in which one can distinguish three zones: the activity zone, the passivity zone and the transpassivity zone (Fig 1.4) [2].
In the figure above three potentials can be distinguished and they delimit the three zones mentioned above: from the equilibrium potential to the passivation potential ($E_p$) there is the activity zone, in which the metal behaves as a normal active metal. From the passivation potential to the transpassivity potential ($E_t$) the passivity region is determined, where the corrosion process is slowed down to a negligible corrosion rate ($j_p < 50 \mu m/\text{year}$ [2]). Above the transpassivity potential the transpassivity region starts: in this region the oxides layer is no more protective.

Actually, even if a metallic material is passive, it can undergo some sort of corrosion on a very small part of the metallic surface compared to the exposed area: the two corrosive attacks that are of interest in this work are the pitting and crevice phenomena.

### 1.3 Pitting and Crevice Corrosion of Stainless Steels

When the anodic and cathodic reactions take place on different surfaces, localized corrosion occurs, affecting only a limited part of the surface exposed to the environment [2]. The separation of the areas leads to the circulation of a current with the circulation of the electrons in the metal from the anodic to the cathodic surfaces and the circulation of ions in the solution. Pitting and crevice corrosion are part of this type of corrosion.

Pitting manifests itself as attacks, leaving pits or cavities, which are extremely penetrating but affect only a very small part of the metallic surface. All metals that exhibit an active-passive behaviour
can be subjected prone to pitting corrosion, although most experimental studies have involved stainless steels, aluminium, and copper. Pitting is caused by the presence of aggressive anions in the electrolyte, usually Cl\(^-\) ions are considered when stainless steel or aluminium are considered. The chloride ion has a special importance in pitting corrosion for two main reasons: Cl\(^-\) ions are ubiquitous, being constituents of seawater, brackish waters, de-icing salts and secondly the chloride ion is a relatively small anion and has a high diffusivity [4].

The tendency of a metal or alloy to undergo pitting is characterized by its critical pitting potential, as illustrated in Fig 1.5. In the absence of chloride ions, the metal retains its passivity up to the electrode potential of transpassivity. In the presence of chloride ions, the passive film suffers localized attack, and pitting initiates at a potential called pitting potential or breakdown potential [4]. Once corrosion pits initiate, they usually propagate rapidly, as shown by the sharp rise in current density at electrode potentials just beyond the critical pitting potential.

![Figure 1.5](image)

**Figure 1.5** - Schematic anodic polarization curve showing the critical pitting potential (for a passive metal) [3].

The critical pitting potential, \(E_{\text{pit}}\) or also called \(E_{\text{loc}}\) the thesis, is a characteristic property of a given metal or alloy in a given environment. For a given chloride concentration, the more positive the critical pitting potential, the more resistant the metal or alloy to pit initiation [4].

The significance of the pitting potential is that below \(E_{\text{pit}}\), pitting does not manifest \((E < E_{\text{pit}})\) while above \(E_{\text{pit}}\), corrosion pits initiate and propagate. \((E > E_{\text{pit}})\)
Moreover not only there is not only a threshold in the potential, but also in chloride concentrations [5]: actually a critical chloride concentration for a given potential can be observed, as depicted in Fig 1.6 [2].

![Figure 1.6 – Dependence of pitting potential in function of the chloride contents [2]](image)

1.3.1 MECHANISM OF PIT INITIATION

Pitting corrosion may be divided into initiation and propagation stages. It is considered that the initiation stage includes both the breakdown of the passive film and the onset of an anodic current at the metal surface. The three-main possible pitting mechanism include the penetration mechanism, the adsorption mechanism and the film rupture mechanism [2, 3].

In the penetration mechanism, aggressive anions are transported through the oxide film to the underlying metal surface where they participate in localized dissolution at the metal/oxide interface. This mechanism is depicted schematically in Fig 1.7. The mechanism by which Cl$^-$ ions penetrate the oxide film is not completely understood, but the radius of the Cl$^-$ ion is only slightly larger than that of an oxygen ion (1.81 vs. 1.40 Å, respectively), so that Cl$^-$ migration through oxygen vacancies is a possible mechanism of chloride entry into the passive film [6].
In the film thinning mechanism, the aggressive anions, in particular chlorides, first adsorb on the oxide surface and then form surface complexes with the oxide film which lead to local dissolution and thinning of the passive film, as shown schematically in Fig. 1.8.

In the film rupture mechanism (Fig. 1.9), chloride ions penetrate the oxide through cracks or flaws in the film. In addition to pre-existing defects in the oxide film, flaws may further develop by hydration/dehydration events in the oxide film and by the intrusion of Cl\(^-\) ions into the film. It has been said that the presence of a high electric field in the oxide can lead to an electromechanical breakdown of the passive film. It should be noted that pre-existing flaws cannot extend down to the underlying metal substrate because the metal would quickly react with water molecules in the electrolyte and would re-oxidize. Then, chloride ions must penetrate the re-formed oxide film by
mechanisms discussed above. Passive films can also be ruptured or disrupted due to metallurgical variables, such as grain boundaries, impurity atoms, and inclusions.

These three mechanisms of pit initiation (chloride penetration, film thinning, and film rupture) are not necessarily mutually exclusive.

1.3.2 MECHANISM OF PIT PROPAGATION

The mechanism of pit propagation is shown in Fig 1.10. When the corrosion pit has started, the corresponding local current density is very high because the current is confined to a small active geometrical area, while the oxide film adjacent to the pit remains passive and act as cathode. As the pit grows, its volume is increased, but dissolved metal cations are confined within the pit and do not diffuse out into the bulk electrolyte due to the confinement of a restricted geometry or a cap of porous corrosion products, which in some cases can be formed. As a result, accumulated metal cations undergo hydrolysis, as in the case of crevice corrosion, and a local acidity develops within the pit. Finally, the $\text{H}^+$ ions and cations are accumulated within an active pit and the $\text{Cl}^-$ ions migrate from the bulk electrolyte to the electrolyte in order to maintain charge neutrality within the pit solution [7].

Hence the propagation stage of pitting, involves the formation of a highly corrosive internal electrolyte which is acidic and concentrated in chloride ions and in dissolved cations of the metal or alloy. When the corrosive pit electrolyte has been formed, pitting is considered to be autocatalytic in nature.
Even at lower potential than the pitting potential, localized attack can occur. These are metastable pits, which can evolve into pits and then propagate, or repassivated.

1.3.3 CREVICE CORROSION MECHANISM

Crevice corrosion can occur in geometrical clearances (under gaskets or seals, under bolt heads, between overlapping metal sheets, within screw threads, within strands of wire rope) under deposits (corrosion products, dust particles). A necessary condition to have crevice attacks is to be in a chloride containing environment.

As for pitting, even for crevice corrosion two distinct stages can be defined: initiation and propagation.

1.3.4 INITIATION OF CREVICE CORROSION

Crevice corrosion initiates due to the operation of a differential oxygen cell. Oxygen reduction occurs both on the metal surface which is exposed to the bulk electrolyte and also on the portion of the metal surface which is contained within the crevice, as depicted in Fig 1.11. The cathodic reaction is the same on both internal and external metal surfaces.

The metal exposed to the bulk electrolyte is in contact with an open supply of oxygen from the atmosphere, so as $O_2$ is consumed near the external metal surface, additional $O_2$ molecules diffuse...
to the metal surface and a steady-state concentration of $O_2$ is maintained near the surface of the external metal. However, when $O_2$ molecules are consumed within the narrow clearance of the crevice, they are not easily replaced due to the long narrow diffusion path formed by the crevice [7].

![Figure 1.11](image)

**Figure 1.11** - Schematic illustration of the initiation stage of crevice corrosion: (c) is an expanded view of (a) and (b) [3].

### 1.3.5 PROPAGATION OF CREVICE CORROSION

Crevice corrosion propagates by changes in the electrolyte composition within the crevice. In particular, the crevice electrolyte will become acidic in nature and will also contain concentrated amounts of cations discharged from the metal or alloy. In chloride solutions, the internal electrolyte
within the crevice will also become concentrated in chloride ions. This internal electrolyte is sufficiently aggressive to break down the passive film on the metal. These changes in the composition of the crevice electrolyte occur because of the narrow geometrical character of the crevice, which allows only restricted exchange between the crevice and bulk electrolytes [8].

![Figure 1.12 - Schematic illustration of the propagation stage of crevice corrosion of iron [5].](image)

The propagation stage of crevice corrosion, like that of propagation of pitting, involves the formation of a highly corrosive internal electrolyte which is acidic and also concentrated in chloride ions and dissolved cations of the metal or alloy, as shown in Fig 1.12. As for pitting, also the initiation stage of crevice corrosion can be quite prolonged (months to years), but propagation may proceed rapidly due to the highly corrosive crevice environment which is formed [6].

### 1.4 EFFECT OF METALLURGICAL FACTORS

Stainless steel are iron-chromium-carbon based alloys and containing other elements like nickel, molybdenum, manganese, nitrogen, tungsten etc. which make them more resistant to corrosion.

The standard UNI ENI 10088-1 defines stainless steels as iron based alloys which contains at least 10.5% of chromium.

Depending on the alloying elements, and so the microstructure, one can divide all stainless steels in three different families: austenitic (FCC), ferritic (BCC), martensitic (TCC), duplex (both austenitic and ferritic phases). Seeing the Fe-Cr and Fe-Ni (Fig 1.13) diagram states that some alloying elements tend to enlarge the α-phase while other tends to enlarge the γ-phase; combining the effect of these elements and the Ni equivalent and Cr equivalent contents are obtained.
These two equivalent number are used in the Schaeffler diagram to define the microstructure (Fig 1.13).

![Schaeffler diagram](image)

**Figure 1.13**– Schaeffler diagram

### 1.4.1 CHEMICAL COMPOSITION OF THE STAINLESS STEEL

As already said, all stainless steel have at least 10.5 % of Cr in their composition to make them more resistant to general corrosion. It is common knowledge [9] that going in more basic solution, the carbon steel becomes more resistant to corrosion and at pH for 12.5 it becomes completely passive; so the Cr addition helps the steel not only to become more corrosion resistant in general, but specifically at pH lower than 11.

Existing data show that Cr, as for Mo, increase the pitting resistance of steels in chloride solutions; this alloying element does not only reduce susceptibility to pit nucleation (Fig 1.14), but also diminish the rate of pit development [4].
It can be seen that, for moderate anodic polarizations in acidic solutions, the passive film consists essentially of chromium in its trivalent state. As the potential increases above the stability limit of chromium III, (about 0.6/0.8 VSHE), the passive film will start to change composition and the fraction of trivalent iron in the film will increase. For acidic solutions, the cation fraction of Cr in the passive film normally amounts to 50/70%. For basic solutions, the solubility of Cr increases, resulting in a higher fraction of iron.

Nickel is less readily oxidized than iron and chromium [13]. Consequently, there is an enrichment of Ni in its metallic state in the metal closest to the oxide/metal interface. This enrichment could assist in the formation of a nickel nitride. Nickel could also bring down the overall dissolution rates of Fe and Cr.
Molybdenum is an alloy element with a strong beneficial influence on the pitting resistance of a stainless steel [14]. When included as an alloying element in a stainless steel, molybdenum is incorporated into the passive film, showing a complex oxide chemistry with different states of oxidation. Hexavalent Mo is found to be enriched at the surface, whereas tetravalent states show a more homogeneous distribution through the film. There are two possible hexavalent states: MoO$_3$, which is soluble in acidic electrolytes and MoO$_4^{2-}$ which shows a higher stability. Distinguishing between these two states is difficult even with a high resolution XPS spectrometer.

Tungsten is fairly recent as a major alloying element in commercial stainless steels. It has been attributed properties similar to those of molybdenum. An important difference between tungsten and molybdenum oxides lies in the different stability of their oxides in acid solution. While hexavalent molybdenum oxide dissolves at potentials well below oxygen evolution, the stability of hexavalent tungsten oxide extends to anodic potentials of several tens of volts.
Nitrogen is the element attributed the strongest beneficial influence on localised corrosion in the pitting resistance equivalent formula (PREN). As for molybdenum, nitrogen also shows strong concentration gradients in the passive film [15]. A possibility is the formation of a nitride at the metal/film interface which brings down the dissolution rates for the individual elements in the alloy [16]. Nitride has also been put forward as a possible mechanism for synergy between nitrogen and molybdenum.

Recently, addition of Mn to stainless steel has been used to increase the solubility of nitrogen and molybdenum, both of which have a strong beneficial influence on the pitting resistance [12].

To compare different stainless steels and to have a qualitative evaluation of the resistance of the stainless steel in a chloride containing solution can be used the PREN (Pitting Resistance Equivalent Number).

This number can be evaluated with the following equations, depending on the composition of the stainless steel:

\[ \text{PREN} = \%Cr + 3,3\%Mo + 16\%N \]  
\[ \text{Eq. 1.1} \]

\[ \text{PREN} = \%Cr + 3,3(\%Mo + 0,5\%W) + 16\%N \]  
\[ \text{Eq. 1.12} \]

The first equation is used when the content of Mo is less than 1,5\%, while the second takes into account also the presence of W when the content of Mo is more than 1,5\%.

All the equation above are used for austenitic stainless steel, if other type (ferritic or martensitic), the coefficient which multiply the contents of the different alloying elements.

The effect on pitting potential of the various alloying elements is shown in Table 1.1 [4]

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>Content (max)</th>
<th>( E_{\text{loc}} ) shift (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>11</td>
<td>50</td>
</tr>
<tr>
<td>Ni</td>
<td>25</td>
<td>200</td>
</tr>
<tr>
<td>Cr</td>
<td>30</td>
<td>900</td>
</tr>
<tr>
<td>Mo</td>
<td>4,5</td>
<td>900</td>
</tr>
</tbody>
</table>

Table 1.1 – Approximated effect of the major alloying elements [4]
1.4.2 STEEL MICROSTRUCTURE AND METALLURGICAL DEFECTS

In general, it can be said that the resistance of the passive film to the breakdown is related to the properties of the base metal. If zones adjacent to the grain boundaries are impoverished in chromium, and this does occur in sensitized stainless steels for example, the passive film is less protective in these regions and localized corrosion is likely to occur.

Also, at sites where non-metallic inclusions emerge on the metal surface, the film is weaker and pits may nucleate [4]. For example, the vicinity of MnS inclusions is known as a preferential location for pit nucleation on stainless steels in the presence of aggressive ions like chlorides. The pitting susceptibility of MnS in chloride-containing solutions is often attributed to the preferential adsorption of chloride ions on MnS rather than on the surrounding passive metal, leading to a decrease in the activation potential of the inclusion [17].

Mechanisms have been proposed to explain the role of the MnS inclusions on pitting initiation [18]. Nevertheless, the phenomenon is subject of intense discussion. Schmuki et al. [19] demonstrated that corrosion can start around or inside the inclusions, in high oxidising environments, and also that some of the inclusions can remain inactive, even in very oxidising conditions. Pitting attack, in or around inclusions, depends upon several factors such as inclusion composition, shape, and geometry.

1.4.3 COLD WORKING

Austenitic stainless steel is used in various applications not only due to its high corrosion resistance but also for its good ductility.

However, the application of these types of steel is limited due to its low yield strength (about 200 MPa), hence the focus is to find some methods to provide ultrafine-grain (UFG) in order to attain a higher strength without losing the ductility and the corrosion resistance that are characteristic of this type of material [4]. To achieve UFG, there are three different families of process that can be used: severe plastic deformation (SPD), advanced thermomechanical process (ATP), mechanical milling (MM) called also shot-peening.

A study [20] says that the cold working affects the pitting initiation frequency: essentially the frequency of initiation increase with the increase of the cold-rolling reduction (Fig 1.9). The
frequency of initiation have been measured as the number of metastable pits.

![Graph showing effect of cold rolling on AISI 304 in 0.1 NaCl + 2x10^-4 FeCl₃](image)

**Figure 1.9** – Effect of cold rolling on AISI 304 in 0.1 NaCl + 2x10^-4 FeCl₃ [20]

### 1.4.4 SURFACE FINISHING AND ROUGHNESS

One major technological concern associated with the electrochemical behavior of stainless steels is the surface finishing.

This has been found to affect the corrosion resistance of stainless steels being related to different forms of localized corrosion, such as stress corrosion cracking and pitting corrosion.

It has been seen that the pitting potential decrease as the surface becomes rougher, indicating a less stable condition owing to localized corrosion. Actually the surface roughness cause a local weakness in the protective oxide layer, where a critical Cl⁻ concentration can be attained and so the number of active siter for pit nucleation can increase.

This effect would be related to the so-called openness of the pit, which is related to the aspect ratio of surface groove: smoother surfaces are characterized by high aspect ratios and are more resistant to pitting corrosion.
This is explained by saying that the metastable pitting is a diffusion-controlled process where the metal dissolution depends on the concentration of chlorides and of corrosion products inside the pits [4].

Higher aspect ratios of surface grooves decrease the chloride concentration inside the pits, thus leading to a reduced current density, and therefore decreasing the pitting nucleation rate [21]. Fig 1.10 show how different surface finishing operations influence the pitting potential for AISI 304.

![Figure 1.10 - Potentiodynamic polarization curves for AISI 304 stainless steel samples submitted to different surface finishing operations in 0.1 M NaCl at room temperature; potential is taken respect to Ag/AgCl/KCl sat reference electrode [21]](image_url)

As shown in the picture, it is clear that the pitting potential of the as-received sample is lower than the others, meaning that it is more prone to have pitting attacks.

Also in another paper [22] the same trend, as shown in Fig 1.11. The specimen 2B is to be considered the untreated sample.
Even if no big difference can be noticed for the treated samples, a clear difference can be seen with the as-received sample.

1.5 EFFECT OF ENVIRONMENTAL FACTORS

Pitting initiation depends not only on the chemical composition and on microstructure of the material that has to bear this kind of corrosive attack, but also on the type of environment that surround it.

Four major environmental factors can be took into account:

- Chloride concentration
- Temperature
- pH
- Flow rate

The general trend is that increasing the chloride concentration, decreasing the pH, increasing the temperature and increasing the flow rate the pitting potential lowers.
1.5.1 Chloride concentration

As already mentioned in the section of 1.2 (Pitting and crevice corrosion in stainless steel) the effect of chloride content on pitting susceptibility of stainless steel has been widely investigated [24] and it is well established that it decreases the pitting potential (Fig 1.6 and Fig 1.12).

It is suggested that transition between passivity and pitting can be explained by a competitive adsorption mechanism in which chloride ions move into the oxide/liquid interface and be able to displace the adsorbed oxygen species.

The chloride tends to reduce the passivity region of the anodic curve of stainless steel reducing the pitting potential.

The anodic processes associated with a metal depassivation are strongly affected by the chloride concentration in the solution: a large amount of chloride the passive film becomes susceptible to pitting corrosion and can suffer localized damage; a simple equation can be found that correlates the pitting potential, $E_{\text{pit}}$, with the concentration of chlorides:

Eq. 1.14 \[ E_{\text{pit}} = A - B \times \log [Cl^-] \]

Where $A$ and $B$ are constants that depend on both environmental and metallurgical condition [4].

Figure 1.12 – Effect of Cl\(^-\) to the pitting potential
1.5.2 TEMPERATURE

A decrease of the pitting potentials at high temperature has been seen and can be explained by a more intense agglomeration and stronger chemisorption of chloride ions on the metal surface, causing easier breakdown of passivity. The pit number also increases with increasing temperature because at higher temperature more site are susceptible to pit nucleation. An increase in temperature accelerates the transport of reagents and reaction products to or from the electrode. However, the effect of temperature on transport rate is considerably less than the effect on the chemisorption of chloride ions and on the ionization of metal. Therefore, the changes in the electrolyte concentration inside pits occurs more rapidly with increasing initial current density in pits. These concentration changes lead to increased concentration polarization, and to ohmic polarization, when salt layers or other corrosion products are deposited in pits. Consequently, inhibition of the metal dissolution, both by transport processes and decreases of the current density in pits vs exposure time, are more pronounced at higher temperatures. It is notable that at certain temperatures, pitting can occur without chloride ions, which is presumably related to some changes in film structure at these temperatures [4].

Fig 1.13 [25] shows how the pitting potential varies with varying the temperature for the Alloy 600, a nickel based alloy. As can be seen there is a clear dependence of pitting potential respect to the temperature.

![Figure 1.13 – Effect of the temperature on the pitting potential of Alloy 600 in deaerated 0.282 m NaCl solution [25]](image)

Another study [26] that the combination of an high temperature and the presence of chloride favour
the breakage of the film.

1.5.3 pH

It is known that the pH of the solution directly affects the cathodic process of hydrogen evolution, but pH also has a strong influence on the kinetics of the anodic processes through the solubility of corrosion products and their protective properties [27]. A lot of studied showed that the pitting potential becomes lower as the pH is more acidic, while at high pH values pitting potential is moved in the noble direction, because of the inhibition effect due to a higher concentration of OH⁻ ions (Fig 1.14).

![Figure 1.14](image)

*Figure 1.14– Effect of pH on pitting corrosion [30]*
A study [28] reported that values below 2.2 are important for pitting corrosion: actually they claimed that no much difference in pitting potential between 2.2 and 5 pH is seen.

As said before, higher values of pH have an inhibiting effect on the pitting corrosion, as the tests done for pH ranging from 4 to 9 show [29].

1.5.4 SOLUTION FLOW

Pitting of stainless steels is often associated with stagnant conditions, but with the increasing of the speed of the solution, positive effects have been detected. Table 1.2 show the results and the difference between pit initiation when there is a flow of the solution (1,2m/s) from when the water is still. The metal tested was a welded 316 stainless steel in seawater. No pitting initiate when the solution is agitated, while attacks appears when the solution is stagnant.

<table>
<thead>
<tr>
<th>Material</th>
<th>Agitated Number of pits</th>
<th>Stagnant Number of pits</th>
</tr>
</thead>
<tbody>
<tr>
<td>316 Plate weld</td>
<td>0</td>
<td>87</td>
</tr>
<tr>
<td></td>
<td>0</td>
<td>47</td>
</tr>
</tbody>
</table>

It is possible to explain this phenomenon by saying that when the solution is in motion the three mechanism described in section 1.2.1 (Pitting initiation mechanism) are hindered.

1.6 THE PEDEFERRI’S DIAGRAM OF STAINLESS STEELS

Pedeferri diagram illustrates conditions for passivity and corrosion in terms of chloride concentrations (Fig 1.15). In the specific, Fig 1.15 depict the original Pedeferri’s diagram used to evaluate the type of cathodic protection of rebars in the concrete in presence of carbonation or in presence of chlorides [9].

In accordance with Pourbaix diagram, in this diagram three important zones can be individuate:

- Perfect passivity, where no pit can initiate or propagate
• Imperfect passivity, where pits can propagate but not initiate

• Pitting, where pits can both initiate and propagate

The definition of these zones has a high industrial values because it makes possible to stop, or even to make it impossible, the pitting corrosion.

The importance of Pedenerri diagram lays in the capability of predicting the pitting and repassivation potentials for certain environmental potential.

Figure 1.15– Pedeferri diagram for the cathodic protection or prevention for the rebars in the reinforced concrete work is both to evaluate a suitable electrochemical methodology to obtain the Pedeferri diagram and to evaluate the influence of method parameters (scan rate, chloride content, size of the sample) for the AISI 304 stainless steel.
ELECTROCHEMICAL TEST METHODS FOR PITTING AND CREVICE SUSCEPTIBILITY MEASUREMENTS

There are various electrochemical methods that can be used to determine the characteristics of corrosion resistance, which are divided in two main families divided in the use of DC and AC.

The first family can be divided in other two subcategories that are: tests that use as an input a variation in polarisation potential and the output will be a current and test that use as an input a current ad the output will be a potential difference.

Electrochemical polarization is the change of electrode potential due to the flow of current. The technique is built on the idea that predictions of the corrosion behaviour of a metal in a specific environment can be achieved by forcing the material away from its steady state condition and monitoring how it responds to this displacement.

In the second family one method is the most known: the electrochemical impedance spectroscopy (EIS).

In all these types of test the conductivity of the electrolyte is a very important factor that should be considered, because the electrolyte resistance can cause potential drop between the working and the reference electrode and may cause errors. This effect has an important impact on the interpretation.
2.1 MEASUREMENTS WITH A POTENTIOSTAT

The first family of tests, where the control is on the potential, can be divided in three types of possible method:

- Potentiodynamic, where the potential is changed continuously at a constant rate
- Quasi-stationary, where the potential is changed stepwise at a desired rate
- Stationary, where the potential is held at an assigned potential

2.1.1 CONTINUOUS POTENTIODYNAMIC POLARIZATION

In this case the potentiostat is controlled with a computer, which control the change of the potential, which is called potential scan rate.

The potentiodynamic polarization are performed using the three electrode configuration, which are: working electrode, reference electrode and counter electrode.

The working electrode is the sample to analyse and it is the electrode to polarize, the reference electrode is the one that monitor and provide the zero for the potential measurements, the counter electrode supply the needed current to the working electrode and close the electrochemical circuit.

![Figure 2.1 – Plot of a potentiodynamic polarization [31]](image-url)
The system works by maintaining the potential of the working electrode at a specific potential, that will change in time, with respect to the reference electrode by adjusting the current supplied by the counter electrode. In the case of localized corrosion the curve is generally analysed in terms of free corrosion, breakdown or pitting and repassivation potentials (Fig. 2.1 [31]).

The initiation of corrosion is detected when a sudden increase in current density, some order of magnitude, is observed and the potential at which this phenomenon happens is called breakdown potential or pitting potential ($E_{\text{pit}}$ or $E_{\text{loc}}$). When the current density reached to a threshold value, the backward potential scan start. In this way the repassivation potential can be obtained ($E_{\text{prot}}$ or $E_{\text{rep}}$). The value of this potential has been debated because some authors consider it the potential at which the current density is zero, others the one at which the forward and backward potential scan intersect [4, 32]. This type of test can be done also only in the forward potential scans, so to have a faster test, but only the $E_{\text{loc}}$ can be obtained [33].

One of the regarding on the use of potentiodynamic, both continuous and stepwise, is that the results of $E_{\text{loc}}$ and of $E_{\text{rep}}$ are dependant on the experimental parameters, which the most important is the scan rate: the higher the scan rate the higher the $E_{\text{loc}}$ is expected. This is due to incubation process for pitting in which a slower scan rate permits more time for a pit to occur at a more negative potential during the forward mode [34, 35]. The effect of potential scan rate on the $E_{\text{pit}}$ can be seen clearly in Figure 2.2 [36].

![Figure 2.2 – Dependence of breakdown potential on the scan rate [36]](image)
2.1.2 STEPWISE POTENTIODYNAMIC POLARIZATION

Stepwise potentiodynamic polarization is a method that produces polarization in which the potential is changed periodically with discrete steps, usually ranging from 25 to 50 mV each [33].

2.1.3 POTENTIOSTATIC POLARIZATION

Potentiostatic polarization is a long-term test that gives the best information regarding the localized corrosion of a metal in a given environment because, being at a fixed potential, it reproduces better the real condition of corrosion. Basically, a constant DC anodic potential is applied to the sample and the current is recorded as a function of time. When pitting initiate, a sudden increase in the current density occurs. There are two methods to measure the pitting potential related to the chloride content of the solution: make tests with a constant chloride content and define a time limit, initiation time, for the pitting to occur (Figure 2.3), or to make tests with a varying chloride content, which is added to the solution after a period of time. The first method is thought to be more accurate in reproducing the environment found in the field (constant chloride content and potential) but too much time consuming [4].

Figure 2.3 – Current density vs Time depending on the polarization potential [37]
While the second method seek to approach the pitting potential in a “horizontal” way. Essentially in the potentiodynamic test the pitting potential is found increasing the potential and not changing the chloride contents (vertical way), while for potentiostatic tests the critical chloride content is found for a specific potential (horizontal way).

![Figure 2.4](image1.png)

**Figure 2.4** – Current density vs Time depending on the polarization potential [38]

As shown in Figure 2.4 [38] when the polarization potential is below the pitting potential, the current decays to a constant value; on the other hand, when the potential is equal to the pitting potential or higher, the current increases due to the pits initiation, at the beginning, and growth.

![Figure 2.5](image2.png)

**Figure 2.5** – Current density when pitting already initiate depending on the polarization potential: $E_a < E_b$; plotted vs time [37]
It has been found [37] that the current density of a stable pit has an increasing trend, until the polarization is stopped and the pit growth ceased and so the current density returned near zero. As the Figure 2.5 shows, not only the current density increases when the pit propagates, but also increases when the potential increases, showing a sharper trend.

It can be concluded that the metal dissolution rate increased significantly with the increasing in the applied potential, and thus the stable pit would have a faster growth at higher potential.

Even if it is possible to obtain a value for the re-passivation potential using this technique, it is rarely used.
2.1.4 COMPARISON BETWEEN POTENTIODYNAMIC AND POTENTIOSTATIC POLARIZATION

Localized corrosion phenomena has a low reproducibility due to the stochastic nature of the phenomenon, anyway there are many authors that measured breakdown potential and repassivation potential using both potentiodynamic and potentiostatic polarization [39, 40].

For example Figure 2.6 shows the results of the potentiodynamic and potentiostatic polarization curves obtained for UNS S32404.

![Figure 2.6](image)

Figure 2.6 – Potentiodynamic polarization curve (a) and potentiostatic polarization curve (b) obtained for UNS S32404 [39]

As can be seen the value for breakdown potential are similar: for the potentiostatic test, the current increase for a value of potential of about 1000 mV SCE, which is also confirmed from the potentiodynamic polarization curve, which is also easier to read.

2.2 MEASUREMENTS WITH A GALVANOSTAT

The second family can be divided in two different modes: stationary, where the specimen is held at an assigned current density, quasi-stationary, where the current density is changed stepwise at a desired rate.
2.2.1 GALVANOSTATIC POLARIZATION TEST

In opposition to the test explained before, in the galvanostatic polarization the current density, and not the potential, is controlled between the working and the counter electrode. The potential of the working electrode is measured against the reference electrode.

This method consists of applying a constant anodic current and measuring the potential as a function of time and the result is a chronopotentiometric curve with three distinct regions:

- Nucleation region, where the maximum potential reached corresponds to the breakdown potential
- Propagation region, where the potential gradually decrease until it reaches a stationary value
- Protection region, where the potential attained can be considered as the repassivation potential

These three regions are represented in Figure 2.7 [41]

![Figure 2.7](image)

*Figure 2.7* – The three region of the chronopotentiometric curve: nucleation (I), propagation (2) and protection (3) [41]
It has been shown that the galvanostatic method can be used for the determination of breakdown and repassivation potential without incurring in crevice phenomena [41]: owing to the rapid pit activation imposed by this technique, crevice corrosion is eliminated at the specimen/holder interfaces, even without any specific care in designing electrode holders. This technique permits also to have low scattering in the value of pitting potential.

2.2.2 STEPWISE GALVANIC POLARIZATION

In this method, changes in electrode potential are recorded until the breakdown potential is achieved; at further increase of the current density the potential decrease until a stationary value is attained and repassivation potential is achieved.

Figure 2.8 shows a curve obtained with this method [4]

![Figure 2.8](image)

**Figure 2.8** – Curve obtained with the stepwise galvanic polarization [4]

2.3 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

Electrochemical impedance spectroscopy (EIS) is a technique that determines a numerical value for the degree of corrosion protection provided by the passive film to a metal substrate. This numerical value is called film impedance and is defined as the ability of the passive layer to resist corrosion through the combination of barrier and adhesive properties: the more the film protects the substrate, the higher the impedance value.
EIS data are collected using a three-electrode cell, which is like the configuration of the potentiodynamic polarization.

Initially the open circuit potential is determined and is defined as the voltage between the reference and the working electrode, then a sinusoidal voltage is applied with an amplitude of 10 mV respect to the open circuit potential of the electrochemical cell: this result in a sinusoidal response. The sample is scanned both over a range of frequencies and a period of time.

There are two limits for the behaviour of the system:

- In phase behaviour, which occurs only in pure resistor
- Out of phase, which occurs only in pure capacitor

When dealing with AC we can decompose the output signal in two parts: the in-phase component and out-of-phase component. For sake of simplicity lets think of the input as a sinusoidal, the in-phase part will be a sinusoidal with the same phase of the input, while the out-of-phase part will be a sinusoidal with a delay of 90°. Because a passive material contains both resistive and capacitive elements, the phase shift of the current, and also potential, will be between 0° and 90°.

The impedance of a sample is determined from the information provided by these two sinusoidal curves. The impedance can be determined by:

\[
Z = \frac{|E_0| \sin(\omega t + \Phi_v)}{|I_0| \sin(\omega t + \Phi_i)}
\]

Eq. 2.1

Where \(|E_0|\) and \(|I_0|\) are the amplitudes of the AC voltage and current, \(\omega\) is the angular frequencies, \(\Phi_v\) and \(\Phi_i\) are the phase angles of the voltage and current respectively. From this definition of impedance, the modulus can be obtain, which is also equal to:

\[
|Z| = \sqrt{(Z_{in-phase})^2 + (Z_{out-of-phase})^2}
\]

Eq. 2.2

\[
Z = |Z|e^{i\theta} = Z_{in-phase} + iZ_{out-of-phase}
\]
Impedance data are normally illustrated in Bode plots, with log impedance modulus shown versus the log of frequency of the imposed signal [43]. This method is efficient at measuring how much the passive layer, or any other protective layer that has been deposited onto the surface of the sample, is adherent to the substrate: larger the impedance measured, better the adhesion on the substrate. From these measurements the thickness of the layer can be obtained [42].

Even if the adhesion and thickness of the passive layer can be used as a qualitative evaluation of the corrosion protection, this method do not give a numerical value of potential of interest (pitting and repassivation potentials)

### 2.4 SCRATCH METHOD

The last electrochemical method presented is the scratch method: in this method the test specimen is held in the electrolyte at different constant potentials. The protective film is broken by scratching with a hard material, diamond or carborundum, and then the current density is monitored to determine whether the metal is capable of repassivation or not. A sharp increase in repassivation time is usually found at the repassivation potential. The advantage of this method is that the results are independent on the surface finishing, but the potential measured is usually nobler than the re-passivation potential but lower than the breakdown potential found with other methods [4].

In this work two main electrochemical methods, i.e. potentiostatic and potentiodynamic polarization tests, have been chosen from a vast variety of possible choices. These electrochemical methods were chosen as an alternative to field testing method as they are less time consuming.
MATERIALS AND METHODS

3.1 MATERIAL

The material used as working electrode for the experiment was AISI 304L, UNS S30400, chemical composition is shown in the Table 3.1

<table>
<thead>
<tr>
<th>Fe</th>
<th>C</th>
<th>Cr</th>
<th>Ni</th>
<th>Mn</th>
<th>Mo</th>
<th>N</th>
</tr>
</thead>
<tbody>
<tr>
<td>71.899</td>
<td>0.018</td>
<td>17.271</td>
<td>8.422</td>
<td>1.458</td>
<td>0.076</td>
<td>0.063</td>
</tr>
</tbody>
</table>

This chosen alloy has a PREN around 18.

3.2 SAMPLE PREPARATION

Three types of specimen are chosen for the analysis, with different surface area.

For the most used specimen, an AISI 304 stainless steel plate was cut into rectangular samples in 30x20x2 mm size (in Fig 3.1). Sample preparation for all the tests (potentiodynamic, potentiostatic and stepwise polarisation) were carried out with this type of configuration. The steps are presented in the Table 3.2

<table>
<thead>
<tr>
<th>Step 1</th>
<th>The sample are polished with 100, 320, 600 and 800 SiC paper on one side</th>
</tr>
</thead>
<tbody>
<tr>
<td>Step 2</td>
<td>A wire is soldered to the unpolished surface, that is first activated with phosphoric acid to have a better adhesion between wire and surface; the connection is then tested physically by pulling the wire by hand</td>
</tr>
<tr>
<td>Step 3</td>
<td>The surface is polished again with a 1200 SiC paper</td>
</tr>
<tr>
<td>Step 4</td>
<td>The surface is cleaned with acetone to remove contamination and then the specimen is fitted into a plastic tube with a designed geometry to hold the sample</td>
</tr>
<tr>
<td>Step 5</td>
<td>The sample is then covered with an anti-corrosive silicon resin, leaving an</td>
</tr>
</tbody>
</table>
Other two types of specimens are used in this work, with two different exposed surface area: 10cm² (cut in a squared shape of 40x40x2 mm) and 50cm² (cut in a rectangular shape of 90x70x2 mm). The preparation of both of them is similar with the 2 cm² sample, with the only difference that for the 50 cm² sample the soldered wires are two and not one, to have a better mechanical support.

### 3.3 APPARATUS AND TOOLS

A Princeton Applied Research potentiostat (model 273A) was used for potentiodynamic tests and an AMEL Instruments model 2049 potentiostat was used for stepwise potentiodynamic tests and potentiostatic tests (Figure 3.2), then switched to a multi channel potentiostat/galvanostat AMEL Instruments model 1480/A.

As seen in Figure 3.2, the setup is a container with 25 litres capacity. One container was filled with 20 litres containing 1000ppm of chloride concentration (slow potentiodynamic). Another container was filled with 20 litres initially containing 100ppm of chloride concentration (potentiostatic) and later the chlorides concentration was increased. A polymeric plate with holes drilled in a circular fashion to fit the sample holder was used to cover the container. 10 samples for each setup was considered. Each sample has a cable that can be connected to resistors (10 KΩ and 1 KΩ). The connection is made only to one of the resistors (10 KΩ) and later changed to (1 KΩ). Each cell/container contains a reference electrode, working electrode and a counter electrode that are connected to the potentiostat.

A hole was drilled in the centre of the plastic plate for the reference electrode (Ag/AgCl/KCl sat) and a hole for the counter electrode (activated titanium mesh). Two separate holes were drilled for the temperature and pH measuring probe.
Fast potentiodynamic tests were recorded on a computer through a software and analysed on Microsoft Excel® as shown in Fig. 3.3.

3.4 PRE-CONDITIONING TIME

This is the time required to gain passivity of the surface by immersing the sample in the solution. According to the tests conducted (Fig. 3.4), for different concentrations of chlorides it was seen that the potential became stable after 6 hours. For flexibility in conducting the experiments taking the work timings into consideration, 24 hours was chosen as the pre-conditioning time.
Figure 3.4 - The pre-conditioning time for AISI 304 at concentration of 3000 and 1000 ppm

3.5 POTENTIODYNAMIC POLARIZATION TEST

The electrolytic solutions were composed by H₂O and NaCl. The solution had a pH between 6 and 6.5.

For potentiodynamic tests, the chosen chloride concentrations were: 100 ppm (2.8 x 10⁻³ mol/L), 300 ppm (8.5 x 10⁻³ mol/L), 1000 ppm (28 x 10⁻³ mol/L) and 3000 ppm (85 x 10⁻³ mol/L). These were obtained by respectively adding 0.82 g, 2.47 g, 8.24 g and 24.72 g of NaCl to 5 L of H₂O.

For the fast potentiodynamic test various scan rates are considered for different concentrations of chlorides, in particular for 1000ppm and 3000ppm, for which both continuous and stepwise potentiodynamic polarization have been conducted.

In Table 3.3 it is displayed the tests done for every concentration.
Table 3.3- Tests performed with different concentrations of chloride for different scan rates and surface area

<table>
<thead>
<tr>
<th>Chloride concentration (ppm)</th>
<th>Molar concentration (mol/L)</th>
<th>Surface area (cm²)</th>
<th>Scan Rate (mV/h)</th>
<th>Type of potentiodynamic test</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>2.8 x 10⁻³</td>
<td>2</td>
<td>600</td>
<td>continuous</td>
</tr>
<tr>
<td>300</td>
<td>8.5 x 10⁻³</td>
<td>2</td>
<td>600</td>
<td>continuous</td>
</tr>
<tr>
<td>1000</td>
<td>28 x 10⁻³</td>
<td>2</td>
<td>10</td>
<td>continuous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>3000</td>
<td>85 x 10⁻³</td>
<td>2</td>
<td>10</td>
<td>continuous</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2</td>
<td>600</td>
</tr>
<tr>
<td>10000</td>
<td>280 x 10⁻³</td>
<td>2</td>
<td>1</td>
<td>stepwise</td>
</tr>
<tr>
<td>1000</td>
<td>28 x 10⁻³</td>
<td>10</td>
<td>600</td>
<td>continuous</td>
</tr>
<tr>
<td>1000</td>
<td>28 x 10⁻³</td>
<td>50</td>
<td>600</td>
<td>continuous</td>
</tr>
</tbody>
</table>

For the slow potentiodynamic test, 10 AISI 304L samples were taken into consideration. At the start, a constant potential of -0.05 V vs Ag/AgCl/KCl sat was taken as it was the E_corr of the system and allowed to stay in this condition for 48 hours (pre-conditioning time). After the period of 48 hours, a potential of 50 mV for every 48 hours was applied stepwise. The electrolyte solution being 10000ppm of chloride concentration, room temperature and pH of 6.

The test cell allows the following items to be inserted in the solution chamber: the working electrode, the reference and counter electrode. The sample was properly mounted into the sample holder, inserted in the test cell and connected to the potentiostat as working electrode. Both reference and counter electrode were inserted in the cell and connected to the potentiostat as well.

3.6 POTENTIOSTATIC POLARIZATION TEST

Potentiostatic tests were performed for a total of 131 days for 20 samples (10 each test) with preconditioning time of 48 hours. A constant potential was applied (0.42 V and 0.336 V vs
Ag/AgCl/KCl sat) based on the minimum localized corrosion potential obtained from potentiodynamic tests. The specifications of the test are shown in Table 3.4.

**Table 3.4** - Potentiostatic test specifications, conducted at room temperature.

<table>
<thead>
<tr>
<th>Surface area (cm²)</th>
<th>E_corr V (SSC)</th>
<th>Initial chloride content</th>
<th>Addition of chlorides</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>0.42</td>
<td>100ppm</td>
<td>50 ppm (every 48 hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Then 100ppm (every 48 hours)</td>
</tr>
<tr>
<td>2</td>
<td>0.335</td>
<td>100ppm</td>
<td>100ppm (every 24 hours)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Then 500ppm (every 48 hours)</td>
</tr>
</tbody>
</table>

Temperature and pH were measured every day, as well as the current density for each specimen.

Two resistors are involved in the experiment (10 KΩ and 1 KΩ). At the beginning of the test the samples are first connected to 10 KΩ. This is because the current is too small to measure the voltage across the resistor. When an increase in the voltage across the resistor is measured, the resistor is changed to 1 KΩ and care was taken to avoid interruption of the connection to the sample during this operation.

Depending on the test, the addition of the chloride change from once every 48 hours 50ppm of chlorides for the test of 0.42 V vs SSC and once every 24 hours of 100ppm of chlorides for the 0.33 V vs SSC. The addition was hen increased to 100 every 48 hours for the first and 500ppm every 48 hours for the latter when they reached 1400ppm and 4500ppm respectively. Before every chloride addition, the voltage difference across the resistors was measured, and the current density was found by simple mathematical calculations i.e.

\[ i = \frac{E}{S \cdot R} \]
Where I is the current density, E is the potential measured through the resistors, S is the surface of the sample in m² and R is the resistance.

The breakdown potential is reflected by a sudden increase in the current density by some orders of magnitude and the resistor is changed to 1KΩ to reduce the ohmic drop across the resistor. Essentially the ohmic drop on the resistance don’t have to be too high (maximum 10 mV) so the polarization potential does not change excessively.

After this step, the voltage difference across the 1 KΩ resistor was checked once every day and when electrical charge (calculated by integration of the measured current) was observed to be more than 5 C the sample was removed. A study [44] suggested that 5 coulombs corresponds to stable pit propagation and could be the threshold charge based on the tests.
RESULTS

This chapter deals with the results obtained for the experiments conducted on potentiodynamic and potentiostatic tests.

4.1. POTENTIODYNAMIC POLARIZATION TESTS

Potentiodynamic tests (continuous) are performed to obtain localized corrosion features such as breakdown potential and re-passivation potential. The influence of some parameters such as the potential scan rate, variation of chloride concentrations and the effect of surface area on localized corrosion of the 304 stainless steel are evaluated. The tests conducted are mentioned in chapter 3 and the results are shown below.

In some cases, most when the chloride contents are low (100ppm and 300ppm), some results have been discarded. The reason is that for the pH measured (pH=6) the threshold of oxygen reduction is set to be 0.68 V vs SSC. This threshold define if the breakdown of the passive layer can happen also in real exposure or it undergoes the localized corrosion because of a too high potential applied by the potentiostat.

4.1.1 EFFECT OF CHLORIDE CONCENTRATION

The first potentiodynamic tests are conducted to study the effect of chloride concentration on 304 stainless steel. Three sets of test have been conducted to study the effect of chloride concentration: 10 potentiodynamic curves are obtained for 100 ppm chloride concentration, 15 for 300 ppm chloride concentration and other 10 for 3000 ppm chloride concentration. The cumulative polarization curves are shown in Figure 4.1 to 4.4.
Figure 4.1 - Polarisation curves of 100 ppm chloride, scan rate 600 mV/h, 2 cm², room temperature.

As can be seen from both the Figure 4.1 and Table 4.1 (Appendix A), the corrosion potential of the samples is around 0V vs SSC, the breakdown potential ranges from about 550 mV to over 800 mV vs Ag/AgCl/KCl sat.

Figure 4.2 - Polarisation curves of 300 ppm chloride, scan rate 600 mV/h, 2 cm², room temperature.
Chapter 4

For the set of tests at 300 ppm chloride can be distinguished two different runs: one with a complete loop, on with only forward polarization. The latter is due to an excessive presence of corrosion products, for this reason the tests had to be stopped.

As for the set of 100 ppm, in some cases the breakdown potential exceed the oxygen evolution threshold. The corrosion potential remains quite stable and does not change value from one another, while the pitting potentials are significantly lower.

Figure 4.3 - Anodic polarisation curves of 300 ppm chloride, scan rate 600 mV/h, 2 cm², room temperature.

Figure 4.4 - Polarisation curves of 3000 ppm chloride, scan rate 600 mV/h, 2 cm², room temperature.

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As can be seen from the Figure 4.1 to 4.4, there is a decrease in pitting potential and repassivation in function of the chloride content, while the corrosion potential does not vary much.

### 4.1.2 EFFECT OF SURFACE AREA

Potentiodynamic tests were conducted on AISI 304 stainless steel sample with surface area 10 cm$^2$ and 50 cm$^2$ to study the effect of surface area on the localized corrosion potential. For the two different exposed surface area the test have been conducted in 1000ppm of chloride. Figure 4.7 and Figure 4.8 represent the polarisation curves of those tests.

![Figure 4.7](image1.png)

**Figure 4.7**-Polarisation curves of 1000 ppm chloride, scan rate 600 mV/h, 10 cm$^2$ at room temperature.

![Figure 4.8](image2.png)

**Figure 4.8**-Polarisation curves of 1000 ppm chloride, scan rate 600 mV/h, 50 cm$^2$ at room temperature
The range of $E_{\text{loc}}$ and $E_{\text{rep}}$ are similar for both the two set of experiments, and range from 0.35 to 0.5 V vs Ag/AgCl/KCl sat and from 0 to 0.1 V vs Ag/AgCl/KCl sat respectively.

### 4.1.3 EFFECT OF SCAN RATE

These tests are conducted to evaluate the effect of different scan rates on the corrosion and pitting potential of stainless steels. For the concentration of 1000 ppm chlorides three scan rates were used: 600 mV/h, 100 mV/h and 10 mV/h. The results are presented in Table 4.1 and 4.2.

#### Table 4.1- Results of previous research, 1000 ppm, scan rate 100 mV/h, 2 cm$^2$, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (V SSC)</th>
<th>$E_{\text{loc}}$ (V SSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.096</td>
<td>0.322</td>
</tr>
<tr>
<td>2</td>
<td>-0.040</td>
<td>0.409</td>
</tr>
<tr>
<td>3</td>
<td>0.093</td>
<td>0.426</td>
</tr>
<tr>
<td>4</td>
<td>0.084</td>
<td>0.460</td>
</tr>
<tr>
<td>5</td>
<td>0.050</td>
<td>0.468</td>
</tr>
</tbody>
</table>

#### Table 4.2- Results of 1000 ppm, scan rate 10 mV/h, 2 cm$^2$, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{\text{corr}}$ (V SSC)</th>
<th>$E_{\text{loc}}$ (V SSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.028</td>
<td>0.558</td>
</tr>
<tr>
<td>2</td>
<td>0.162</td>
<td>0.575</td>
</tr>
<tr>
<td>3</td>
<td>0.041</td>
<td>0.390</td>
</tr>
<tr>
<td>4</td>
<td>-0.035</td>
<td>0.423</td>
</tr>
<tr>
<td>5</td>
<td>-0.049</td>
<td>0.553</td>
</tr>
</tbody>
</table>

Also for the concentration of 3000 ppm chlorides three scan rate have been used: 10 mV/h and 100 mV/h. The tests at scan Results are shown in Table 4.3 and Table 4.4.
Table 4.3 - Results for 3000 ppm Cl, scan rate 100 mV/h, 2 cm², Horizontal, Silicon, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (V SSC)</th>
<th>$E_{loc}$ (V SSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.040</td>
<td>0.368</td>
</tr>
<tr>
<td>2</td>
<td>-0.115</td>
<td>0.329</td>
</tr>
<tr>
<td>3</td>
<td>0.049</td>
<td>0.351</td>
</tr>
<tr>
<td>4</td>
<td>0.006</td>
<td>0.369</td>
</tr>
<tr>
<td>5</td>
<td>-0.110</td>
<td>0.300</td>
</tr>
</tbody>
</table>

Table 4.4 - Results for 3000 ppm Cl, scan rate 10 mV/h, 2 cm², Horizontal, Silicon, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$E_{corr}$ (V SSC)</th>
<th>$E_{loc}$ (V SSC)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-0.039</td>
<td>0.307</td>
</tr>
<tr>
<td>2</td>
<td>-0.030</td>
<td>0.344</td>
</tr>
<tr>
<td>3</td>
<td>0.043</td>
<td>0.370</td>
</tr>
<tr>
<td>4</td>
<td>-0.090</td>
<td>0.301</td>
</tr>
<tr>
<td>5</td>
<td>-0.059</td>
<td>0.323</td>
</tr>
</tbody>
</table>

As can be seen from both Table 4.4 and Table 4.4, the values for pitting potential lowers with lowering the scan rate.

A single stepwise potentiodynamic polarization, with scan rate of 1 mV/h, has been conducted at the chloride concentration of 10000 ppm.

Fig 4.9 show the results of this stepwise potentiodynamic polarization.

Table 4.5 – Results for the stepwise potentiodynamic polarization, scan rate 1 mV/h, surface area of 2 cm², room temperature

<table>
<thead>
<tr>
<th>Sample</th>
<th>Potential Polarization (mV vs Ag/AgCl/KCl_sat)</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>356</td>
<td>19</td>
</tr>
<tr>
<td>2</td>
<td>556</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>556</td>
<td>24</td>
</tr>
<tr>
<td>4</td>
<td>656</td>
<td>27</td>
</tr>
<tr>
<td>5</td>
<td>656</td>
<td>27</td>
</tr>
<tr>
<td>6</td>
<td>906</td>
<td>35</td>
</tr>
<tr>
<td>7</td>
<td>756</td>
<td>29</td>
</tr>
<tr>
<td>8</td>
<td>506</td>
<td>23</td>
</tr>
<tr>
<td>9</td>
<td>456</td>
<td>22</td>
</tr>
<tr>
<td>10</td>
<td>656</td>
<td>27</td>
</tr>
</tbody>
</table>
4.2 POTENTIOSTATIC POLARIZATION TESTS

Potentiostatic tests were performed at room temperature, pH varying between 6 to 6.5 and a constant potential of 0.42 V and 0.335 V both vs Ag/AgCl/KCl_{sat}. These potentials are chosen based on minimum localized corrosion potential obtained by potentiodynamic tests corresponding to each chloride concentration.

The test on 0.335 V vs Ag/AgCl/KCl_{sat} lasted 131 days and then it has been decided to stop after it reached 20000ppm chloride and it remained at that concentration for 2 weeks. Samples 2, 4, 5, 7 and 9 did not suffer localized corrosion.

The tests on 0.42 V vs Ag/AgCl/KCl_{sat} lasted 131 days and 8 specimen out of 10 reached the localised corrosion.

The results of both potentiostatic tests are presented in the Table 4.6 and Table 4.7 and Fig. 4.10 and Fig. 4.11.
Table 4.6 - Results for potentiostatic polarisation at 0.336 V vs SSC\text{sat}, addition of 100 ppm every day (first 62 days) and 500 ppm every two days, 2 cm\(^2\), Horizontal, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chloride Concentration (ppm)</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>20000</td>
<td>124</td>
</tr>
<tr>
<td>2</td>
<td>20000</td>
<td>124</td>
</tr>
<tr>
<td>3</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>4</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>6</td>
<td>20000</td>
<td>124</td>
</tr>
<tr>
<td>7</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>8</td>
<td>20000</td>
<td>129</td>
</tr>
<tr>
<td>9</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>10</td>
<td>11000</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 4.7 - Results for potentiostatic polarisation at 0.421 V vs SSC\text{sat}, addition of 50 ppm every two days (first 63 days) and 100 ppm every two days, 2 cm\(^2\), Horizontal, room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Chloride Concentration (ppm)</th>
<th>Days</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3100</td>
<td>105</td>
</tr>
<tr>
<td>2</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>3</td>
<td>3100</td>
<td>105</td>
</tr>
<tr>
<td>4</td>
<td>3400</td>
<td>111</td>
</tr>
<tr>
<td>5</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>6</td>
<td>3400</td>
<td>111</td>
</tr>
<tr>
<td>7</td>
<td>3100</td>
<td>105</td>
</tr>
<tr>
<td>8</td>
<td>850</td>
<td>38</td>
</tr>
<tr>
<td>9</td>
<td>3400</td>
<td>111</td>
</tr>
<tr>
<td>10</td>
<td>3400</td>
<td>111</td>
</tr>
</tbody>
</table>
Figure 4.10 - Results for potentiostatic polarisation at 0.42 V vs Ag/AgCl/KCl_{sat}

Figure 4.11 - Results for potentiostatic polarisation at 0.335 V vs Ag/AgCl/KCl_{sat}
DISCUSSION

Comparison between the results obtained during the thesis work and the literature review will be conducted in this chapter. The aim of this discussion is to obtain the Pedeferri diagram, discussing how different electrochemical methods used affect the final drawing of it.

5.1 POTENTIODYNAMIC POLARISATION TEST

The first electrochemical method that is discussed is the potentiodynamic polarisation tests and how the chloride concentration and setup variable influenced the results of this test.

5.1.1 EFFECT OF CHLORIDE CONCENTRATIONS

As shown in the figures of the previous chapter (Fig. 4.1 to Fig. 4.8), the test conducted are presented in the forms of potentiodynamic polarisation curves. In those curves, one can distinct three points, as explained in Chapter 1: the corrosion potential, the pitting or breakdown potential and the repassivation potential.

Many authors confirm this trend, that to an increase of chlorides, or more in general halides, a decrease of breakdown potential follows [3, 4], and as expected also in this work this trend is confirmed.

In order to compare the results obtained with different chloride concentration, a data distribution of the results have been studied and plotted (Fig 5.1) for specimen with 2 cm² and at a scan rate of 600 mV/h. In addition, data from previous thesis work are taken into account, for a total of six sets of test considered, ranging from 100 ppm to 19000 ppm chloride concentration. To build this integral probability curves it has been taken the whole pool of data of a single set and to each value a percentage of failure have been attributed: for example, for the test of 1000ppm chloride (Fig. 5.1c), the value 500mV vs Ag/AgCl/KCl_sat has been attributed the 80% of failure, meaning that in the tests carried out in this thesis 80% of the specimen undergo pitting corrosion at 500mV. Dually it can be said that a specific percentage of failure has been attributed a polarization potential: taking the curve for 3000ppm chloride concentration (Fig 5.1d), the potential at which the 50% of the specimen failed is about 400mV vs Ag/AgCl/KCl_sat.
The same consideration can be done for the re-passivation potential, but instead of failure of the specimen (pitting attack occurs), the success of the specimen is considered (the re-passivation is achieved). For this reason, there is a formation of the peculiar funnel shape of the two curve. For each percentage considered, the difference between the pitting potential and repassivation potential give an estimated value of the imperfect passivity range; taking the Pedeferri’s diagram of Chapter 1 (Fig. 1.15) can be seen that the imperfect passivity lays between the two values of $E_{\text{loc}}$ and $E_{\text{rep}}$.

**Figure 5.4**- Probability curves for all the concentration tested. a) 100 ppm, b) 300 ppm, c) 1000 ppm, d) 3000 ppm, e) 10000 ppm, f) 19000 ppm [45] for samples of 2 cm$^2$, 600mV/h
It can be seen that for the set of 100 ppm and 300 ppm (Fig. 5.1a and Fig. 5.1b respectively) some percentage of failure are missing, this is due to the results obtained in those tests. Recalling the Pourbaix diagram (Chapter 1.2, Figure 1.2) for the oxygen two zones are defined: the oxygen reduction and oxygen evolution. In Chapter 1.1 it has been point out that at neutral or basic pH the cathodic reaction is oxygen reduction, so potential where oxygen reduction is not possible are not consider significant. For this reason the pitting potentials values above 0.68 V vs Ag/AgCl/KCl sat are not considered.

To compare and to place the result in a single plot, two percentage have been considered: 10% and 90%. The first has been chosen because it has been decided as the limit of safety: 10% means that only 1 specimen out of 10 reached to the localized corrosion and so it is near the imperfect passivity and it is the first point for which we observed pitting phenomena. The second has been chosen as the limit for the pitting corrosion: it means that at that potential 9 specimen out of 10 reached to the localized corrosion and so it is practically sure to be in the pitting corrosion zone. A similar, but reverse, thought can be done for the re-passivation phenomena: when the 10% of the specimen reached to the re-passivation, there it is the limit between the perfect and imperfect passivity; when the 90% of the specimen re-passivate, it is very probable to be in the perfect passivity zone.

Isoprobability curves have been drown taking the 10% and 90% of failure (pitting) and re-passivation. From these curves can be distinguished the three zones of the Pedeferri’s diagram (Chapter 1.6, Fig. 1.15): the perfect passivity zone below the 90% of the re-passivation, the imperfect passivity between the 10% of re-passivation and 10% of pitting, and the pitting corrosion zone above the 90% of pitting.

Both linear and logarithm plot are shown in Fig 5.2 and Fig 5.3.

It can be noticed that the linear relationship between the pitting potential and the logarithm of chloride contents expressed in Chapter 1.5.1 (Eq. 1.14) has been found for both pitting potential and re-passivation potential. The only discrepancy is for high chloride contents, for which re-passivation is more difficult.
In high concentrations (19000 ppm), it was difficult to attain re-passivation potential points for 90% of the specimen that attained localized corrosion due to the fact that at high concentration most of the time the specimens suffer a very severe localised corrosion and they are not able to repassivated if not at very low polarization potential (lower than -200 mV vs Ag/AgCl/KCl_{sat}).
For sake of completeness, a statistical study has been conducted, measuring the average values, the standard deviations and the dispersion index of the data. Although the average value of breakdown potential and repassivation potential do not give a complete understanding of the phenomenon, being localized corrosion stochastic by nature, they are needed for the definition of dispersion index value. The dispersion index is the ratio between the standard deviation of a set of value and the average of the same set [46].

Both standard deviations and dispersion index define the replicability of the test conducted: the lower is the value of these two, the more probable it is to obtain results similar of the ones obtained in previous tests.

Before the calculation of the above mentioned statistical number, another quantity has been introduced: the interval of passivity, which is defined as the difference between the corrosion potential and the pitting potential.

The average and standard deviation of the pitting potential and repassivation potential are shown in Table 5.1, while in Table 5.2 the average, standard deviation and dispersion index of the interval of passivity are calculated.

Table 5.1- Average values and standard deviation of breakdown potentials ($E_{loc}$) and repassivation potential ($E_{rep}$)

<table>
<thead>
<tr>
<th>Cl- (ppm)</th>
<th>$E_{loc}$ (V vs SSC) Average</th>
<th>$E_{rep}$ (V vs SSC) Average</th>
<th>Standard Deviation $E_{loc}$ V</th>
<th>Standard Deviation $E_{rep}$ V</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.643</td>
<td>0.095</td>
<td>0.085</td>
<td>0.064</td>
</tr>
<tr>
<td>300</td>
<td>0.576</td>
<td>0.056</td>
<td>0.073</td>
<td>0.053</td>
</tr>
<tr>
<td>1000</td>
<td>0.462</td>
<td>0.035</td>
<td>0.043</td>
<td>0.061</td>
</tr>
<tr>
<td>3000</td>
<td>0.408</td>
<td>0.030</td>
<td>0.085</td>
<td>0.064</td>
</tr>
<tr>
<td>10000</td>
<td>0.405</td>
<td>-0.027</td>
<td>0.042</td>
<td>0.035</td>
</tr>
<tr>
<td>19000</td>
<td>0.405</td>
<td>-0.159</td>
<td>0.017</td>
<td>0.101</td>
</tr>
</tbody>
</table>

Table 5.2- Average values, standard deviations and dispersion indexes (DI) of the interval of passivity($E_{loc}$-$E_{corr}$)

<table>
<thead>
<tr>
<th>Cl- (ppm)</th>
<th>$E_{loc}$-$E_{corr}$ (V) Average</th>
<th>Standard Deviation $E_{loc}$-$E_{corr}$ (V)</th>
<th>DI $E_{loc}$-$E_{corr}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.644</td>
<td>0.096</td>
<td>14.9</td>
</tr>
<tr>
<td>300</td>
<td>0.582</td>
<td>0.083</td>
<td>14.2</td>
</tr>
<tr>
<td>1000</td>
<td>0.483</td>
<td>0.072</td>
<td>15.0</td>
</tr>
<tr>
<td>3000</td>
<td>0.450</td>
<td>0.037</td>
<td>8.2</td>
</tr>
<tr>
<td>10000</td>
<td>0.434</td>
<td>0.057</td>
<td>13.2</td>
</tr>
<tr>
<td>19000</td>
<td>0.408</td>
<td>0.025</td>
<td>6.1</td>
</tr>
</tbody>
</table>
As can be seen both values of standard deviation and dispersion index show us the stochastic aspect of localised corrosion: it is easy to deduct it by the values of dispersion index, 4 set of tests out of 6 have a volatility above 10% and only one it’s near 5%, that it is consider a good replicability. The sets of tests done at 3000 ppm and 19000 ppm have a much lower volatility value than the others. For 19000 ppm the explanation can be that the chloride contents becomes the predominant factors for the break of the passivity (the dependence on pH and temperature are lower), while for other results a minimal and/or variation of pH or temperature scatter influenced more the results; while for 3000ppm no explanation can be given.

5.1.2 EFFECT OF SURFACE AREA

In order to evaluate the effect of the surface area, specimens with different surface areas (1, 2, 4, 10 and 50 cm²) were selected.

The results of the test conducted are shown in Fig 5.4, with the criterion of failure probability mentioned above.

Even if a dependence on the exposed area is expected (Fig 5.5), no trend is found in this work.

![Figure 5.3- Isoprobability curves of different surface area](image)
Figure 5.5- Potentiodynamic polarization curves samples of AISI 304 in 3.5\% NaCl, at 35°C with potential scan rate of 480 mV/min for various surface area [47]

The same authors [46] claims that if the potential scan rate is kept low enough, no differences are found in the respect the surface area. From Fig 5.6 it can be seen that for potential scan rate of 20 mV/min (1200 mV/h) no dependence is found.

This explained why in this work the trend is not found: essentially the fastest potential scan rate used (600 mV/h) is far below the value found in literature.

Figure 5.6- Dependence of pitting potentials on the surface at fixed scan rate for samples of AISI 304 in 3.5\% NaCl and 35°C [47]
5.1.3 EFFECT OF POTENTIAL SCAN RATE

The scan rate taken into account in this work range from 1 mV/h to 600 mV/h, which is the potential scan rate imposed by the standard, so from a very fast potentiodynamic polarization to a very slow potentiodynamic.

The tests have been run with three different concentration: 1000 ppm, 3000 ppm and 10000 ppm. For the first, three potential scan rate (1 mV/h, 10 mV/h, 600 mV/h) have been used, while for the chloride concentration have been used or only the continuous potentiodynamic polarization (10 mV/h, 100 mV/h, 600 mV/h for 3000 ppm) or only the fastest and slowest (1 mV/h and 600 mV/h for 10000).

From Fig 5.7 to Fig 5.9 it is shown the effect of the various scan rate, with all the data. Some values have been removed because above the oxygen evolution threshold.

![Graph](Figure 5.7 – Pitting potentials at 1000 ppm with three different potential scan rate (1 mV/h [45], 10 mV/h and 600 mV/h))
A scan rate dependence is expected: lowering the scan rate, at lower polarization potential the pitting occur.

It can be clearly seen in Fig 5.7 and Fig 5.9, where pitting potentials value are lower as the potential scan rate lowers.

For 10000ppm the inverse is observed, no explanation can be given for that phenomenon.

### 5.2 POTENTIOSTATIC POLARISATION TESTS

The potentiostatic test the aim was to find the critical chloride concentration.

Based he result obtained in the work, only 5 out of 10 reached to the localised corrosion in the test of 0.335 V vs Ag/AgCl/KCl sat, and 4 of them reached the corrosion at 20000ppm chloride. Even if the breakdown is reached at a very high concentration, this results do not go against the results obtain with the potentiodynamic, since a pitting potential of 0.42V vs Ag/AgCl/KCl sat can be seen also at high concentration. Fig 5.10 and Fig 5.11 show the percentage of specimens corroded in function of the chloride in the solution.
It can be seen from both figures that the specimen suffered the localized attack much beyond the limit expected from the potentiodynamic. This is due to the form of the Pedeferri’s diagram (Fig 5.8): the critical chloride contents for a specific polarization potential is spread in an order of
magnitude more or less, so at that specific polarization potential the pitting can occur at a very varying chloride contents.

Figure 5.10- Critical chloride concentration for three different polarization potentials

For the other set of potentiostatic tests instead the polarisation potential was very similar to the one of the previous potentiostatic test (0.41 V vs SSC) and the result are similar to that experiment.

5.3 PEDEFERRI DIAGRAM

Fig. 5.11 show the comparison between all the potentiodynamic and potentiostatic polarization tests. It can be seen that the results give approximately the same range of values, with the difference that the potentiostatic give horizontal results (critical chloride contents) while the potentiostatic give vertical results (pitting potential).
The results of 1 cm$^2$, 2 cm$^2$, 4 cm$^2$ for 1000 ppm chloride content and the one of 2 cm$^2$ with 10000 ppm chloride content are taken from a previous thesis work [45] and the results of 2 cm$^2$ with 19000 ppm chloride content from an in progress bachelor thesis [48].

So there are two possible way to obtain Pedeferri diagram: using potentiostatic tests to find which is the critical amount of chloride content for a specific polarisation potential or potentiodynamic test to find which is the breakdown potential, and repassivation potential, for a specific chloride concentration. Being the potentiodynamic faster than potentiostatic and giving a similar range of values, as said earlier, potentiodynamic tests have been chose to get both faster and reliable result.

To plot a Pedeferri’s diagram for AISI 304 stainless steel (Fig 5.8), from all the potentiodynamic tests, the ones with samples of 2cm$^2$ and with a potential scan rate of 600 mV/h has been chosen to have uniformity in the data.

As can be seen one can distinguish the three area discussed in chapter one:

- The perfect passivity zone, where the potential is less than the last repassivation potential
- The imperfect passivity zone, where the potential is between the highest repassivation potential and the lowest breakdown potential
- The corrosion potential, where the potential is higher than the highest breakdown potential measured

![Figure 5.11 - Comparison between all the tests conducted in this thesis and the previous one](image-url)
To these three zones other two zones have been added:

- The no corrosion zone, that is similar to the perfect or imperfect passivity zone, where the chloride content is not high enough to break the passive film, and it is at around 50 ppm of concentration, that is in the same order of magnitude of the calculation made considering the PREN (calculated with Eq. 5.1 considering PREN=18, K=10, pH=6 and temperature at 25°C)

- The oxygen evolution zone, that defines the limit to consider a potential as possible in nature

Eq 5.1

\[
\log[C\text{-}\text{crit}] = \frac{PREN}{K} - \frac{7 - pH}{7} - \frac{T - 25}{25}
\]

Figure 5.8- Final Pedeferrri diagram, with all the areas highline; used potentials are the one for 600mV/h, 2 cm², room temperature
CONCLUSIONS

In this thesis, potentiodynamic and potentiostatic anodic polarization tests were carried out on austenitic UNS 304000 stainless steel in order to define the most proper test method for the definition of Pedeferrri diagram. Potentiodynamic tests were performed in the presence of different chlorides concentration (from 100 to 20,000 mg/kg) and potential scan rates (10 mV/h, 100 mV/h, 600 mV/h) in aerated and neutral solution. Then, potentiostatic tests were carried out at tailored polarization potential value in order to compare the two methods.

The results of potentiodynamic tests show that:

1. As expected, localized corrosion potential depends on the chlorides content in solution; the potential varies linearly with the logarithm of chlorides concentration as reported in several papers and books of the last 40 years

2. Localized corrosion potential and its distribution depends on the potential scan rate: generally, the localized corrosion potential increases as the scan rate increases, but this trend was not observed in same of the experimental conditions. This behaviour can be attributed to the kinetic of localized corrosion initiation, which is not instantaneous: the localized corrosion potential corresponds to the potential at which the incubation period of corrosion and the kinetic of the test method are comparable. The distribution (deviation) of localized corrosion potential values depends on potential scan rate and increases as the scan rate decreases. As a possible interpretation, longer test times can affect the electrochemical behaviour of the metal, in particular the properties of the passive film, as its thickness. In other words, longer tests (i.e. low potential scan rate) can induce modification (anodizing) of the passive oxide with the consequent modification of its corrosion resistance during the test;

3. From point 2 it is possible to conclude that low scan rate would be preferable because they provide lower localized corrosion potential (more conservative approach) but at the same times the dispersion of data is generally larger;

4. The potentiodynamic polarization method (continuous scan or stepwise) affects also the localized corrosion potential distribution: in the presence of a stepwise polarization, the data dispersion increases.
The performed potentiostatic tests showed that the two test methods are comparable, and a large deviation from the mean value is observed also for potentiostatic test. In principle, potentiostatic polarization test seems preferable because approach to the real condition where the oxidizing power of the electrolyte in contact with the metal is fixed (oxygen reduction process) while potentiodynamic test is strongly accelerated and does not simulate any practical condition. As already said.

A first attempt to draw the Pedeferri diagram UNS 304000 stainless steel in near neutral pH and at room temperature has been carried out. The results are promising even if the selection of the best tests method is ongoing.
BIBLIOGRAPHY


