

# **POLITECNICO DI MILANO**

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## **Effect of intermittent cathodic protection on potential and corrosion rate of carbon steel in soil simulating solution**

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## Abstract

The study of the effects of the interruption of the cathodic current in cathodic protection (CP) system is nowadays in a preliminary stage. Indeed, in real application cathodic protection is applied in a stationary way by means of a direct current that guarantees the reduction of corrosion rate. Nevertheless, often accessibility to energy sources is limited or cheaper solutions are preferred. In particular, nowadays a possible solution is represented by the use of renewable energy sources, as photovoltaic panels, whose energy production is confined to the hours of light (thanks to the batteries, energy is often available even at night, but not always sufficient for protection).

In this work, the effects of the interruption of cathodic protection on potential monitoring and corrosion rate of carbon steel are evaluated. Laboratory tests on carbon steel specimens in soil simulating condition under intermittent CP condition were carried out, varying the ON period (i.e. when the CP current is applied) and the OFF period (without cathodic protection). Long-term tests (about four months) were performed, during which potential has been monitored for 24 hours each week, in order to study the effect of current interruption on the potential of the metal, which is the most important parameter monitored in the field to verify CP condition of a structure ( $E < -0.85$  V CSE). At the end of the test, mass loss rate was determined and compared to the corrosion rate of a control specimen in free corrosion condition.

Results show that, in most of the cases, the potential remains below (more negative) the protection level ( $-0.85$  V CSE) after the interruption of the current, so that the metal can maintain the protection condition: the duration of this time depends mainly on the duration of the ON and OFF periods. In particular, during the ON period, oxygen is consumed and alkalinity is produced due to the cathodic current. These effects are not immediately lost after the interruption of the current. Longer ON periods favour the maintaining of CP condition. After this period, the potential increases up to the free corrosion condition, with an increase of corrosion rate. The mass loss rate values have been finally analyzed considering three interpretation models. In many cases lower corrosion rates than those evaluated considering the metal with active electrochemical behaviour were measured. This means that the CP has non-negligible chemical effects that extend for a short time

even after its interruption. The formation of passive condition on steel in CP condition is a possible explanation.

**Key words:** cathodic protection, carbon steel, mass loss, potential monitoring, corrosion rate.

## Sommario

Lo studio degli effetti della protezione catodica (PC) intermittente, vale a dire con corrente di protezione interrotta periodicamente, è attualmente in una fase preliminare. Nelle applicazioni di campo della protezione catodica, la corrente è applicata in modo stazionario, garantendo l'abbassamento del potenziale del metallo e la conseguente riduzione della velocità di corrosione. Tuttavia, spesso l'accessibilità alle fonti energetiche è limitata o si preferiscono soluzioni meno costose. In particolare, oggi una possibile soluzione è rappresentata dall'utilizzo di fonti energetiche rinnovabili, come i pannelli fotovoltaici, la cui produzione di energia è limitata alle ore di luce (grazie alle batterie, l'energia è spesso disponibile anche di notte, ma non sempre sufficiente per garantire permanentemente la protezione).

In questo lavoro di tesi sono valutati gli effetti dell'interruzione della protezione catodica sul potenziale e sulla velocità di corrosione dell'acciaio al carbonio. Sono stati effettuati test di laboratorio su provini di acciaio al carbonio in condizioni di protezione catodica intermittente in soluzione simulante terreno, variando il periodo di attivazione, detto periodo ON, cioè quando viene applicata la corrente di PC, e il periodo OFF (senza protezione catodica). Sono stati eseguiti test a lungo termine (circa quattro mesi), durante i quali il potenziale è stato monitorato per 24 ore a settimana, al fine di studiare l'effetto dell'interruzione corrente sul potenziale del metallo, che è il parametro più importante monitorato in campo per verificare la protezione di una struttura (definita da  $E < -0,85 \text{ V CSE}$ ). Alla fine della prova, la velocità di corrosione mediante perdita di massa è stata determinata e confrontata con la velocità di corrosione di un campione di riferimento in condizioni di corrosione libera.

I risultati mostrano che, nella maggior parte dei casi, il potenziale rimane inizialmente inferiore (più negativo) al livello di protezione ( $-0,85 \text{ V CSE}$ ) dopo l'interruzione della corrente. Ciò significa che il metallo è in grado di mantenere la condizione di protezione anche a seguito dell'interruzione di corrente: la durata di questo tempo dipende principalmente sulla durata dei periodi ON e OFF. In particolare, durante il periodo ON, l'ossigeno viene consumato e l'alcalinità viene prodotta dalla corrente catodica. Questi effetti non sono immediatamente persi dopo l'interruzione della corrente, ma permangono fino ad annullarsi in tempi più lunghi. In particolare, periodi di ON più lunghi favoriscono

il mantenimento della condizione di PC. I valori di velocità di corrosione sono stati infine analizzati considerando tre modelli di interpretazione. In molti casi sono stati misurati valori di velocità di corrosione inferiori a quelli valutati considerando il metallo con comportamento elettrochimico attivo. Ciò significa che la PC ha effetti chimici non trascurabili che si estendono per un breve periodo anche a valle della sua interruzione. La formazione di condizioni di passività sull'acciaio è una possibile spiegazione.

**Parole chiave:** protezione catodica, acciaio al carbonio, perdita di massa, monitoraggio del potenziale, velocità di corrosione.



## Introduction

In this thesis work, the effects of the interruption of cathodic protection (CP) current on potential monitoring and corrosion rate of carbon steel are investigated. This work is part of a research started in 2015 in which the chemical effects of cathodic protection, namely oxygen consumption and the promotion of passive condition on carbon steel due to the alkalinity formed in CP, were studied in the presence of d.c. interference corrosion. Then, due to the promising results, the interest of the research was addressed on the study of a CP system in which the cathodic current is interrupted periodically. The goal is to understand if, due to the interruption of the current, the protection is maintained due to the permanency of the positive chemical effects of CP. The main difference with the interference case is given by the duration of the OFF period (i.e. when the current is interrupted): while in the case of the anodic interference peaks this period is very short, in the case of intermittent CP is in the order of hours, and no anodic current is applied.

This research is just in a preliminary stage. Indeed, in real application cathodic protection is applied in a stationary way by means of a direct current that guarantees the reduction of corrosion rate. Nevertheless, often accessibility to energy sources is limited or cheaper solutions are preferred. In particular, nowadays a possible solution is represented by the use of renewable energy sources, as photovoltaic panels, whose energy production is confined to the hours of light (thanks to the batteries, energy is often available even at night, but not always sufficient for protection).

Laboratory tests on carbon steel specimens in soil simulating solution under intermittent CP condition were carried out, varying the ON period (i.e. when the CP current is applied) and the OFF period (without cathodic protection). ON period varies from 2 to 18 hours, while OFF period varies from 2 to 6 hours. Indeed, previous experimental tests showed that OFF period longer than 6 hours are not acceptable because of the high corrosion rate. Long-term tests (about four months) were performed; potential has been monitored for one day each week, in order to study the effect of current interruption on the potential of the metal, which is the most important parameter monitored in the field to verify CP condition of a structure (according to international standards, carbon steel is in CP condition if the potential is lower than  $-0.85$  V CSE). At the end of the test, mass loss rate was determined

and compared to the corrosion rate of a control specimen in free corrosion condition (24 hours CP-OFF). Results show that, in most of the cases, the potential remains more negative than the protection level (-0.85 V CSE) after the interruption of the current, so that the metal can maintain the protection condition: the duration of this time depends mainly on the duration of the ON and OFF periods and in some cases it can reach values higher than 2 hours. This slow depolarization is due to the chemical effects during the ON period: oxygen consumption in the ON period and its slow replacement in the OFF period and the production of alkalinity due to the cathodic current. These effects are not immediately lost after the interruption of the current. After this period, the potential increases up to the free corrosion condition, with an increase of corrosion rate.

The mass loss rate values have been finally analyzed considering three interpretation models. In many cases lower corrosion rates than those evaluated considering the metal with active electrochemical behaviour were measured. In particular, the lowest corrosion rates were measured in conditions with OFF period lower than 2 hours. This means that the CP has non-negligible chemical effects that extend for a short time even after its interruption. The formation of passive condition on steel in CP condition is a possible explanation.

The thesis is organized in three main parts:

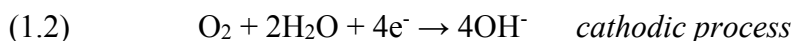
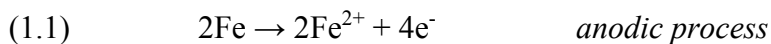
- Part I (Chapter 1 e Chapter 2), which reports the basic theory of cathodic protection and a review of some cases reported in the literature on the use of intermittent cathodic protection;
- Part II (Chapter 3), which reports a description of the experimental apparatus and methods;
- Part III (Chapter 4 e Chapter 5), which reports and discusses the obtained experimental results.

## Corrosion and cathodic protection overview

### 1.1 Corrosion of metals: thermodynamic and kinetic aspects [1]

Corrosion of metals is defined as the degradation of the material due to its interaction with the surrounding environment. Corrosion can occur in the presence of water (*wet corrosion*) or in the presence of high temperature gas (*dry corrosion*).

The first form, which is dealt with in this thesis work, takes place with an electrochemical mechanism, resulting from an anodic process, namely the dissolution of the metal, and a cathodic process that is the reduction of chemical species present in the environment, typically oxygen. Considering a metal (as iron or carbon steel) in natural environments (water, atmosphere, soil), the anodic process is metal dissolution and the cathodic process is oxygen reduction:

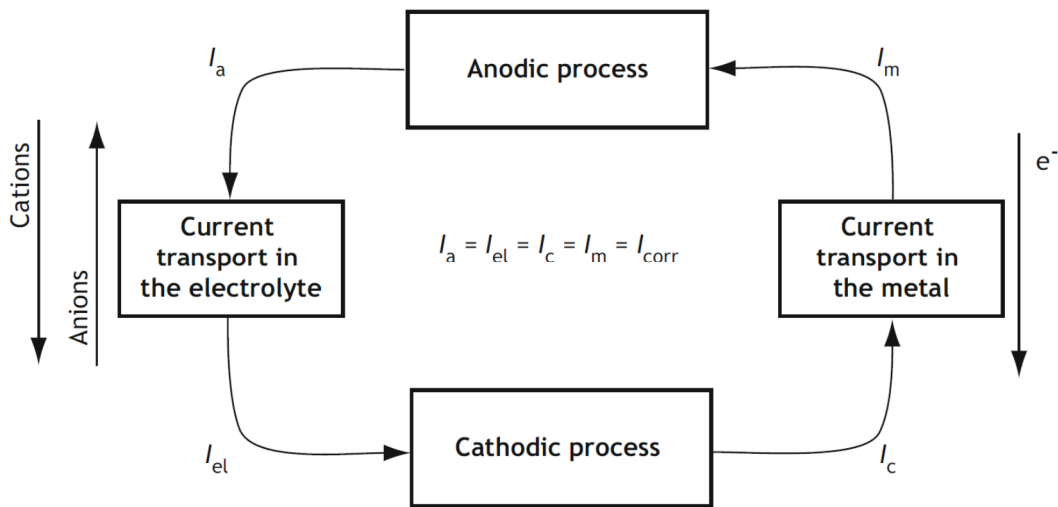


A further cathodic reaction can take place at low potentials or low pH, which is hydrogen evolution ( $2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$ ). A corrosion process implies two further processes, namely: 1) an electron flow within the metal from the anodic area, where electrons are released, to the cathodic zone, where electrons are consumed, 2) a current flow within the electrolyte by ion transportation, from the anode to the cathode zone. In short, a corrosion process consists of four processes in series, as depicted in Fig. 1.1. These four processes occur at the same rate. In fact, the number of electrons released by the anodic reaction, i.e., the anodic current,  $I_a$ , exchanged on the metal surface, the number of electrons consumed by the cathodic reaction, i.e., the cathodic current,  $I_c$ , the current flowing within the metal

from the cathode to the anodic zone,  $I_m$ , and the current circulating within the electrolyte,  $I_{el}$ , must be the same:

$$(1.3) \quad I_a = I_c = I_m = I_{el} = I_{corr}$$

This common current flow,  $I_{corr}$ , measures, in electrochemical units, the corrosion rate.



**Fig 1.1** – Electrochemical mechanism of a corrosion process. [2]

Since corrosion is an electrochemical mechanism, Faraday laws can be applied establishing the relationship between the corroding mass and the circulating electric charge (number of electrons) through the electrochemical equivalents: for iron, the equivalence between the corrosion current density (in mA/m<sup>2</sup>) and corrosion rate (in mm/y) is: 1 A/m<sup>2</sup> = 1.17 mm/y.

From thermodynamic considerations, it is possible to calculate for any partial reaction (anodic and cathodic) the *equilibrium potential* ( $E_{eq}$ ), which is a measure of the free Gibbs energy, i.e. the spontaneity of the reaction. Indicating with  $E_{eq,a}$  the equilibrium potential of the anodic reaction (dissolution of the metal) and with  $E_{eq,c}$  the equilibrium potential of the cathodic reaction (reduction of oxygen or hydrogen evolution) the thermodynamic condition of spontaneity of the corrosion process is:

$$(1.4) \quad E_{eq,c} > E_{eq,a}$$

For any electrochemical reaction ( $aA + bB + \dots \rightarrow cC + dD + \dots + ze^-$ ), the equilibrium potential is defined by the Nernst equation:

$$(1.5) \quad E_{eq} = E^0 + \frac{RT}{zF} \ln \frac{a_C^c \cdot a_D^d}{a_A^a \cdot a_B^b}$$

Where  $E^0$  is the standard potential of the reaction at standard conditions (i.e., unitary activity for dissolved species and fugacity 1 atm for gas);  $z$  is the number of electrons involved and  $F$  is the Faraday constant (964856 C), and,  $a_i$  are the activities of species,  $i$ , elevated to their stoichiometric coefficient. At 298 K, for metal dissolution reaction,  $M = M^{z+} + ze^-$ , the Nernst equation becomes:

$$(1.6) \quad E_{eq} = E^0 - \frac{0.354}{z}$$

where metal ion concentration is assumed  $10^{-6}$  mol/L, as suggested by Pourbaix, for electrolytes not containing metal ions, as in the case of metals exposed to waters or buried in soil and activity of solids and liquids are unitary. For the iron dissolution reaction ( $Fe = Fe^{2+} + 2e^-$ ), the equilibrium potential is -0.62V SHE (-0.92 V CSE)<sup>1</sup>.

The equilibrium potential of the two main cathodic processes (oxygen reduction and hydrogen evolution) are:

$$(1.7) \quad E_{eq} = -0.059 \cdot pH \quad \text{hydrogen evolution}$$

$$(1.8) \quad E_{eq} = 1.23 - 0.059 \cdot pH \quad \text{oxygen reduction}$$

---

<sup>1</sup> The standard hydrogen electrode (SHE) is a redox electrode used as reference on all half-cell potential reactions. The value of the standard electrode potential is fixed at zero at all the temperature.

The copper-copper sulphate electrode (CSE) is a reference electrode commonly used for corrosion monitoring in soil and concrete. The potential of CSE is +0.318 V vs. SHE (standard hydrogen electrode).

The thermodynamic conditions of a metal varying the pH of the electrolyte are reported in the so-called Pourbaix diagram. The diagram reports the domain of *metal immunity* (no corrosion is possible), *metal corrosion* (dissolution of the metal) and *passivation* (formation of stable oxides and/or hydroxides on the metal surface which reduction of corrosion rate).

The potential of the metal deviates from the equilibrium value when the metal exchanges a current. This can occur in the presence of a more noble cathodic process than metal oxidation or in the presence of an external polarization current. The relation between metal potential and the current density (current exchanged between the metal and the electrolyte for unit surface,  $S$ ) is defined by Butler-Volmer equation. Without going into mathematical details, out of this this thesis work, it is possible to consider the following general equation:

$$(1.9) \quad E = E_{eq} \pm f(i)$$

Where  $i$  is current density ( $i = I/S$ ) and  $f(i)$  is generally a logarithmic equation which sign is positive for the anodic process, while the negative one is valid for the cathodic process. The term  $f(i)$ , which measures the deviation of potential from the equilibrium condition, is called *overvoltage* ( $\eta$ ). In the case of an *active metal* (as iron in a neutral and acidic environment), Tafel's law is valid:

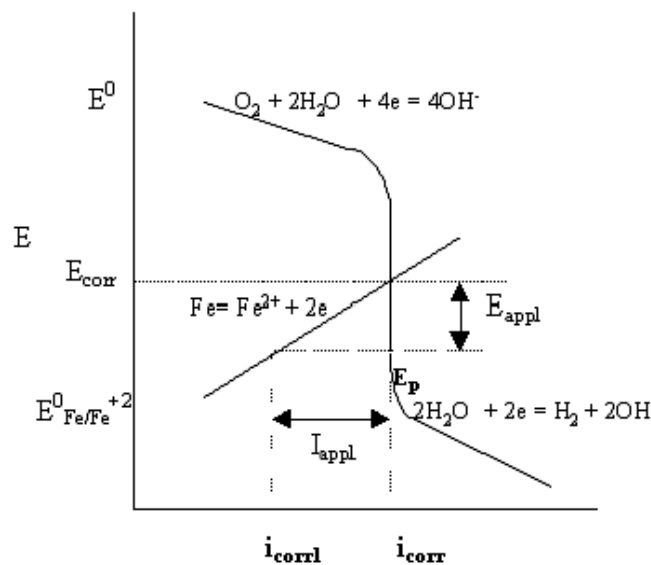
$$(1.10) \quad \eta_a = a + b \log i = b \log \left( \frac{i}{i_0} \right)$$

where  $i_0$  is called *exchange current density*, which represents the current density at the equilibrium potential, and  $b$  is *Tafel's slope* (60 mV/decade for bivalent metals, 120 mV/decade for monovalent metals). The oxygen reduction process involves two dissipation contributions: one corresponding to the process of charge transfer to the metal surface (Tafel behavior) and the other to the transport of oxygen in the solution. The overall overvoltage can be written as:

$$(1.11) \quad \eta_c = \eta_{act, O_2} + \eta_{conc, O_2} = -b \log \frac{i}{i_{o, O_2}} + 0.015 \log \frac{i_L - i}{i_L}$$

where  $i_L$  is called *oxygen diffusion limiting current density* and measure the maximum current density due to the concentration (i.e. diffusion) of oxygen in the electrolyte.

The kinetic behavior of a metal in the presence of a more noble cathodic process (oxygen reduction) can be reported in a potential vs. current density diagram (*E-logi*), called *Evans diagram*.



**Fig 1.2** – Cathodic and anodic characteristic for a corrosion process in an aerated environment.

The anodic and cathodic curves in the Evans diagram are called *characteristic curves*. The intersection point between the two curves determines the electrochemical working point of the system, i.e. *free corrosion potential* ( $E_{corr}$ ) and *corrosion current density* ( $i_{corr}$ ). Fig. 1.2 reports the Evans diagram for carbon steel in aerated soil. As depicted in Fig. 1.2, corrosion current density corresponds to the oxygen diffusion limiting current density ( $i_{corr} = i_L$ ), which means that corrosion rate is determined by the maximum amount of oxygen available on the metal surface.

At lower potential, hydrogen evolution sums to oxygen reduction (Fig. 1.2); the overvoltage of hydrogen evolution follows Tafel's law with a slope of 120 mV/decade.

Corrosion rate in a diffusion-controlled process is defined by the equilibrium at the metal surface between oxygen diffusion and consumption, i.e. by Second Fick's law and Faraday

law. In stagnant condition (absence of turbulence), the oxygen diffusion limiting current density, i.e. corrosion rate, can be calculated as:

$$(1.12) \quad i_{corr} = i_L \cong 10 \cdot [O_2] \cdot 2^{\frac{T-25}{25}}$$

Where  $[O_2]$  is oxygen content in ppm,  $T$  is temperature ( $^{\circ}C$ ) and  $i$  is in  $mA/m^2$ . Oxygen diffuses from atmosphere and its solubility in waters varies with temperature and depends on the salinity of the solution. The limit current density of oxygen diffusion varies from about  $50 mA/m^2$  to about  $100 mA/m^2$  between  $20-30^{\circ}C$ . In the presence of turbulence, the limit current can therefore rise up to a few  $A/m^2$ . In soil, at  $25^{\circ}C$ , oxygen content ranges from 1-2 ppm in wet soils, as clay where oxygen diffusion is low, to 7-8 ppm in sandy aerated soil. Accordingly, steel corrosion rate ranges between 10 and 80 mm/year, depending on soil characteristics.

## 1.2 Corrosion forms in soil [2]

The corrosion forms in soil can be divided in three main groups in accordance with corrosion mechanisms involved: oxygen-related corrosion, microbiological induced corrosion, particularly by sulphate-reducing bacteria under anaerobic conditions, and stray current corrosion.

### 1.2.1 Oxygen related corrosion

Oxygen in soils as well as in water is the most important factor determining corrosion in the absence of bacterial activity. The amount of oxygen reduced in the corrosion process is that arriving through diffusion, hence regulated by Fick's law. Forms of the oxygen-related corrosion are *uniform corrosion* in homogeneous aerated soils with low conductivity and in acidic soils, *localized corrosion* with formation of pustules in the presence of chlorides and sulphates, *differential aeration corrosion* in the presence of non-uniform distribution of oxygen and corrosion by *galvanic coupling* due to the contact with noble metals.

The corrosion rate is equal to oxygen availability in the case of uniform corrosion, while is



proportional to it in case of localized attack, as in galvanic and differential aeration mechanisms.

**Uniform corrosion:** it is the simplest form of corrosion. This phenomenon occurs in the atmosphere, in liquids and in the soil, usually under normal working conditions. The attack can be quick or slow, while the metal surface can remain clean or covered by the same corrosion products. The uniform corrosion usually occurs on metal surfaces with a chemical composition and homogeneous microstructure. Access to metal from the corrosive environment is generally free and homogeneous. In the presence of oxygen, the *maximum uniform corrosion rate* is given by the following equation:

$$(1.13) \quad C_{rate} \cong 12 \cdot 2^{\frac{T-25}{25}} \cdot [O_2]$$

where  $C_{rate}$  is expressed in  $\mu\text{m/y}$ ,  $[O_2]$  is the oxygen content in mg/L ( $\approx$  ppm) and  $T$  is the temperature ( $^{\circ}\text{C}$ ).

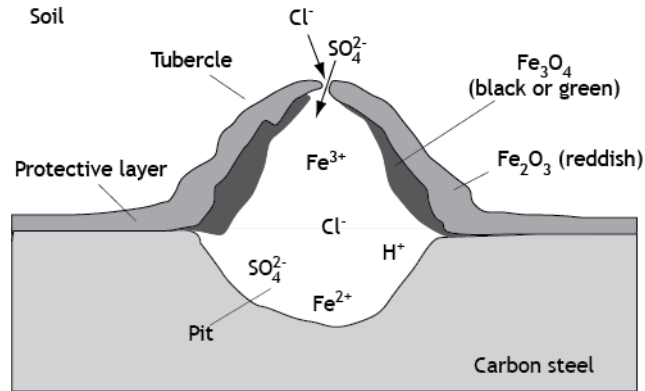
After extensive experimentation carried out in the United States, the National Bureau of Standards through a statistical approach derived an equation of corrosion rate that correlates the metal thickness loss ( $X$ ,  $\mu\text{m}$ ) of different metals to the period of exposure and soil resistivity:

$$(1.14) \quad C_{rate} = k' \cdot t^{n-1}$$

The value of  $n$  for carbon steel, extrapolated from the results obtained by NBS, ranges from 0.1 (good soil aeration) to 0.8 (poor soil aeration).

**Localised corrosion:** The presence of high content of chloride and sulphate influences the corrosion rate through the tendency to depassivation and formation of soluble corrosion products with low protective properties and promotes conditions for localized corrosion attacks. In particular, corrosion attack localizes beneath corrosion products or deposits, forming so-called *pustules* or *tubercles*, where oxygen can not be replaced, while surrounding surface works as cathode. So, inside the tubercle, the oxidation and hydrolysis reactions produce  $\text{Fe}_3\text{O}_4$  and  $\text{Fe}_2\text{O}_3$ , increasing the acidity (the pH drops below 4) due to

the poor diffusion towards the outside zones. At the same time, sulphates and chlorides enter inside the tubercle transported by the macrocell current, creating an aggressive local environment.

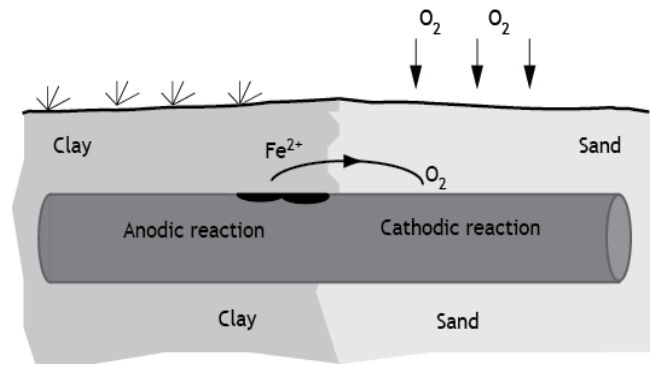


**Fig 1.3** – Pustules on carbon steel due to sulphates and chlorides presence.

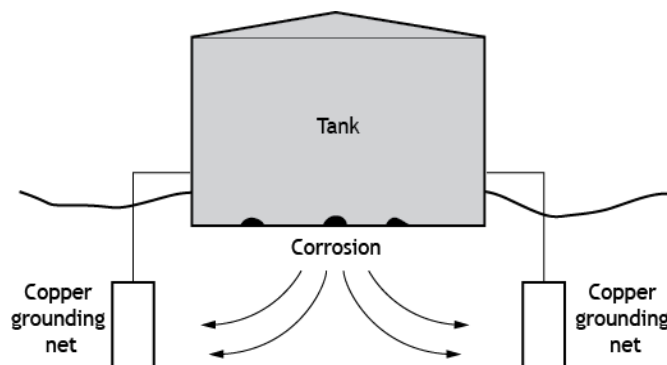
The corrosion rate becomes high, greater than  $100 \mu\text{m}/\text{y}$ , when threshold values of 200 ppm of chlorides and 1,000 ppm of sulphates are exceeded.

**Differential aeration:** local corrosion through differential aeration takes place when the soil surrounding the structure is not homogeneous and shows variable oxygen permeability, as in the presence of corrosion products or deposit, which limits the oxygen diffusion.

A typical case study is the presence of both a clayey layer and a sandy layer. The metal surface in contact with clay, which is not permeable to oxygen, becomes anodic and metal dissolution takes place ( $\text{Fe} = \text{Fe}^{2+} + 2\text{e}^-$ ). On the other hand, metal in contact with sand, which is highly permeable to oxygen, becomes cathodic and oxygen reduction takes place ( $\text{O}_2 + \text{H}_2\text{O} + 4\text{e}^- = 4\text{OH}^-$ ). The corrosion rate is given by the cathodic process rate, equal to the oxygen diffusion limiting current density multiplied by the cathodic/anodic surface area ratio; when cathodic surfaces are much larger than anodic ones, the corrosion rate can be as high as about  $1 \text{ mm}/\text{y}$ .



**Fig 1.4** – Example of differential aeration corrosion



**Fig 1.5** – Galvanic corrosion of the bottom of a carbon steel tank due to the coupling with the copper net

**Galvanic Corrosion:** the presence of two metals having different nobilities may lead to galvanic corrosion. The less noble metal, which has a lower potential in the natural environment, assumes anodic behaviour, and the more noble metal assumes cathodic behaviour. Galvanic corrosion is favoured in low resistivity soils: the lower the resistivity the greater the corrosion effects, both as corrosion rate and extension of involved zones. For example it is possible to have corrosion of steel structure if they are coupled with the copper of the grounding system. The corrosion rate is high when a small anodic zone is coupled to an extensive cathodic one.

### 1.2.2 Microbiological corrosion (de-aerated soil)

It takes place mainly in neutral or alkaline soils, rich in organic content, and is absent in acidic or neutral soils with a high salt content. The most damaging family of these micro-organisms is made up of sulphate-reducing bacteria (SRB) that develop and live in anaerobic environments like clayey soils. Literature data agree on a corrosion rate even

above 1 mm/y. The SRB corrosion mechanism is quite complex and not yet completely understood. Bacteria make use of hydrogen produced at the cathode to reduce sulphate ions through the following reactions:

- $4\text{Fe} = 4\text{Fe}^{2+} + 8\text{e}^-$
- $8\text{H}^+ + 8\text{e}^- = 8\text{H}$
- $\text{SO}_4^{2-} + 8\text{H} = \text{S}^{2-} + 4\text{H}_2\text{O}$
- $\text{Fe}^{2+} + \text{S}^{2-} = \text{FeS}$
- $3\text{Fe}^{2+} + 6\text{OH}^- = 3\text{Fe}(\text{OH})_2$

Redox potential measurements with a platinum electrode make it possible to establish if a soil is prone to the development of SRB, through the  $E_H$  factor (Table 1.1).

**Table 1.1** – Relationship between redox potential and bacterial corrosion probability

$E_H$ (mV SHE)	$E_H$ (mV CSE)	SRB corrosion probability
< 100	< -200	High
100 – 200	-200 to -100	Moderate
200 – 400	-100 to 100	Limited
> 400	> 100	Nil

### 1.2.3 DC stray current corrosion

It occurs when a DC electric field influences a buried metallic structure, determining cathodic and anodic surface areas. The latter may suffer severe corrosion called *stray current corrosion*. Interference can be *stationary* and *non-stationary*:

- *Stationary interference* takes place when the structure is immersed in a stationary electric field generated, for example, by a cathodic protection system, and the effect is greater as the structure is closer to the groundbed.
- *Non-stationary interference* occurs when the electric field is variable, as in the typical case of stray currents dispersed by DC traction systems; in this case interference takes place only during the trains' transit, and often, in spite of the limited duration, a few minutes; the effects may be severe due to high circulating current.

In both cases, corrosion attacks are localized and very severe, with corrosion rates even higher than 1 mm/y, depending on current densities reached locally. If the interfered structure is provided with an integral coating, interference cannot take place, but when the coating has a number of faults, corrosion is very severe since current concentrates in them.



Fig 1.6 – Stray current corrosion on a coated carbon steel pipe

### 1.3 Cathodic protection: an overview

Cathodic protection (CP) is an electrochemical technique used to prevent or reduce corrosion of metal such as underground structures (gas pipelines, oil pipelines, tanks, etc.), marine structures (port or offshore structures, ship's hulls, etc.), internal surfaces of chemical equipment, and to prevent and protect the rebars of reinforced concrete contaminated with chlorides.

It is carried out by a continuous current flow between an electrode (anode) placed in the environment and the surface of the structure to be protected (cathode). The current circulation reduces or stops the corrosion rate of the cathode. CP can be applied in two ways: by a galvanic anode system and by an impressed current system.

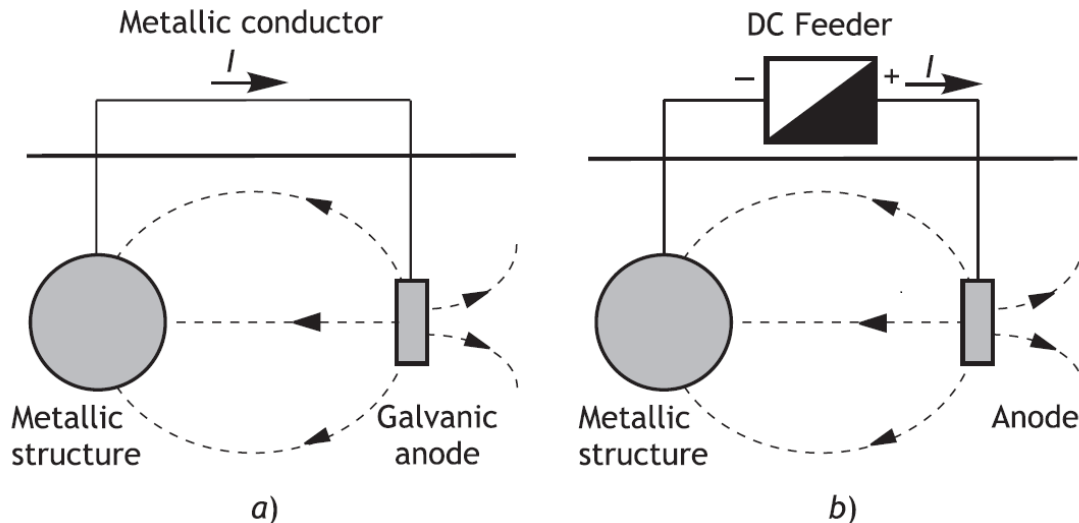
#### 1.3.1 Cathodic protection by galvanic anodes

CP by *galvanic anodes* is obtained with any metal, provided its working potential is less noble than the protection potential of the metal to protect (Fig. 1.7a). To protect carbon

steel structures, aluminium, magnesium and zinc alloys are employed for practical applications. Two parameters determine CP performance:

- *working potential*: used to define the anode driving voltage and the anode current output and therefore the minimum anode number necessary to reach protection;
- *current capacity*: is the charge per unit mass, and it defines the anode's consumption and therefore determines the weight necessary to ensure the duration of protection.

A galvanic anode is also characterized by the anode output, which is the current the anode is able to supply, simply obtained by using the first Ohm's law:  $I = \Delta E/R$ , where  $\Delta E$  is driving voltage (in V), and R is total resistance of the electrical circuit anode – electrolyte – cathode (in  $\Omega$ ). The driving voltage is given by the difference between the anodic working potential and the protection potential. The driving voltage of steel structures typically assumes a value of 250 mV, 300 mV and 800 mV respectively for Zn, Al and Mg anodes. To maximize the current output, the electrical resistance should be reduced to the minimum; accordingly, anodes are fabricated in suitable shapes or surrounded by a suitable low resistivity backfill.



**Fig. 1.7** - Types of cathodic protection: a) by galvanic anodes b) by impressed current system [1]

Anode type is chosen based on environmental resistivity; in soil, the environment surrounding the anodes is changed by a suitable backfill to allow anodes a more stable potential by avoiding risk of their passivation. Typical backfill is based on a mixture of clay, to guarantee high humidity and low resistivity, and gypsum, to maintain anode in active state. From an economic point of view, aluminium alloys are the most convenient,

since the relative cost of producing the same electrical charge is 1 for aluminium, 3 for zinc and 8 for magnesium.

### 1.3.2 Cathodic protection by impress current system

In impress current CP (ICCP) systems, a DC feeder provides current through an anode, which is able to supply current to the environment (Fig. 1.7b). For soil applications, inert anodes such as iron-silicon alloy or activated titanium are typically used. A backfill, typically calcined carbon coke powders, is used to obtain a low anode resistance, generally less than  $2 \Omega$ , even in relation to a maximum feeding voltage of 50 V, imposed by regulations for safety reasons. When high current output is required, a group of multiple anodes is used.

The anodes supply current by means of an anodic reaction, which depends on the anodic material and the environment. For example, in the case of scrap steel anodes, the anodic reaction is the dissolution of iron. For the so-called insoluble or inert anodes, such as activated titanium or cast iron, the reactions are oxygen and chlorine evolution, depending on the environment (presence of chlorides) and the current density. Since a current feeder is used, the most important design parameter is the minimum feeding voltage necessary to supply the protection current, given by the following relationship:

$$(1.15) \quad V_{min} = \Psi^* + I \cdot R$$

where  $I$  is the protection current required by design (obtained by the product of the protection current density and the surface of the structure to be protected),  $R$  is the circuit's total resistance and  $\Psi^*$  is the thermodynamic and kinetic contributions of electrode reactions. For iron soluble anodes,  $\Psi^*$  is negligible, but it is 2 to 3 V in the case of inert anodes.

### 1.3.3 Cathodic protection effects

The reduction or stop of the corrosion rate, following the application of cathodic protection is based on three distinct effects, both generated by the lowering of potential:

- A *thermodynamic effect*, related to the reduction of the driving force;
- A *kinetic effect*, related to the increase of the reaction resistances.
- A *chemical effect*, related to the increase in alkalinity due to the protection current.

#### 1.3.3.1 *Thermodynamic effect (protection potential)*

If the potential of the metal is lower than the equilibrium one ( $E < E_{eq}$ ), the process of oxidation of the metal (i.e. the anodic process) cannot take place. In other words, at this potential the metal has no tendency to pass to the oxidized form and therefore to form corrosion products; these conditions are called thermodynamic immunity, where the driving voltage is zero or negative.

If the potential lowering compared to the free corrosion potential ( $E_{corr}$ ) is not sufficient to cancel the driving force (i.e.  $E_{eq} < E < E_{corr}$ ), the corrosion rate is reduced but not stopped. From an engineering point of view, the so-called quasi-immunity conditions are reached. Indeed the potential is brought to values close to those of equilibrium, making the corrosion rate negligible.

#### 1.3.3.2 *Kinetic effect*

The kinetic effects are not related to the reduction of the driving force, but regarding the fact that the metal potential lowering causes an increase in the resistance of the anodic reaction. This happens in cases where the lowering of the potential can bring the metallic material into conditions of passivity, so for the metals with active-passive behavior. In these cases, passivity protection conditions are established.

#### 1.3.3.3 *Chemical effect*

The cathodic reactions at the metal-to-electrolyte interface produce alkalinity; the effect is positive for carbon steel because the pH increase (up to values between 10.5 and 12) is a condition that can favor the precipitation of protective products (for example a calcareous deposit,  $\text{CaCO}_3$ , in seawater) and passive conditions. Moreover, in an electrolyte the current is transported by the ions: the cations move in the direction of the current, the anions in the opposite direction. When the CP is applied, the current flows from the electrolyte to the metal: then the cations are transported to the metal surface while the anions are removed. Chlorides are harmful negative ions (they reduce the passivity range



of active-passive materials) and their removal from the metal surface is a positive effect obtained by applying the PC.

### 1.3.4 Protection current density

The cathodic protection conditions are obtained by imposing an external current between an anode and the structure to protect; in particular, the current value necessary to reach the protection condition depends on the cathodic process, therefore on the environment in which the structure is placed. In presence of an external cathodic current ( $I_e$ ), the currents associated to the cathodic and anodic processes ( $I_c$  and  $I_a$ ) assume the values necessary to satisfy the current balance:

$$(1.16) \quad I_a = I_c - I_e$$

According to Eq. 1.16, the current of the anodic process is eliminated if the external cathodic current, provided to the metal, equals the current of the cathodic process. In other words, the corrosion is stopped in presence of a protection current equal to the electron demand of the cathodic processes occurring on the metal surface:

$$(1.17) \quad I_e = I_{prot} = \sum I_c$$

In case of oxygen reduction, the protection current density is therefore equal to the limit current density of oxygen diffusion,  $i_L$ ; the possible increase of the cathodic current leads to the hydrogen development at the cathode, since this reaction has a less noble potential than the oxygen reduction.

For example, the protection current density in sandy (aerated) soils is greater than in clayey soils saturated with water (poorly aerated). It passes from 50-80 mA/m<sup>2</sup> in the first case to 2-10 mA/m<sup>2</sup> in the second case.

**Table 1.2** – Values of protection current densities in industrial applications [2]

Environment	Protection current density (mA/m <sup>2</sup> )
<i>Bare steel</i>	
Soil	
– Neutral aerated	20–150
– Water saturated	2–20
– Hot metal surface	30–60
Concrete	
– Atmospherically exposed	2–20
– Water saturated	0.2–2
Fresh water	
– Cold	30–160
– Warm	50–160
Seawater	50–600
Seamud	20–33
Acidic electrolytes	50–1500
<i>Coated steel</i>	
Soil	0.01–1
Seawater	0.1–10

**Table 1.3** – Values of protection potentials for metals most commonly used in soil and seawater [2]

Metals	Soil	Seawater	
	V CSE	V Ag/AgCl	V Zn
Carbon steel:			
– Aerobic	–0.85	–0.80	+0.25
– Anaerobic	–0.95	–0.90	+0.15
– In concrete	–0.75	–0.70	+0.35
Copper	–0.30	–0.20	+0.70
Lead	–0.50	–0.45	+0.50
Zinc	–1.00	–1.05	0
Aluminium	–0.80	–0.90	+0.15
Stainless steel	–0.40	–0.50	+0.55

Table 1.2 reports indicative values of the protection current density in natural environments for carbon steel. Natural environments and all those in which the cathodic reaction is the reduction of oxygen, are the most suitable for CP application because protection currents, equal to the limit current of oxygen diffusion, are low.

The CP in other environments is less suitable: for example, acid environments, in which the cathodic reaction is the hydrogen evolution, require high protection currents, generally one or two orders of magnitude higher than the current limit of oxygen diffusion.

### 1.3.5 Protection potential

The potential below which the metal is in immunity conditions (or almost immunity) is called protection potential,  $E_{prot}$ . Table 1.3 reports the values of protection potentials of some metals (including carbon steel) in soil and in seawater.

### 1.3.6 Cathodic protection effectiveness and monitoring

The general criteria used to verify CP of a structure is based on potential measurement. According to the scheme in Fig. 1.8, this is done using a reference electrode placed in contact with the environment surrounding the structure (soil, fresh water, seawater, concrete) and a high impedance voltmeter whose positive pole is connected to the structure and its negative one to the reference electrode. This measurement technique is simple because it requires only a voltmeter and it is of easy interpretation, provided one takes into account that the potential reading may include errors that should be eliminated.

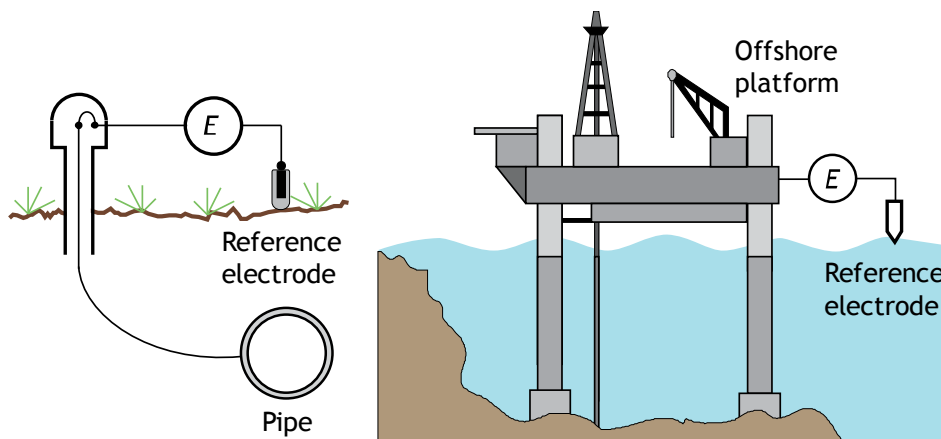


Fig. 1.8 - Potential measurement for a buried pipeline and a submerged platform [1]

ISO 15589-1 standard in Section 6 describes the principle of cathodic protection criteria to assure a residual corrosion rate less than  $0.01 \text{ mm}\cdot\text{a}^{-1}$ . Same criteria were present in the past EN 12954. The basic criterion is IR-free potential lower than protection potential (Table 1.3):

$$(1.18) \quad E_{IR-free} < E_{prot}$$

The protection potential of a metal depends on the corrosive environment (soil) and on the type of metal used (carbon steel). ISO 15589-1 standard also states “application of potentials that are too negative can result in cathodic over-protection leading to coating disbondment and blistering and hydrogen embrittlement of some metals.” Therefore, the IR-free potential should not be more negative than a threshold value. For carbon steel, *overprotection* corresponds to potential lower than -1.2 V CSE.

When measuring the potential by locating a reference electrode nearby the metal surface (Fig. 1.8), there is an ohmic drop contribution,  $IR$ , due to the flowing current in the electrolyte. This contribution alters the potential reading, hence has to be eliminated. The measured value,  $E_{ON}$ , is the sum of two contributions:

$$(1.19) \quad E_{ON} = E_{IR-free} + IR$$

where  $E_{IR-free}$ , often referred as “true potential” in the industrial practice, is the potential deperated by the ohmic drop. The ohmic contribution is the spurious term that contaminates the measurement of potential. It depends on the position of the reference electrode with respect the monitored structure,  $d$ , the resistivity of the electrolyte,  $\rho$ , and the flowing current density,  $i$ :

$$(1.20) \quad IR = \rho \cdot i \cdot d$$

Ohmic drop decreases when the reference electrode is placed close to the pipeline, therefore, the simplest technique to minimize it consists in placing the reference electrode as close as possible to the structure. Of the three parameters determining ohmic drop, resistivity plays the most important role. For example in seawater, where resistivity is low, even if current is high, the ohmic drop is often negligible. On the contrary, in concrete and in soils, especially in the most resistive ones, the ohmic drop is not at all negligible, even if small current circulates.

Therefore, for a correct measurement of potential, ohmic drop has to be evaluated or eliminated. For carbon steel in aerated soil, the protection potential is -0.85 V CSE (as

defined by the international standard ISO 15589-1); under anaerobic conditions and in the presence of sulphate-reducing bacteria, the protection potential is -0.95 V CSE. These values are considered for quasi-immunity conditions and correspond to corrosion rates lower than 0.01 mm/year, so technically negligible.

CP effectiveness is evaluated in two phases, according to ISO 15589-1:

- For a *CP general assessment*, ON potential should be measured at all test points, at a certain frequency; the structure is protected if the ON potential is more negative than the free corrosion potential;
- For a *detailed and comprehensive assessment of the CP*, two alternatives are possible:
  - ✓ OFF potential readings at all measuring points at least every three years;
  - ✓ If OFF potential reading is not possible (for example in the presence of stray current), coupons or potential probes are required.

Regarding the latter, it is important to underline that OFF potential is not a synonymous of IR-free potential, being the latter the potential measured with local reference electrode or potential probe.

In other cases it may be more convenient to apply the "*100 mV depolarization criterion*" which consists in verifying a depolarization of at least 100 mV starting from the Off potential (potential measured after the interruption of the protection current) after a reasonable time, usually more than four hours after the interruption of the cathodic protection. This criterion is based on the fact that, after the interruption of the protection current, the potential approaches the free corrosion potential. Moreover, a depolarization of 100 mV indicates that the residual corrosion rate (before the shutdown) was at least one order of magnitude lower than the free corrosion rate of the metal (the slope of the Tafel line is of the order of 100 mV/decade).



# Chapter 2

## Intermittent cathodic protection (ICP)

The study of the effects of the interruption of the cathodic current in CP systems is nowadays only theoretical. Indeed, in real application cathodic protection is applied in a stationary way by means of a direct current that guarantees the reduction of corrosion rate. In this work, the effects of the interruption of CP on potential monitoring and corrosion are evaluated, although this study is only preliminary and based on theoretical aspects.

Moreover, often accessibility to energy sources is limited or cheaper solutions are preferred. In particular, nowadays a possible solution is represented by the use of renewable energy sources, as photovoltaic panels, whose energy production is confined to the hours of light (thanks to the batteries, energy is often available even at night, but not always sufficient for protection).

For the reasons above, there are very few studies about the effect of the interruption of protection current on corrosion rate and on protection condition. However, some works in literature can be considered, even if they are not strictly related to intermittent CP of carbon steel in soil. For example, some applications of the interruption of the protection current are related to the protection of steel bars for reinforced concrete, subjected to corrosion due to the presence of chlorides. However, although the electrolyte is different, a brief summary of some works on the effects of the current interruption on corrosion and protection of reinforced concrete can be useful to understand the possible extension to other electrolytes such as soil and waters. Here some examples are reported.

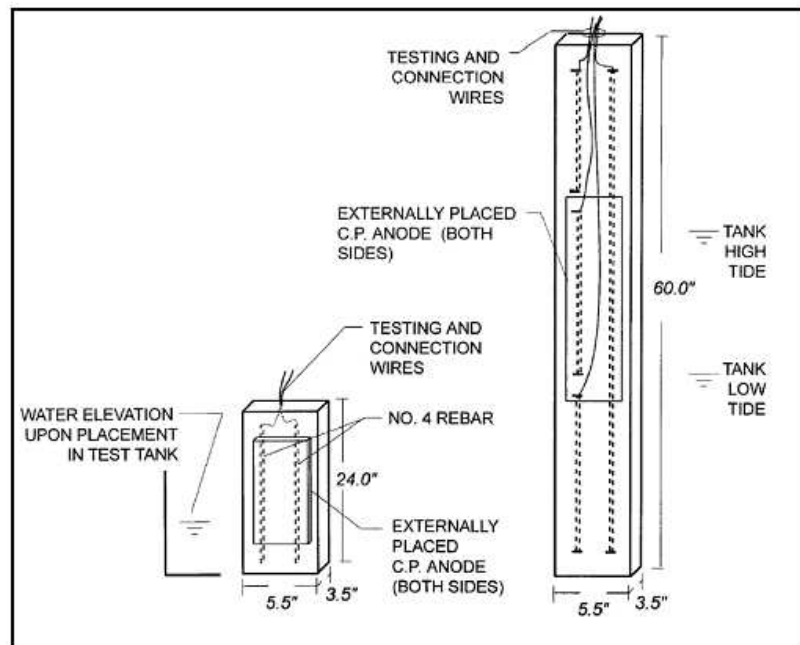
### 2.1 Some examples from literature

R.J. Kessler et al. [5] have obtained important results regarding the application of intermittent cathodic protection. Authors evaluated the feasibility of the ICP to protect the

carbon steel rebars of the concrete structures placed in the marine environment by means of laboratory and field tests.

The importance of this study lies in the fact that the cathodic protection has been realized through the solar panels use, that guarantee a direct current only during the day, while at night or in low sunlight hours the cathodic protection is deactivated; so, it simulates a real protection system realizable without any feeder or any battery that store energy.

Regarding the laboratory tests, two sets of samples in reinforced concrete contaminated by chlorides (Fig. 2.1) were prepared; samples were immersed in a tank containing seawater in order to simulate the conditions of high and low tide acting on a bridge pillar.



**Fig. 2.1** – Samples representation for experimental laboratory tests. [5]

Two specimens have been connected to an anodic system and to the photovoltaic panel: the first specimen in direct mode, while the second specimen through a diode that allows the current passage only in one direction in order to avoid other current passages between the rebar and the anode during the off period. Both the samples are subjected to a protection current equal to  $21 \text{ mA/m}^2$ , stable respect to the surface of the bar.

A third sample, instead, has been left in free corrosion condition. Regarding instead the field tests, they were carried out on ten pillars of pre-stressed reinforced concrete of a bridge located in the North Sea of Florida, in a particularly aggressive marine environment



and, even in this case, the intermittent cathodic protection was achieved through solar panels. In this case, the protection current is equal to  $15 \text{ mA/m}^2$  (with respect to the reinforcement surface). For both laboratory and field tests, the rebar potential monitoring was performed during all the test phase. Fig. 2.2 shows the specimens potential (V vs. Ag/AgCl) submitted to the laboratory test: it is noted that the potential, even always maintaining a protection value, moves towards values that are more positive during the night, when current is off.

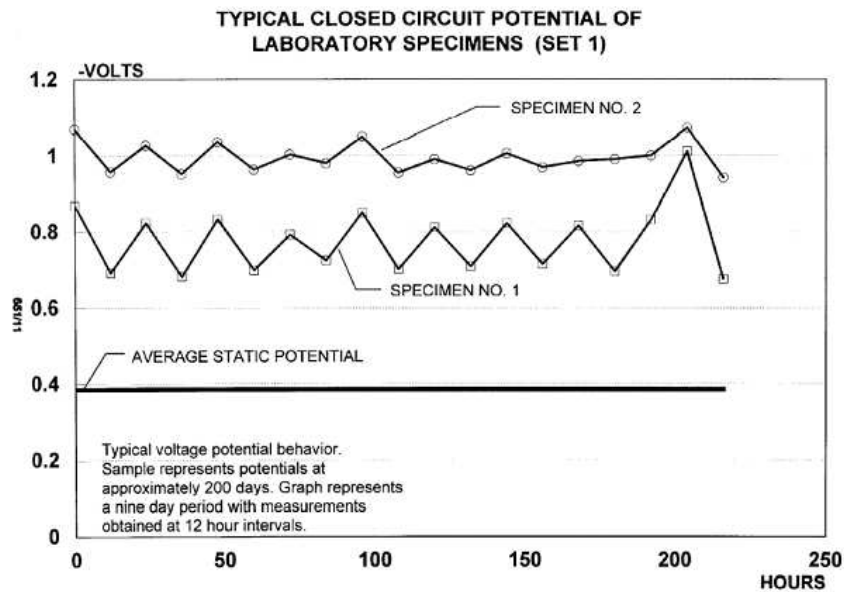


Fig. 2.2 – Samples potential (V vs Ag/AgCl) with 12 h interval of potential measures. [5]

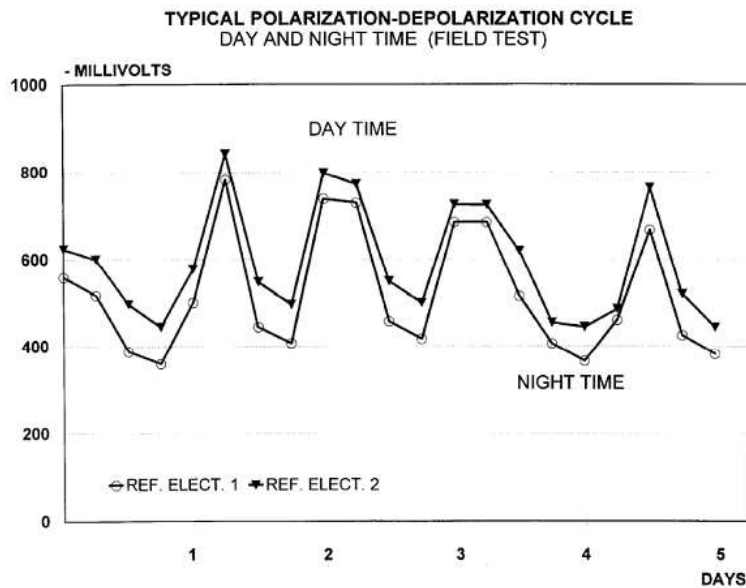


Fig. 2.3 – Potential profile (V vs. Ag/AgCl) of the steel bar; test carried out in field. [5]

At the end of the three-year test period, it was possible to notice that the steel reinforcement of specimens 1 and 2, protected by intermittent current, shows only some traces of corrosion compared to the armature of the sample 3, maintained in free corrosion condition, which showed severe pitting corrosion. As said, it is visible on the following table (table 2.1):

**Table 2.1** –  $R_p$  values in different experimental conditions tests. [5]

<b>Specimen No.</b>	<b>Pol. Res. Test Started After Instant Off (ohm-cm<sup>2</sup>)</b>	<b>Pol. Res. Test Started 18 Hours After Depo. (ohm-cm<sup>2</sup>)</b>	<b>Pol. Res. Test Started 72 Hours After Depo. (ohm-cm<sup>2</sup>)</b>
<b>1</b>	<b>2,114</b>	<b>4,003</b>	<b>1,979</b>
<b>2</b>	<b>2,854</b>	<b>2,618</b>	<b>2,653</b>
<b>3</b>	<b>1,080</b>	<b>---</b>	<b>---</b>

Field tests confirmed a potential profile similar to that obtained from laboratory tests, as showed in Fig. 2.3.

In fact, the field-tests with depolarization values above 100 mV (100 mV criterion), demonstrated that polarization of the metal reinforcement by cathodic protection was more than adequate.

In general, authors' conclusions are of considerable importance regarding the applications of the ICP, especially because they have shown that it is possible to maintain the protection conditions by applying cathodic protection with periodic intervals. The potential measurements, in fact, have shown that by the use of a sufficient current density it is possible to maintain the reinforcement polarization at a protection level, even when the cathodic protection is deactivated. Secondly, they have demonstrated the applicability of cathodic protection through photovoltaic panels that require the presence of a diode in the electric circuit to allow the unidirectional, since, in the absence of it, during the off period

there is a current in the sample-panel direction (opposite direction) which favours the depolarization of the specimen towards higher potential values.

From the analysis of the chlorides quantity present in the concrete, it has also been determined that, although the intermittent cathodic protection is not able to reduce the concentration of chlorides already present in the concrete, it prevents the presence of others. In another research [8], on the other hand, it has been shown that intermittent cathodic protection can favour a removal effect of the chlorides already present in the reinforced concrete.

As this bibliographic research work could have guessed, intermittent cathodic protection proved to be a valid possibility to the existing prevention methods, regarding the protection of rebars in reinforced concrete structures.

G.K. Glass et al. [6] have done some laboratory tests applying intermittent cathodic protection to reinforced concrete structures contaminated by chloride, in an environment simulating the tidal (spray) zone.

In these tests, the samples were concrete cylinders with a steel reinforcement placed on the cylinder axis. After curing for one month, the cylinders were immersed in two tanks of artificial seawater for 0.5 hours every 12 hours and exposed to an air stream for the remainder 12 hours to simulate the conditions of dry-wet alternation. An anode applies a protection current pulse lasting 30 minutes and, while the current is active, the samples are partially immersed. While the current was applied, some specimens were only partially submerged, 80%, 65% or 50% of the specimens being below the water level. At the end of the laboratory tests, it has been observed that as the intensity of the protection current increases, there is a significant reduction of the amount of corrosion products present on the reinforcements, until they are completely eliminated.

In fact, it has been observed that the reinforced concrete specimens subjected to ICP have shown lower or totally absent surface breakings compared to the specimen left in free corrosion condition. Authors have demonstrated that the intermittent protection current is able to generate an alkaline environment on the cathode surface similar to that generated by a direct current and equal to the value of the integral average of the intermittent currents. Authors realize that intermittent cathodic protection is effective mainly for two reasons: 1) it causes a lowering of the potential and 2) it changes the electrochemical

conditions close to the steel surface such as a re-establishment of the passivity conditions and the oxygen and chlorides removal from the metal surface.

These changes in the re-establishment of the local alkalinity, the removal of chlorides and the formation of a reducing environment is maintained even after the interruption of the current and it is precisely this factor that justifies, according to the authors, the applicability of intermittent cathodic protection for rebars.

In support of the effectiveness of ICP, in Oregon, S. Cramer et al. [3,7] carried out an ICP system realized by means of zinc anodes (thermal sprayed zinc), on reinforced concrete bridges subjected to corrosion in an environment rich of chlorides.

In this test, they performed a corrosion rate monitoring in order to evaluate the appropriate time to reignite cathodic protection on concrete. This method ensures that the protection can be used for a much shorter period, also depending on the environmental conditions present on site. In fact, during the off period of ICP, the chlorides present in the concrete destroy the passive film thus causing an increase in the corrosion rate. During the on period, instead, the metal reinforcement is re-populated and there is a local increase in alkalinity, which favours the formation of a stable layer of oxides that guarantee the conditions of passivity. In this case, the use of intermittent protection allows an increase in service life of the anodes and therefore the bridge's life protection costs are lower.

In this case, however, the studied environment is rich in chlorides, which damages the protective passive film and makes it necessary to apply cathodic protection: the bar is polarized and the pH gradually increases.

The study is performed on cylindrical samples of concrete, which cover a steel bar placed on the cylinder axis. The counter electrode is an external cylinder in galvanized steel. The cathodic protection condition provided for a 28-day maturing in a wet room before corrosion measurements. Sponges were used to keep the contact between the counter electrode and the concrete surfaces; moreover, they allow keeping the surfaces damp, but not saturated and so letting the oxygen to spread into the concrete.

In the test, specimens were subjected to an intermittent cathodic protection, polarizing the bar for 24 hours with a current density of  $1.1 \text{ A/m}^2$  and then 24 hours of open circuit depolarization. Fifteen polarization cycles were performed. The Figure 2.4 shows the polarization curves of the rebars subjected to intermittent cathodic protection.

The potential varies between -0.250 to -0.500 V vs. CSE, with higher potential when the protection is switched off, as expected. It is also noted that when the concrete starts to dry out, the potential assumes lower values: this is probably due to the decrease in the value of diffusivity of the oxygen in the cell.

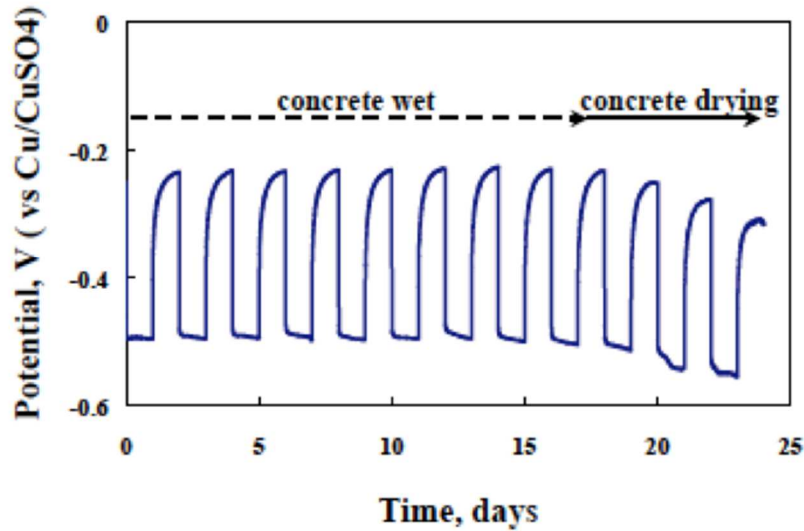


Fig. 2.4 – Potential monitoring during on/off current cycles applied to a rebar in a concrete cylinder. [7]

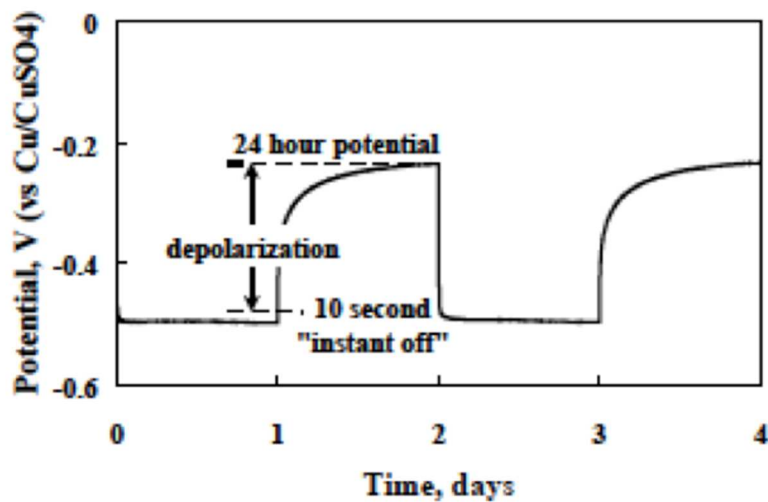


Fig. 2.5 - Depolarization curve of a reinforcement subjected to intermittent cathodic protection. [7]

A characteristic feature of this type of protection is the gradual shift of the potential values from the protection value to the corrosion value, according to a curve, shown in Fig. 2.5. The standard depolarization of 100 mV in 24 hours or less is commonly used to indicate

adequate protection of the reinforcement from corrosion. In this case, depolarization greater than 200 mV were detected after 24 hours for each of the 15 cycles. This result is quite satisfactory, and it has been achieved with almost dry concrete. The effect of ICP is equivalent to halving the density of the anodic current, effectively duplicating the service life of the zinc anode.

From the study of S. Cramer et al., we thus conclude that PCI can be successfully applied to steel reinforcements, also ensuring an extension of the service life of the zinc anodes with a consequent economic advantage. Even if it has not been possible to have evidence, in literature, on the ICP effectiveness for cases different from the one previously exposed, it can be hypothesized that some considerations remain valid also for ICP on structures placed in water and soil. In fact, the cathodic reactions at the metal-to-electrolyte interface produce alkalinity and decrease the oxygen mobility on the sample surface, so they create a more favourable environment and passivity conditions, reducing the corrosion rate. A study of N. Sridhar et al. [10] seems to confirm the last statement: they observed changes in crevice pH and potential when the steel was maintained at its open-circuit potential, with the ferrous hydrolysis in lowering the pH in absence of cathodic protection. The application of a negative polarization (-0.8 V SCE), instead, results in an increase in the internal pH to values close to about 11. The internal potential increases slightly by about 50 mV. This created an alkaline environment that have reduced dissolution rate of iron.

As we have understood from this work, even if no universal solutions are reached, intermittent cathodic protection has proved to be a valid alternative to existing prevention methods and offers an additional protection tool, not necessarily connected to photovoltaic panels but inserted into a wider view of energy protection.

# Materials and Methods

### Intermittent CP test in soil simulating solution

Aim of the test is to evaluate the weight loss rate of carbon steel specimens under intermittent cathodic protection condition, varying the duration of the on period, i.e. when CP is applied, and off period, i.e. CP current absent. During the test, potential has been monitored. In the following, the experimental method is described.

#### 3.1 Material

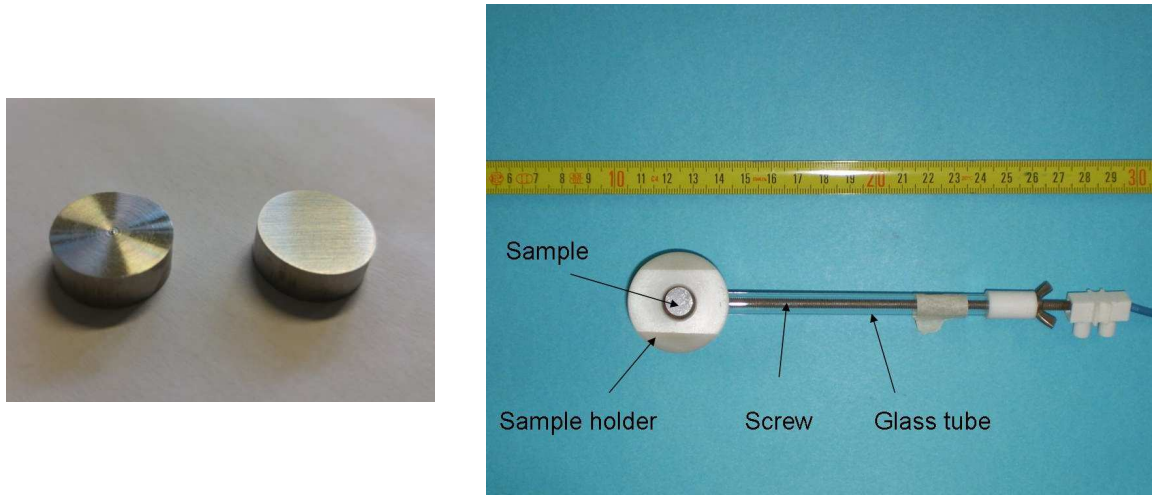
Carbon steel samples were cut from a bar (diameter 14 mm) and used in the test. Steel chemical composition, similar to that of steel pipes for hydrocarbon transport, is reported in Table 3.1.

**Table 3.1** – Carbon steel chemical composition (by weight)

Grade	%C max	%Mn max	%P max	%S max
API 5L X52 (Equivalent to EN L360)	0.30	1.40	0.030	0.030

After preparation with abrasive paper up to 1200 grit and cleaning with acetone, carbon steel specimens were placed in a PTFE cylindrical sample holder (Figure 3.1) made of two watertight caps. A circular area of 1 cm<sup>2</sup> of the metal was exposed to the electrolyte. A metal rod was screwed in a hole on the top of the sample holder to provide the electrical contact with the specimen inside the cap. In order to prevent the contact between the metal rod and the surrounding environment, a plastic tube was placed around the screw and was pressed against the sample holder interposing an o-ring joint between them (Figure 2.1).

Before testing, carbon steel specimens were weighted by a balance with an accuracy of  $\pm 0.1$  mg, in order to evaluate, at the end of the test, the weight loss due to corrosion.



**Figure 3.1** – Carbon steel specimen (left) and sample holder (right)

### 3.2 Electrolyte

Carbon steel specimens were immersed in a becher (1 L) containing a solution composed of distilled water containing 0.33 g/L of NaCl and 0.28 g/L of CaSO<sub>4</sub>, equal to 200 ppm of chlorides and 200 ppm of sulphates. The electrical resistivity of the solution measured at the beginning of the test by means of a conductivity probe is 50  $\Omega \cdot m$ . This solution aims to simulate a corrosive and aerated soil, as regards ions composition and conductivity. Nevertheless, the fluid dynamic condition, namely the diffusion of chemical species as oxygen, cannot be considered the same as soil. In order to avoid change in ions concentration and electrical resistivity due to the evaporation of water, distilled water was added weekly to restore the initial condition.

### 3.3 Intermittent CP conditions

14 specimens were tested:

- 12 specimens have been subjected to intermittent CP condition;
- 1 specimen was kept in free corrosion condition, i.e. no CP was applied;



- 1 specimen was kept continuously in CP condition, without interrupt the cathodic current.

Test conditions are summarized in Table 3.2. Repeatability for each intermittent CP condition is two, so that six conditions were tested. Each condition is defined by the following parameters:

- *on period ( $t_{on}$ ):* hours in a day in cathodic protection condition;
- *off period ( $t_{off}$ ):* hours in a day in absence of cathodic protection condition;
- *on/off time ratio ( $t_{on}/t_{off}$ ):* the ratio between on period and off period.
- *Number of cycles on/off in a day:*  $24 h/(t_{on}/t_{off})$

Conditions were selected in order to study the effect of the length of the on period fixing the off period (specimens 1-2-3-4-7-8-11-12; specimen 5-6-9-10) and fixing the ratio between on and off period (specimens 1-2-5-6).

**Table 3.2** – Intermittent CP condition (on and off time)

Specimens	on period (hours/cycle)	off period (hours/cycle)	On/off time ratio	Number of cycles on/off in a day
1 – 2	2	2	1	6
3 – 4	6	2	3	3
5 – 6	6	6	1	2
7 – 8	12	2	6	1.7
9 – 10	12	6	2	1.3
11 – 12	18	2	9	1.2
13 (CP)	24	0	--	--
14 (free corr.)	0	24	--	--

### 3.4 Test cell

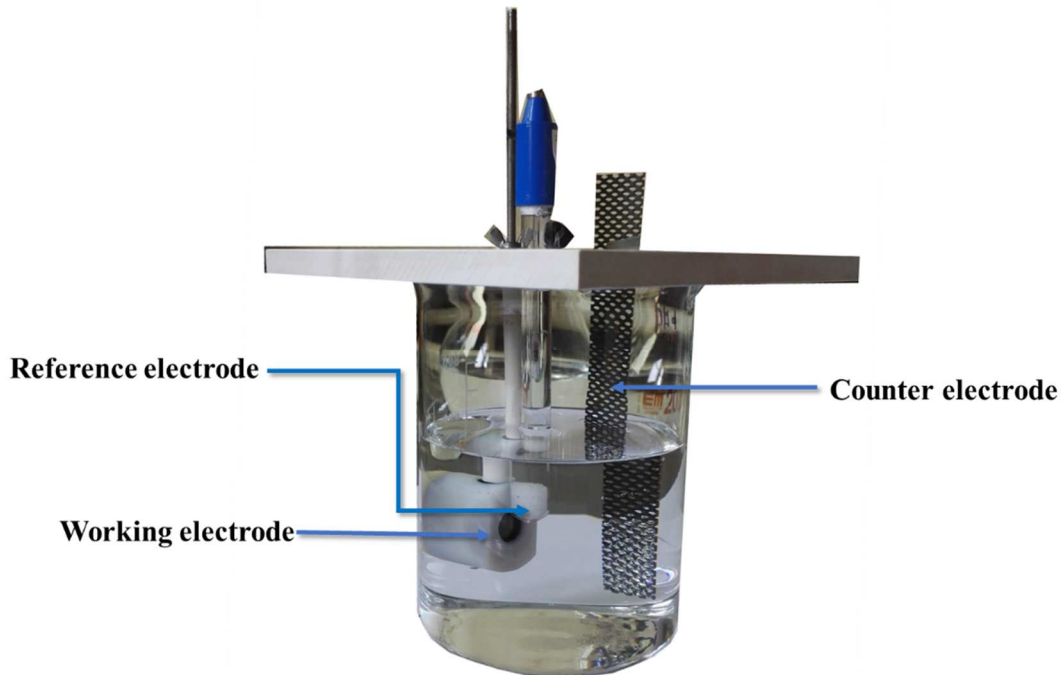
The specimen has been placed inside the becher containing the solution; the becher was covered by a proper PVC cap, which allows the insertion of electrodes for the application of CP and its monitoring (Figure 3.2):

- The working electrode: the specimen to test;
- The counter electrode (or auxiliary electrode): an inert electrode made of a mesh of

activated titanium (Ti-MMO, MMO – Mixed Metal Oxide) for the application of CP condition;

- The Ag/AgCl/KCl<sub>sat</sub> reference electrode for potential measurements.

In addition, supplementary electrodes were used to monitor and control test conditions (pH, temperature, resistivity).



**Figure 3.2** – Cell for cathodic protection tests.

### **3.5 Electrical circuit**

Figure 3.3 shows a scheme of the electrical circuit for the intermittent CP test. There are no particular differences if compared with a traditional CP test, except for the presence of a programmable switch able to stop the circulation of the current in the system during the off period. For each tested condition, the two cells were inserted in series. The working electrode (carbon steel specimen) has been connected to the negative pole of a DC feeder, while the positive pole has been connected to the anode (the counter electrode). In series to the cell, a resistor of 1 k $\Omega$  has been inserted in order to measure the circulating current, given by the ratio between the voltage across the resistor and its resistance ( $I = V/R$ ). The

off and on periods were set based on values reported in Table 3.2. Figure 3.4 shows the internal electrical circuit of the switch: in off condition, the switch moves to channel “18” opening the circuit avoiding current flow between the anode and the specimen.

### 3.6 Cathodic protection condition

Cathodic protection was applied in a galvanostatic way, i.e. at constant current density, by means of a DC feeder. After a period of two weeks during which the current was controlled in order to measure a stable potential, the intermittent CP test started.

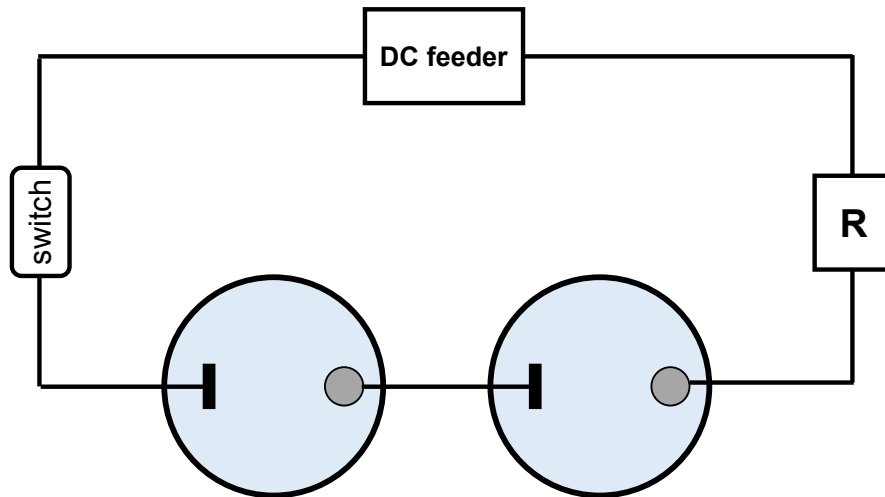


Figure 3.3 – Scheme of the test circuit.

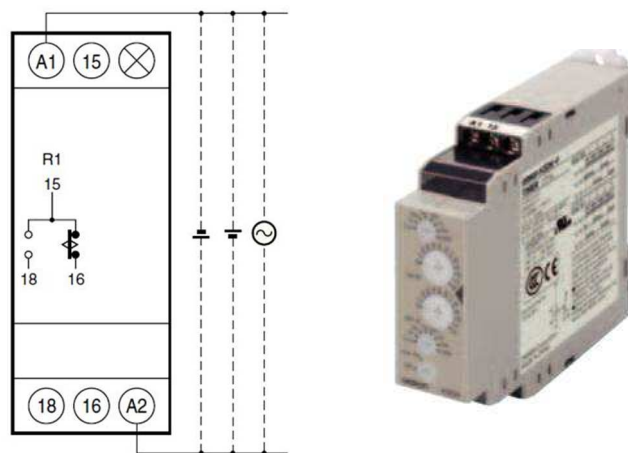


Figure 3.4 – Scheme of the switch.

In stationary condition, cathodic current density is about 0.2 A/m<sup>2</sup>; values are reported in Table 3.3. The polarization potential in on condition is in the range between -0.85 V CSE and -1.20 V CSE. It follows that each specimens reached cathodic protection condition without be overprotected ( $E < -1.2$  V CSE) so that the main cathodic process on steel surface is oxygen reduction.

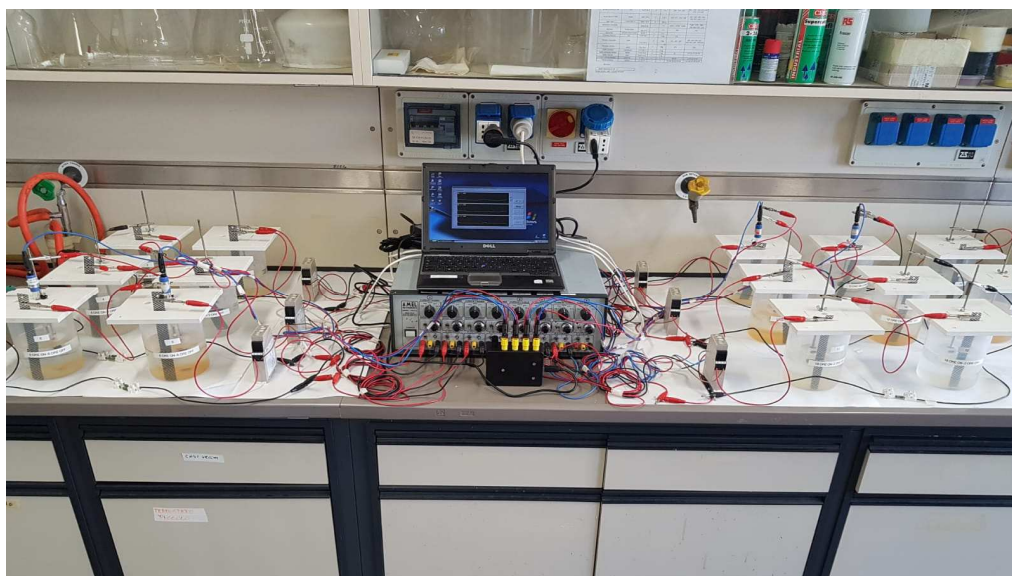
**Table 3.3** – Cathodic protection current density at the beginning of the test and after two weeks of stabilization time

Specimens	Initial current density (A/m <sup>2</sup> )	Final <sup>(*)</sup> current density (A/m <sup>2</sup> )
1 – 2	0.27	0.20
3 – 4	0.23	0.25
5 – 6	0.35	0.20
7 – 8	0.20	0.20
9 – 10	0.30	0.18
11 – 12	0.25	0.20
13 (CP)	0.30	0.20

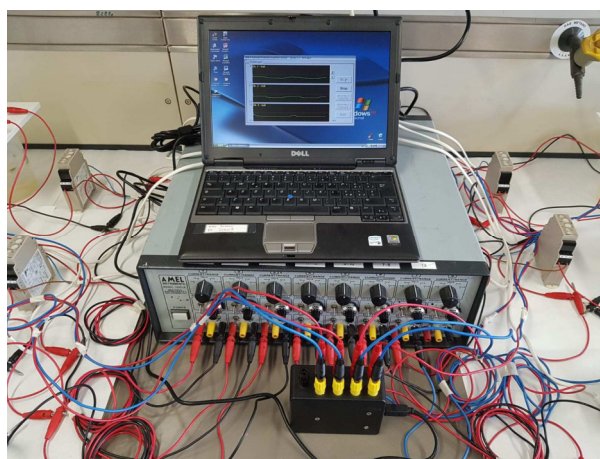
\* After two weeks of polarization

### 3.7 Monitoring

The potential of each specimen was measured continuously for 24 hours each week in order to study the depolarization behaviour during the off period. Potential was measured by means of a Ag/AgCl/KCl<sub>sat</sub> reference electrode (+0.2 V SHE) immersed in solution and placed very close to the metal surface (a few millimetres) in order to avoid ohmic drop contribution in the potential reading. For a sake of simplicity, in all the reported graphs the potential measurements are converted with respect to CSE reference electrode, the same use in field to monitor CP in soil (CSE = +0.32 V SHE). Potential was recorded by means of a data logger with high internal impedance (10 MΩ) and an acquisition frequency of 1 point per minute. Figure 3.5 and 3.6 show the electrical connection to the data acquisition system.



**Figure 3.5 – Potential monitoring.**



**Figure 3.6 – Potential monitoring (detail of data acquisition system).**

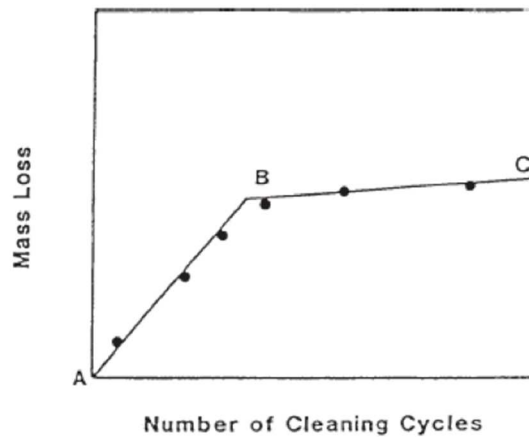
### **3.8 Duration**

Test duration is 6 months.

### **3.9 Weight loss rate (corrosion rate)**

Corrosion products were removed according to the procedure reported in the Standard ASTM G1-03 [14]. This procedure is called “cleaning” and ideally it should remove only corrosion product and not remove any base metal. The cleaning procedure should be repeated on the specimens several times until the complete removal of the corrosion

products. Figure 3.7 shows the mass loss as a function of the number of cleaning cycles as reported on ASTM G1-03; in particular, the segment AB represents the mass loss given by both the corrosion product removal and metal mass loss, while the segment BC represents only the metal mass loss after the corrosion product has been completely removed. Therefore, the optimum number of cleaning cycles is approximately the one that gives the mass loss referred to point B.



**Fig 3.7** – Example of mass loss trend according to the pickling cycles as reported in the ASTM G1 standard

After the test, the specimens have been photographed still dirty and subsequently the surface has been cleaned with chemical washing and ultrasound. The chemical pickling was carried out in a 1: 1 solution of hydrochloric acid (HCl), with addition of 3.5 g of hexamethylenetetramine ( $C_6H_{12}N_4$ ), iron corrosion inhibitor introduced to prevent further corrosion of the base metal. The samples were subjected to washing cycles in an ultrasound machine to facilitate the removal of corrosion products. The mass was measured at the end of each ultrasound cleaning cycle (2 minutes). By plotting the mass loss, according to the number (or duration) of the cycles, a graph similar to the one shown in Figure 3.7 is obtained.

Corrosion rate,  $CR$ , was calculated by means of weight loss measurement:

$$(3.1) \quad CR = \frac{\Delta W}{S \cdot t}$$

where  $\Delta W$  is weight loss (g),  $S$  is the exposed surface of the sample ( $1 \text{ cm}^2$ ) and  $t$  the duration of the test. When steel is in CP condition, namely at potential lower than  $-0.85 \text{ V CSE}$ , the corrosion rate is negligible, which means lower than  $0.01 \text{ mm/year}$ , according to ISO 15589-1 standard [11].





## Experimental results

In this chapter, the results of potential monitoring and mass loss rate of the intermittent cathodic protection tests are presented. The experimental details are reported in Chapter 3. For a sake of clarity, Table 3.2 is reported also in this section. The table reports all the test conditions, varying the length of the on and off period.

**Table 4.1 (as Table 3.2) – Intermittent CP condition (on and off time)**

Specimens	on period (hours/cycle)	off period (hours/cycle)	On/off time ratio	Number of cycles on/off in a day
1 – 2	2	2	1	6
3 – 4	6	2	3	3
5 – 6	6	6	1	2
7 – 8	12	2	6	1.7
9 – 10	12	6	2	1.3
11 – 12	18	2	9	1.2
13 (CP)	24	0	--	--
14 (free corr.)	0	24	--	--

### 4.1 Potential monitoring

#### 4.1.1 Free corrosion condition and polarization period

Figure 4.1 reports the potential values (E, V vs. CSE) of the carbon steel specimen exposed to free corrosion condition (sample N°14, Table 4.1) versus the test time. The free corrosion potential depends mainly on oxygen content in solution; the mean value during the test time is -0.680 V CSE: this value has been considered for the calculation proposed in the next sections. In Figure 4.1 the cathodic protection level, namely -0.85 V CSE, is also shown. In

this condition, corrosion rate corresponds to the oxygen limiting diffusion current density. As discussed in Chapter 3, before the starting of the ON-OFF cathodic protection intermittent cycles, the specimens (except the free corrosion sample) were subjected to a period of cathodic polarization, without any interruption of the cathodic current, in order to stabilize the potential below the quasi-immunity value of -0.85 V CSE. Figure 4.2 and Figure 4.3 show the monitoring of the sample potentials before the onset of the intermittent cycles: this phase lasted 45 days.

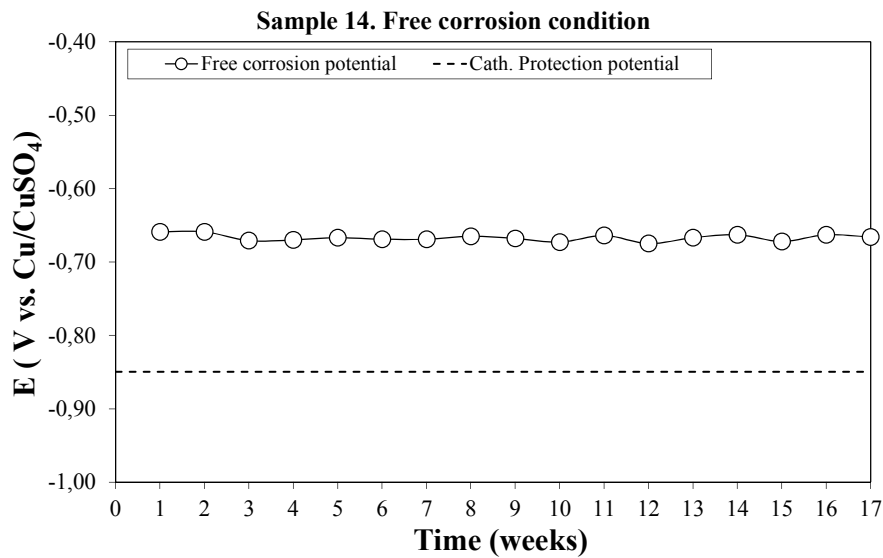


Fig. 4.1 – Free corrosion potential (Sample 14).

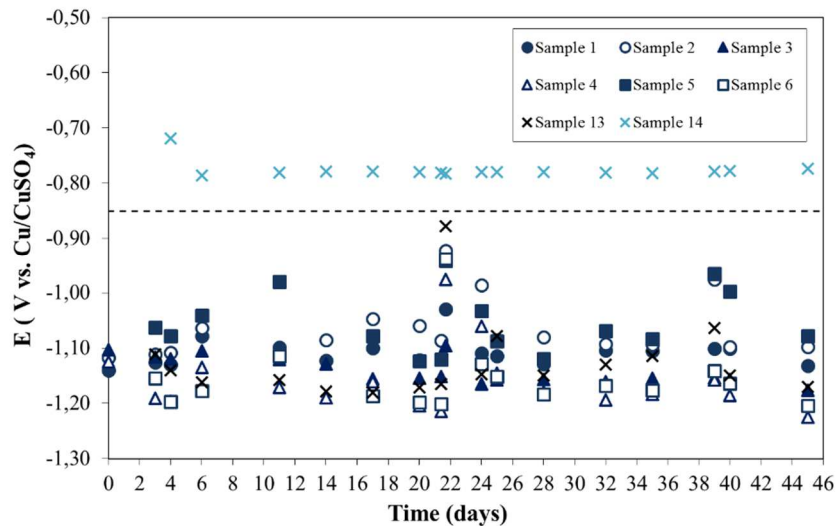


Fig. 4.2 – Potential monitoring during the pre-polarization period (Samples 1-6, 13-14)

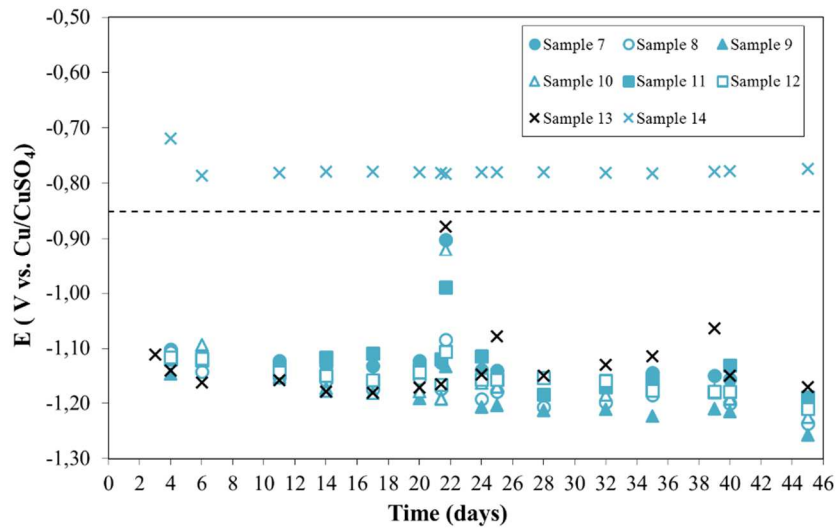


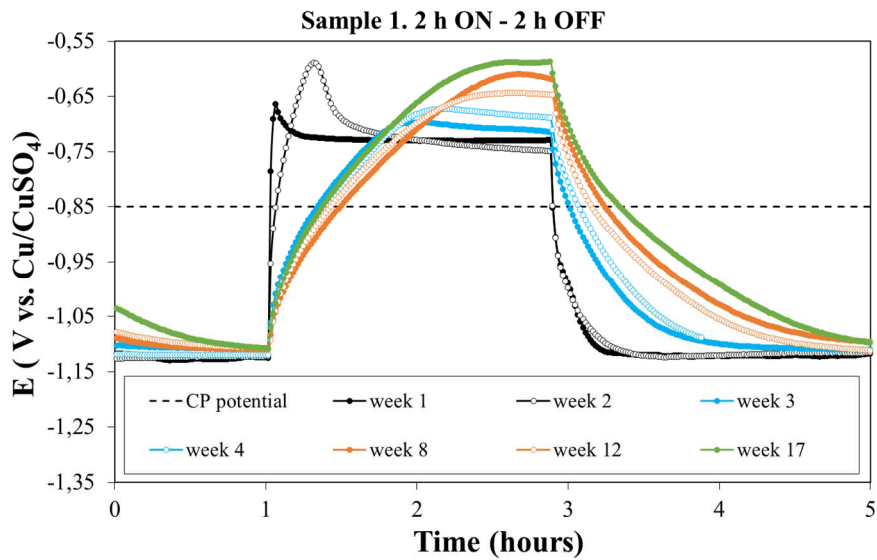
Fig. 4.3 – Potential monitoring during the pre-polarization period (Samples 7-12, 13-14)

#### 4.1.2 Cycles of intermittent cathodic protection

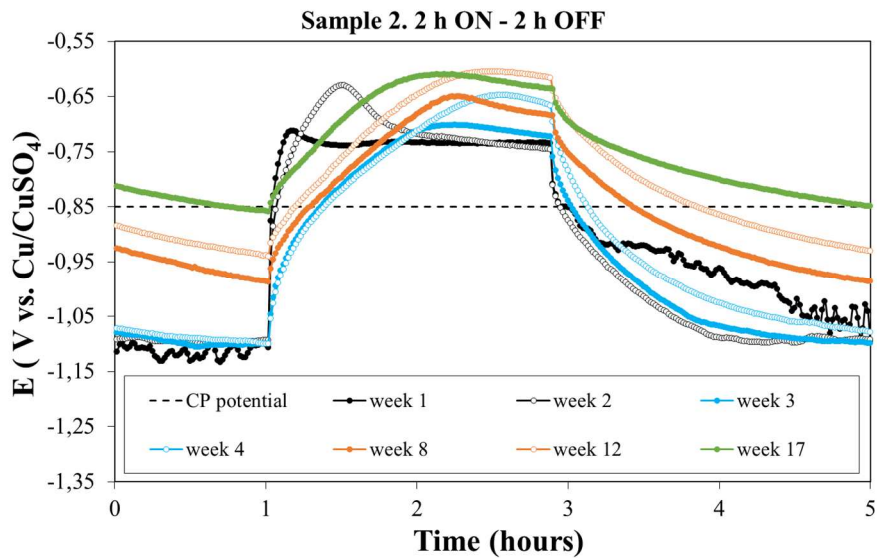
Figures from 4.4 to 4.15 show the IR-free potential monitoring of the specimens from 1 to 12, respectively. For each sample, the potential profile is reported; even if the potential has been registered for 24 hours, the graphs show only one ON-OFF cycle in the monitored day. The duration of each single cycle is reported in Table 4.1. For a sake of clarity, only the following profiles are reported: weeks 1-2-3-4 (one profile each week for the first month)-8-12-17 (one profile each month for the following months).

*Sample 1-2:* Figures 4.4 and 4.5 show the potential profile for Sample 1 and 2 (2h ON - 2h OFF). During the ON period, the potential is between -1.0 V CSE and -1.1 V CSE, lower than the protection potential (-0.85 V CSE). In this condition, corrosion is impossible from a thermodynamic point of view, because the potential is lower than the equilibrium potential of iron dissolution (-0.92 V CSE). When the cathodic current is interrupted, the potential increases assuming progressively more positive values, up to the free corrosion potential. It is observed that the sample depolarization is very rapid during the first weeks of testing, when the potential increases almost instantaneously to the free corrosion potential. After about one month testing, the depolarization is slower. Moreover, in some cases the potential overcomes the free corrosion potential (-0.68 V CSE) at the end of the OFF period.

From an electrochemical point of view, the gradual increase in potential can be explained by oxygen diffusion and replacement from the bulk of the solution towards the metal-solution interface. In fact, during the previous period of cathodic protection, on the surface of the specimen the cathodic reactions of oxygen reduction takes place and lead to a decrease in the concentration of this gas in contact with the metal. When the cathodic protection is interrupted, the sample tends slowly to the free corrosion potential with a kinetic that depends on oxygen mobility (i.e. oxygen diffusion) in solution.



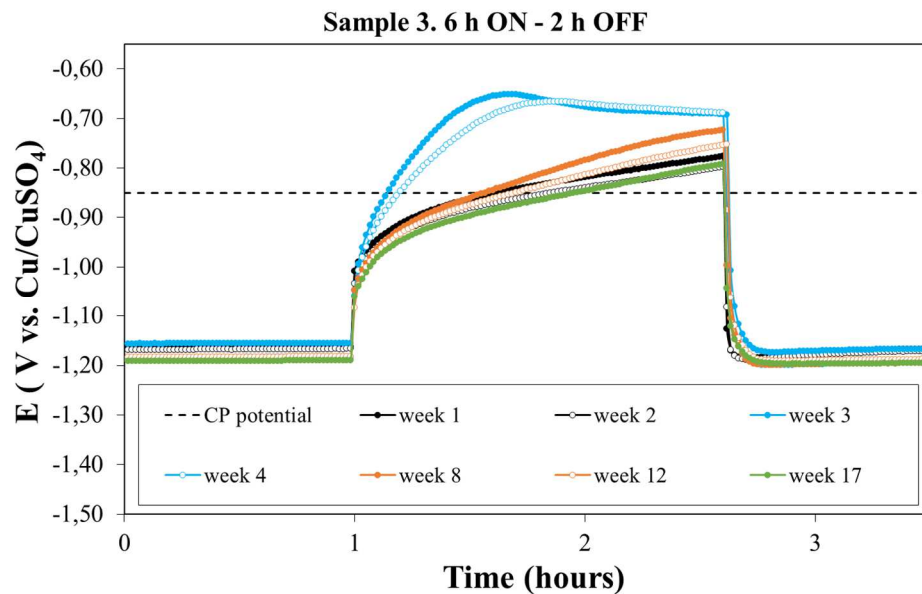
**Fig. 4.4** – Potential monitoring of Sample 1 during intermittent cycles



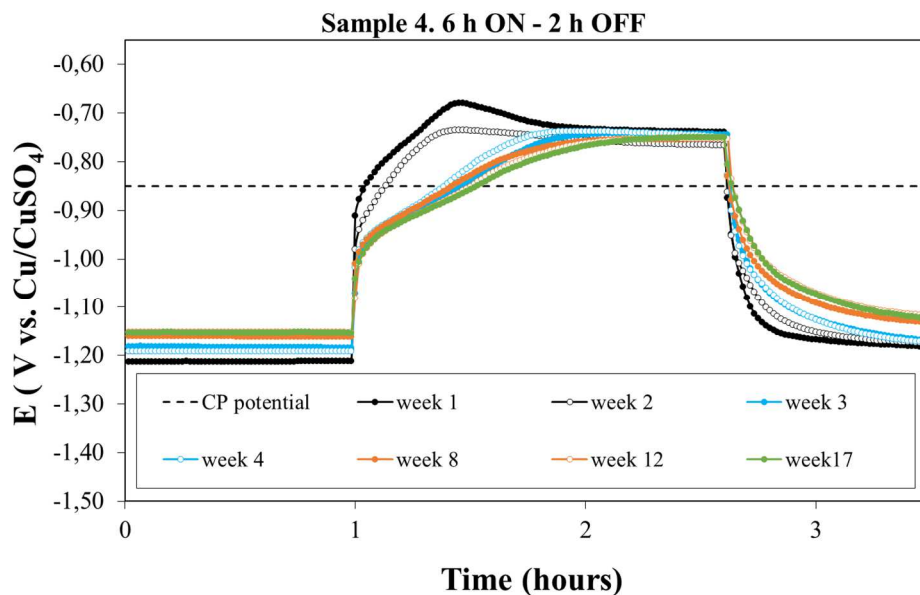
**Fig. 4.5** – Potential monitoring of Sample 2 during intermittent cycles

At the end of the OFF period, when the current is applied again, the samples potential decreases again, returning to the values preceding the interruption of the protection current with a trend that is identical to the previous depolarization phase. For Sample 2 in some cases (week 8-12-17) the potential does not reach easily the protection potential. Indeed, before starting the following cycle, the potential was very close to or slightly higher more positive than -0.85 V CSE; this is not acceptable and in these cases some current output corrections were done.

*Sample 3-4:* Figures 4.6 and 4.7 show the potential profile for Sample 3 and 4 (6h ON - 2h OFF). Similar considerations of Samples 1 and 2 can be extended also to this case. During the ON period, the potential is between -1.15 V CSE and -1.2 V CSE. When the cathodic current is interrupted, the potential increases assuming progressively more positive values, up to the free corrosion potential. As observed for the first two samples, even in this case, the depolarization is very rapid during the first weeks of testing and the potential increases almost instantaneously to the free corrosion potential.



**Fig. 4.6** – Potential monitoring of Sample 3 during intermittent cycles



**Fig. 4.7** – Potential monitoring of Sample 4 during intermittent cycles

After about two weeks testing, the depolarization is slower. For instance, at the week 17, the potential of Sample 3 becomes higher than the protection value, -0.85 V CSE, after about 1 hour from the interruption of the current. For Sample 4, a similar trend is observed but with a more rapid depolarization. Strange potential profiles are observed for Sample 3 at weeks 3 and 4, with respect to the potential profiles at weeks 1 and 2. Indeed, the depolarization is faster at weeks 3 and 4; this has been observed only for Sample 3 and probably is related to an error of potential recording with the instrumentations. Further investigations are needed.

*Sample 5-6:* Figures 4.8 and 4.9 show the potential profile for Sample 5 and 6 (6h ON - 6h OFF). Especially for Sample 5, in some cases a disagreement between the potential profiles is observed. Consider for instance the potential profile after 8 weeks: it seems to be in contrast with the general trend observed for all the potential profiles. Apart this behaviour, it is possible to conclude that also in this condition the depolarization time, i.e. the time needed to reach free corrosion potential, increases as the test time increases. For this test condition, the depolarization time varies from a few minutes in the first weeks to a few hours after 17 weeks.

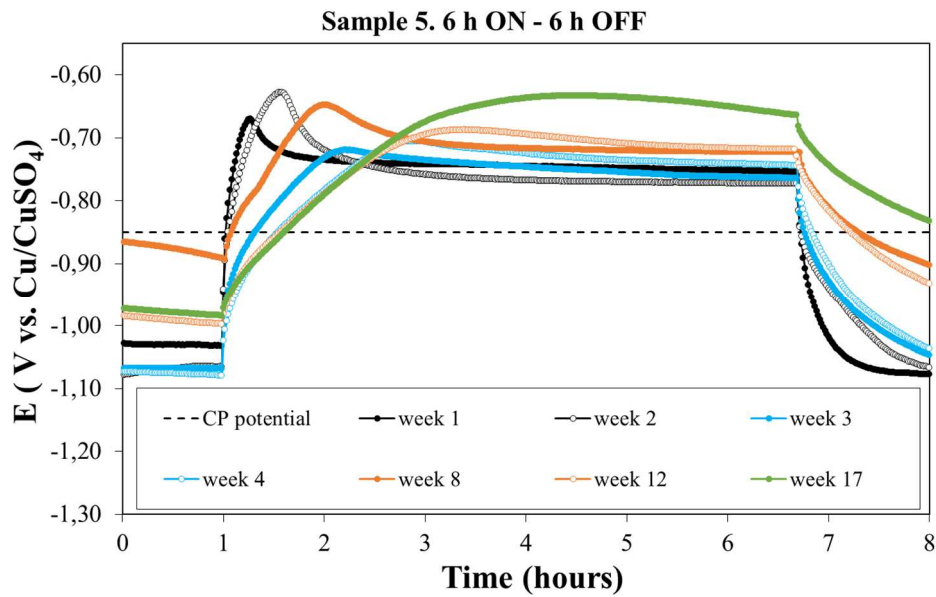


Fig. 4.8 – Potential monitoring of Sample 5 during intermittent cycles

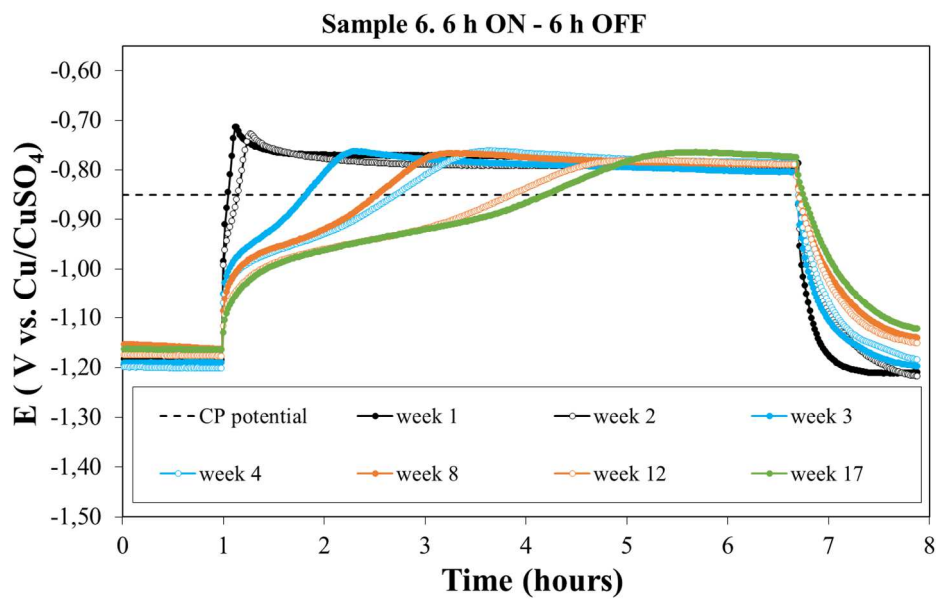


Fig. 4.9 – Potential monitoring of Sample 6 during intermittent cycles

Sample 7-8: Figures 4.10 and 4.11 show the potential profile for Sample 7 and 8 (12h ON - 2h OFF). During the ON period, the potential is between -1.15 V CSE and -1.25 V CSE and the potential is very stable. Indeed, in this case, the ON period is longer (6 hours) than in the first six samples; this probably helps to the stabilization of the polarization potential. The depolarization, similarly to the cases already commented, increases as the test time increases.

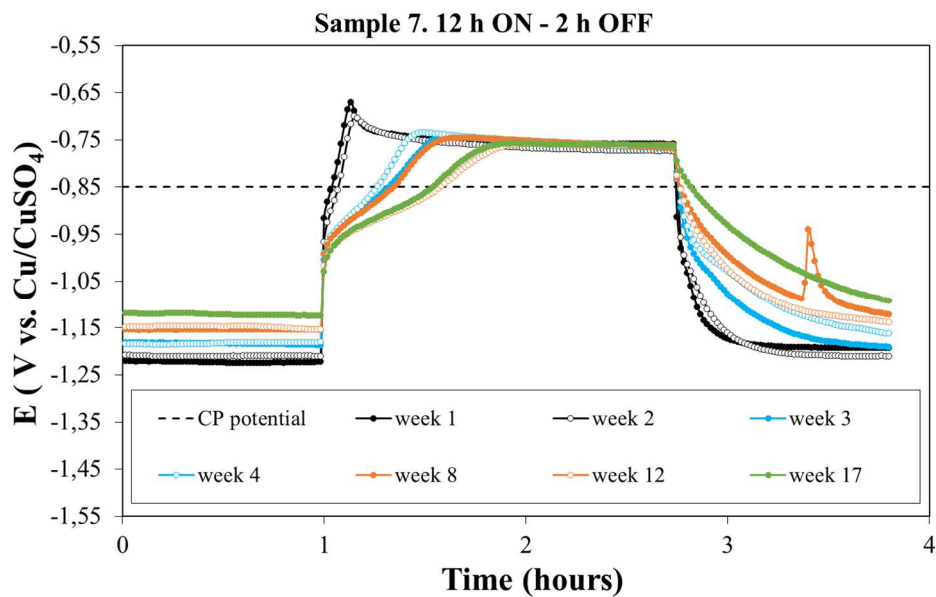


Fig. 4.10 – Potential monitoring of Sample 7 during intermittent cycles

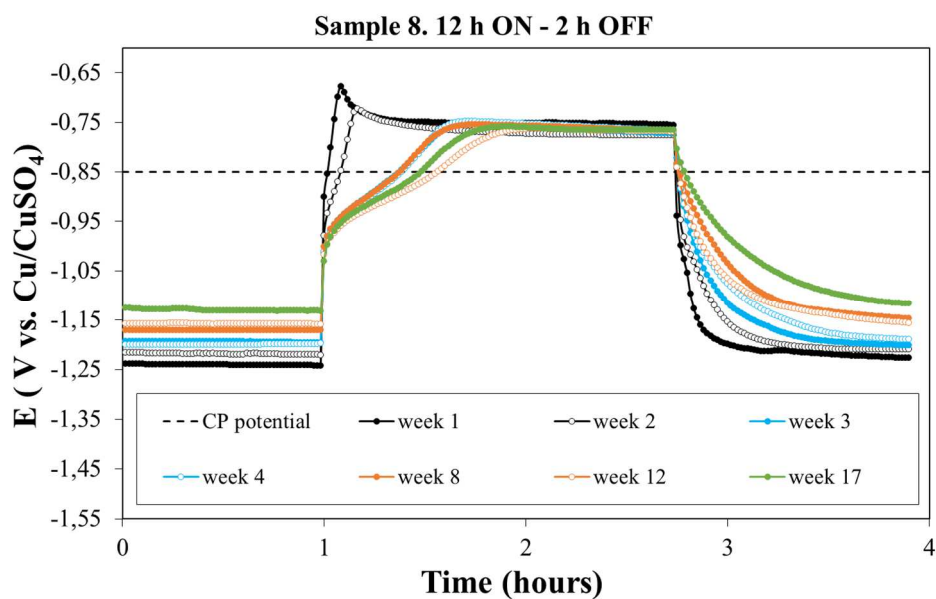
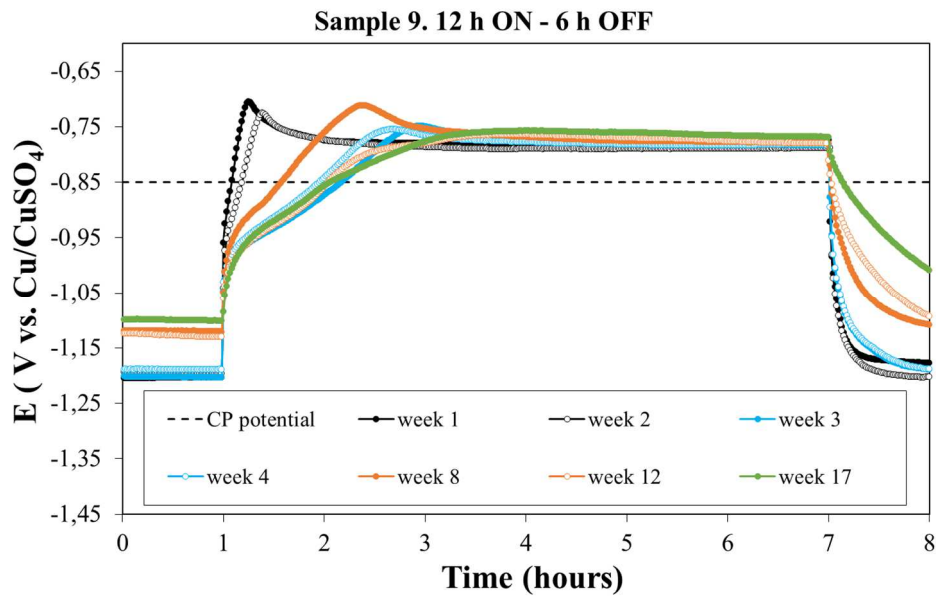


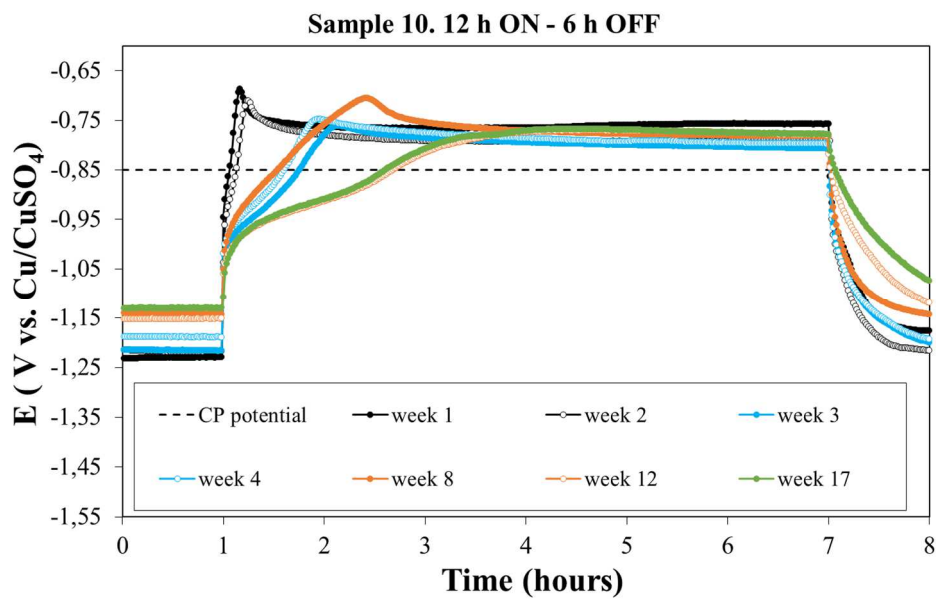
Fig. 4.11 – Potential monitoring of Sample 8 during intermittent cycles

Sample 9-10: Figures 4.12 and 4.13 show the potential profile for Sample 9 and 10 (12h ON - 6h OFF). During the ON period, the potential is very stable, probably due to the long polarization period that makes more stable the electrochemical conditions on the metal surface (consumption of oxygen and increase of pH). As observed for the previous samples, the depolarization time is concluded in about one/two hours after a few months of testing.





**Fig. 4.12** – Potential monitoring of Sample 9 during intermittent cycles



**Fig. 4.13** – Potential monitoring of Sample 10 during intermittent cycles

*Sample 11-12:* Figures 4.14 and 4.15 show the potential profile for Sample 11 and 12 (18h ON - 2h OFF). During the ON period, the potential is very stable due to the long CP period and ranges between -1.15 V CSE and -1.25 V CSE. Some considerations of the other samples can be extended also in this case.

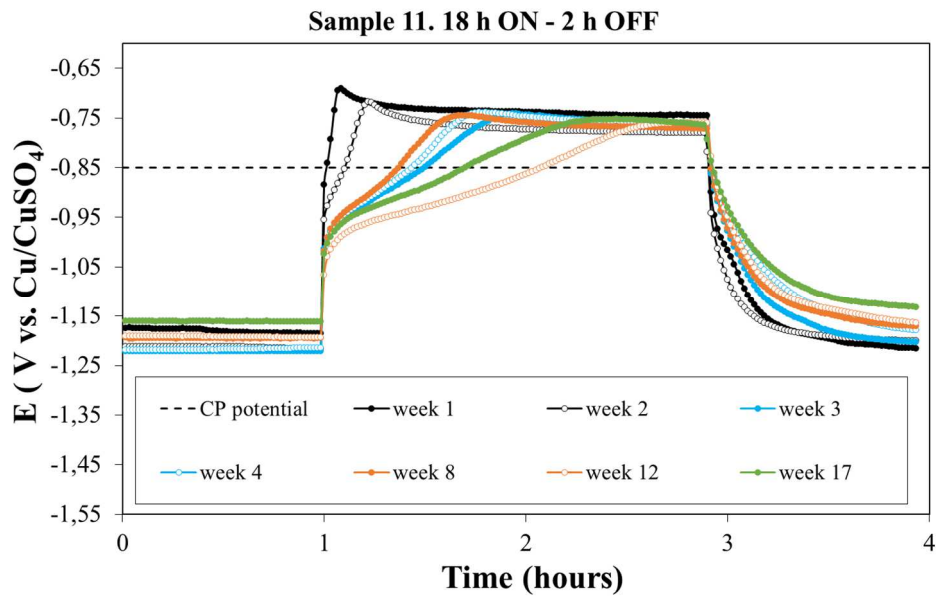


Fig. 4.14 – Potential monitoring of Sample 11 during intermittent cycles

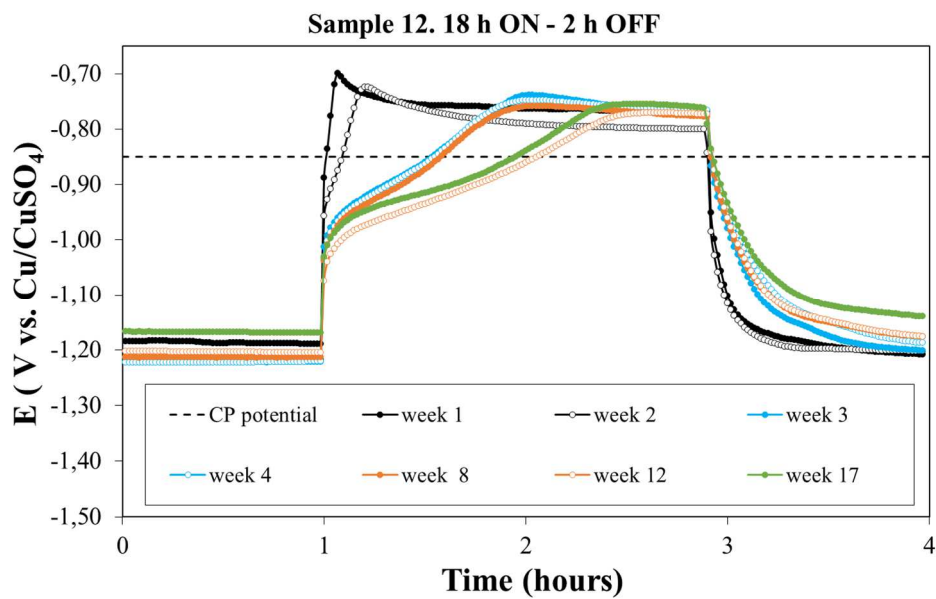


Fig. 4.15 – Potential monitoring of Sample 12 during intermittent cycles

In conclusion, Figure 4.16 shows the IR-free potential values of all the samples (from 1 to 12) measured at the end of the OFF period, varying the test weeks. A detailed investigation of the potential profiles during the off period is reported in Chapter 5.

It is possible to observe that the potential at the end of the OFF period is close to the average free corrosion potential value measured for Sample 14 (-0.68 V CSE) with some exceptions. In particular, for Sample 1 and 2 (2h ON - 2h OFF) this potential is higher than -0.68 V CSE

with some variations probably due to the difficulty for the specimen to reach stable electrochemical condition in the OFF and ON periods which are very short. In the other cases, the potential after the OFF cycle is lower than -0.68 V CSE: CP seems to create electrochemical conditions, which cannot be “eliminated” in a short time. The potential in most of the cases is very close to -0.75 and -0.80 V CSE, between free corrosion condition and the protection level (dotted lines). It follows that corrosion rate, at least theoretically, will be lower than the free corrosion rate.

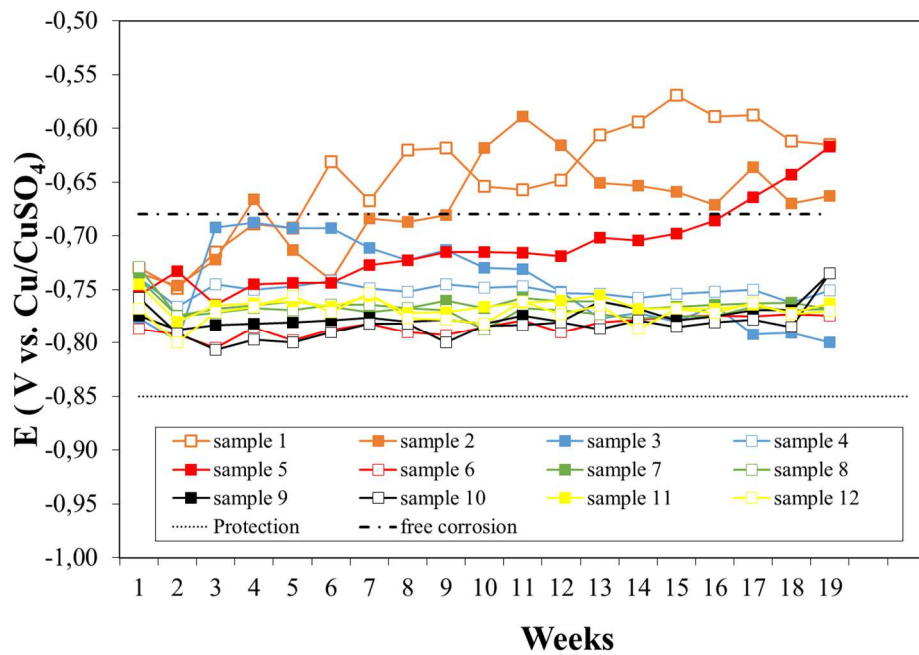


Fig. 4.16 – Potential profiles measured at the end of the OFF cycle.

## 4.2 Mass loss rate

At the end of the immersion tests, the specimens were extracted from the cells, cleaned with acid pickling and ultrasound. Then, they were weighed to evaluate the mass loss rate, calculated as follows:

$$(4.1) \quad CR = \frac{\Delta W}{\rho \cdot S \cdot t}$$

where CR is the corrosion rate (penetration rate of corrosion),  $\Delta M$  is the mass variation in time  $t$ ,  $S$  is the surface of the sample ( $1 \text{ cm}^2$ ) and  $\rho$  the mass density of the steel ( $7.87 \text{ g/cm}^3$ ). Table 4.2 reports the experimental corrosion rate (accuracy  $\pm 1 \text{ }\mu\text{m/year}$ ) of the samples calculated using Eq. 4.1:

**Table 4.2** – Corrosion rate values obtained from mass loss measurements.

<b>Specimens</b>	<b>on period (hours/cycle)</b>	<b>off period (hours/cycle)</b>	<b>On/off time ratio</b>	<b>Corrosion rate (<math>\mu\text{m/year}</math>)</b>
<b>1</b>	2	2	1	<b>12</b>
<b>2</b>				<b>43</b>
<b>3</b>	6	2	3	<b>6</b>
<b>4</b>				<b>15</b>
<b>5</b>	6	6	1	<b>64</b>
<b>6</b>				<b>116</b>
<b>7</b>	12	2	6	<b>20</b>
<b>8</b>				<b>18</b>
<b>9</b>	12	6	2	<b>143</b>
<b>10</b>				<b>137</b>
<b>11</b>	18	2	9	<b>16</b>
<b>12</b>				<b>21</b>
<b>13 (CP)</b>	24	0	--	--
<b>14 (free corr.)</b>	0	24	--	<b>150</b>

A detailed analysis of corrosion rate data is proposed in Chapter 5.

# Chapter 5

## Discussion

In this chapter, the experimental results introduced in the previous chapter are discussed. In particular, an electrochemical model of data interpretation and corrosion rate evaluation is proposed.

### 5.1 Potential profile during the OFF period

Figure 5.1 shows an example of potential profile recorded during the monitoring phase for Sample 3 (6 hours ON, 2 hours OFF). As widely discussed in Chapter 4, when the CP current is interrupted, the potential increases assuming progressively more positive values, up to the free corrosion potential. It is observed that the sample depolarization is very rapid during the first weeks of testing, when the potential increases almost instantaneously to the free corrosion potential. After a few weeks of testing, the depolarization is slower. Moreover, in some cases the potential overcomes the free corrosion potential (-0.68 V CSE) at the end of the OFF period. From the potential profiles it is possible to measure the time in which the sample is immune to corrosion (i.e. the time when the potential,  $E$ , remains below -0.85 V CSE) even if the cathodic protection is switched off.

From the graph reported in Figure 5.1, it is possible to define the following parameters:

- $t_{OFF}$ : duration of the CP current-OFF period (hours/cycle);
- $t_{ON}$ : duration of the CP current-ON period (hours/cycle);
- $t.i.p.$  (Time in Protection): time of CP condition, namely  $E < -0.85$  V CSE, after the interruption of CP current (during the OFF period); in order to compare different test conditions, it is possible to calculate the following parameter:

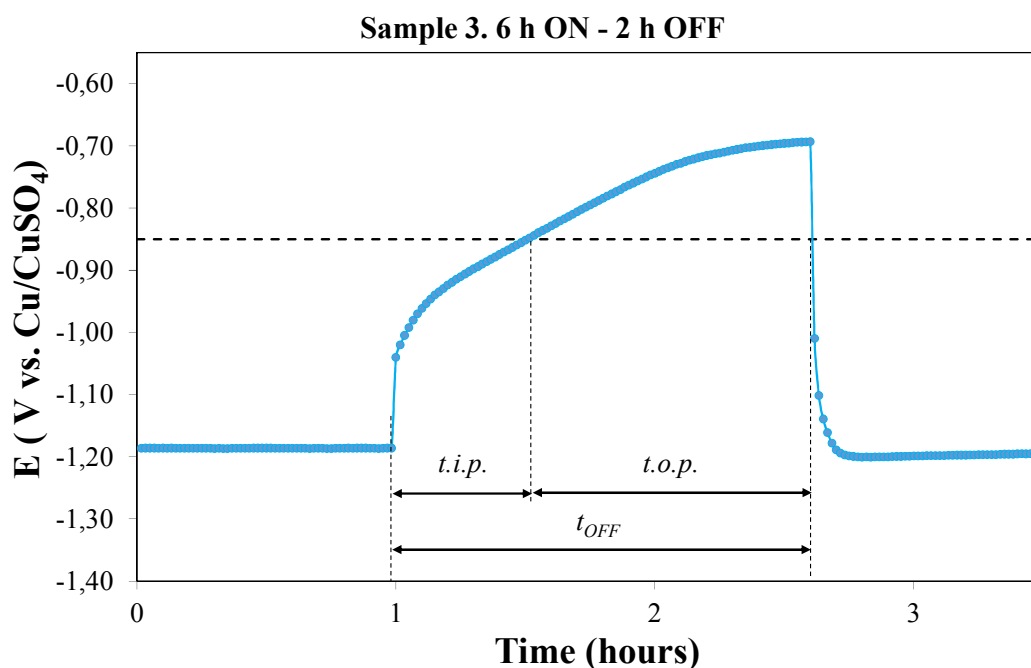
$$(5.1) \quad \%t.i.p. = \frac{t.i.p. \cdot 100}{t_{OFF}} \quad \text{where } t.i.p. \text{ and } t_{OFF} \text{ are expressed in hours.}$$

- *t.o.p.* (Time out of Protection): time out of CP condition, namely  $E > -0.85$  V CSE, after the interruption of CP current (during the OFF period); in order to compare different test conditions, it is possible to calculate the following parameter:

$$(5.2) \quad \%t.o.p. = \frac{t.o.p. \cdot 100}{t_{OFF}} \quad \text{where } t.o.p. \text{ and } t_{OFF} \text{ are expressed in hours.}$$

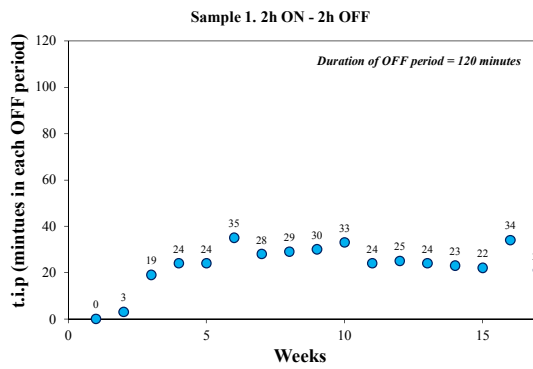
- $t_{OFF} = t.i.p. + t.o.p.$

These parameters have been calculated for each potential profiles recorded during the test time. Results are reported in the following.

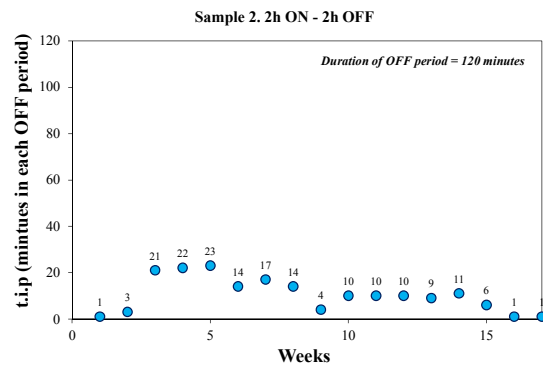


**Fig 5.1** – Parameters obtained from each potential profile. Example

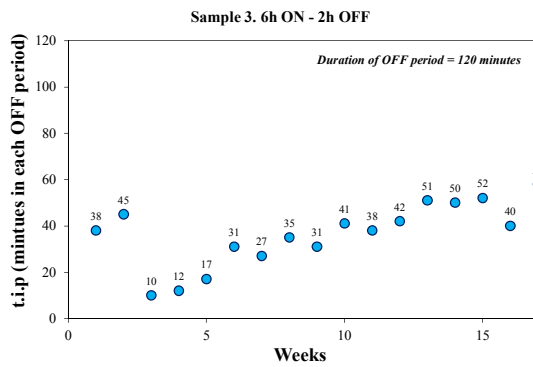
Figures from 5.2 to 5.7 report the value of the time in protection ( $t.i.p.$ , expressed in minutes during the off period) for all the tested samples.



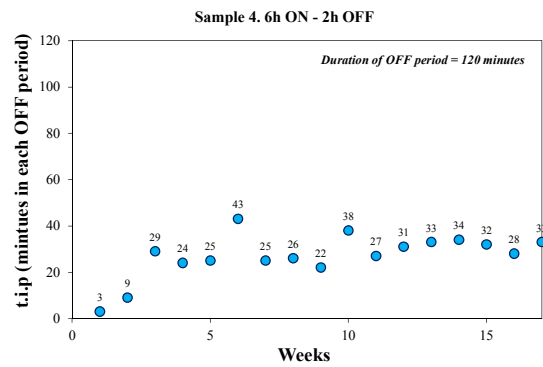
**Fig 5.2a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 1



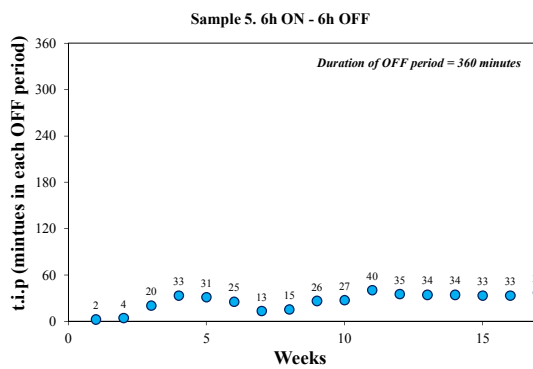
**Fig 5.2b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 2



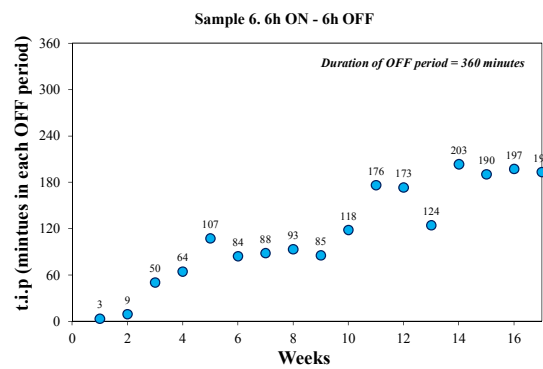
**Fig 5.3a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 3



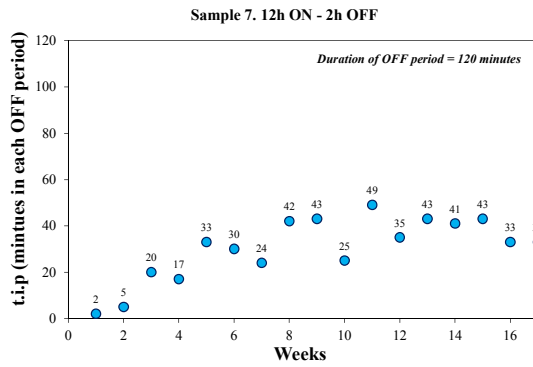
**Fig 5.3b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 4



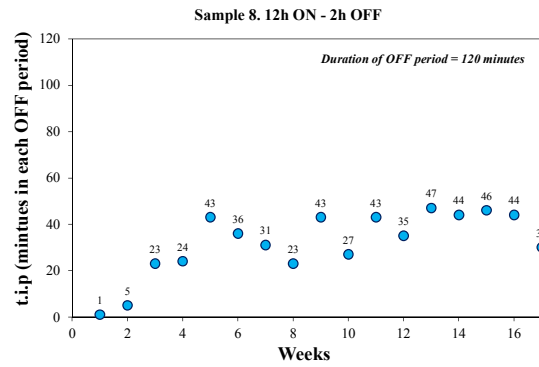
**Fig 5.4a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 5



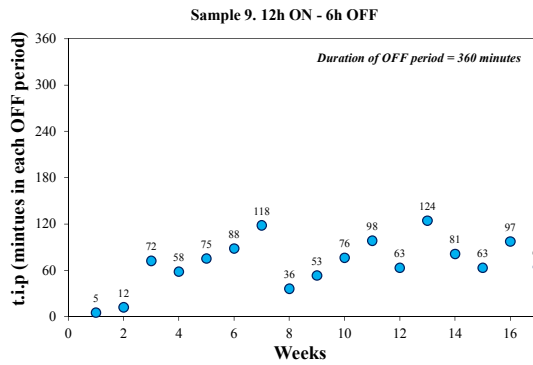
**Fig 5.4b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 6



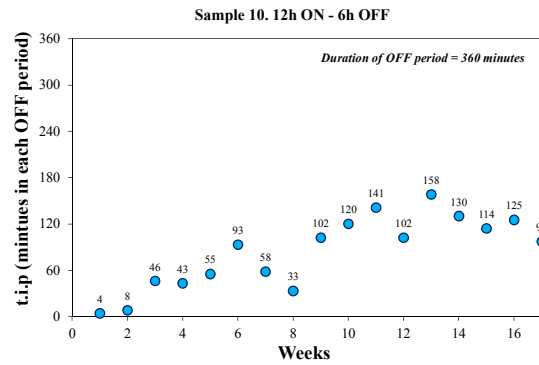
**Fig 5.5a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 7



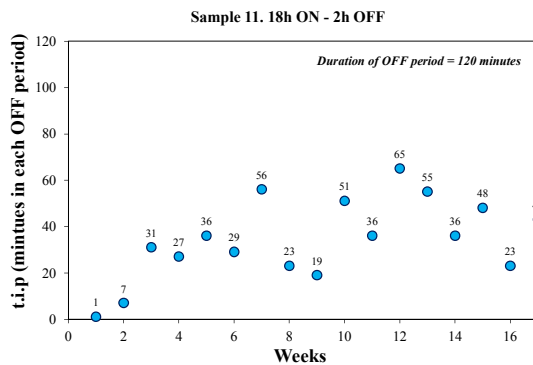
**Fig 5.5b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 8



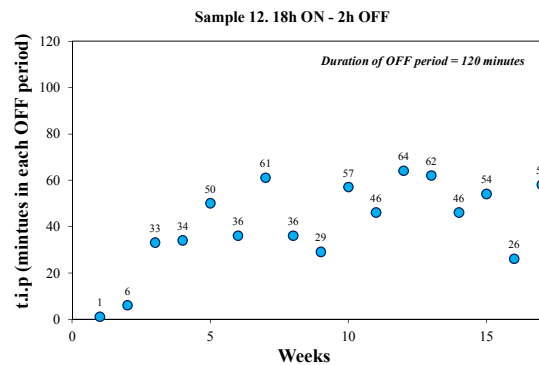
**Fig 5.6a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 9



**Fig 5.6b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 10



**Fig 5.7a** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 11



**Fig 5.7b** – Immunity time (time in protection, *t.i.p.*) during the off period for Sample 12



In order to compare different conditions and to study the effect of ON and OFF periods, the values of % *t.i.p.* (Eq. 5.1) are showed in Table 5.1.

Data are highlighted in four groups:

- **White:**  $\text{tip} < 20\%$  of the OFF time. This condition occurs mainly during the first month of test for all conditions. This could be due to a stabilization time of the electrochemical conditions on the metal surface during alternate CP condition;
- **Yellow:**  $20\% < \text{tip} < 30\%$  of the OFF time. This condition occurs mainly after the first month of test for all conditions;
- **Blue:**  $30\% < \text{tip} < 40\%$  of the OFF time. This condition is absent for Sample 1 and 2, characterized by 2 hours ON and 2 hours OFF. Although the OFF time is short, the two hours of CP seem not able to create stable condition on the metal surface in terms of oxygen consumption. Oxygen is consumed by the cathodic current during the ON period but this effect is weak for very short ON time;
- **Green:**  $\text{tip} > 40\%$  of the OFF time. This condition is particularly evident for very long ON period (Sample 11 and 12, which have 18 hours/day of cathodic protection).

Considering Figures from 5.2 to 5.7 and data in Table 5.1, it is possible to conclude that the main explanation of this behavior is related to the oxygen consumption and diffusion. Indeed, in proximity of the metal surface, oxygen is reduced and consumed by the cathodic current during the ON period; after the current shutdown (OFF period) the oxygen diffuses towards the metal, causing a rise in potential up to the free corrosion potential. Only long ON periods (higher than 12 hours/day) create conditions of high oxygen consumption on the metal surface with a slow diffusion (and so a slow potential increase) during the OFF period. This is evident comparing for example data of Sample 1 and 2 (2 hours On – 2 hours OFF, Figure 5.2) and data of Samples 9-10-11-12 (Figures 5.6 and 5.7). In the first case, the *t.i.p.* period is always lower than 40 minutes, due to the short ON period. When ON period is longer (Samples 9 to 12), the *t.i.p.* increases up to 120 minutes or higher.

Table 5.1 – Immunity time (% *t.i.p.*) during the off period for all the tested conditions

$\%t.i.p. = \frac{t.i.p. \cdot 100}{t_{OFF}}$																						
Samples	$t_{ON}$ (h/cycle)	$t_{OFF}$ (h/cycle)	$t_{ON}/t_{OFF}$	Week 1	Week 2	Week 3	Week 4	Week 5	Week 6	Week 7	Week 8	Week 9	Week 10	Week 11	Week 12	Week 13	Week 14	Week 15	Week 16	Week 17	Week 18	Week 19
1	2	2	1	0	2,5	16	20	20	29	23	24	25	27	20	21	20	19	18	28	18	23	23
2				1	2,5	18	18	19	12	14	12	3	8	8	8	7,5	9	5	1	1	1	1
3	6	2	3	32	37	8	10	14	26	22	29	26	34	32	35	42	42	43	33	48	49	52
4				2,5	7,5	24	20	21	36	21	22	18	32	22	26	27	28	27	23	27	32	26
5	6	6	1	1	1	5,5	9	8,5	7	3,5	4	7	7	11	10	9,5	9,5	9	9	10	9	1
6				1	2,5	14	18	30	23	24	26	24	33	49	48	34	56	53	55	54	42	55
7	12	2	6	1,5	4	17	14	27	25	20	35	36	21	41	29	36	34	36	27	27	46	43
8				1	4	19	20	36	30	26	19	36	22	36	29	39	37	38	37	25	37	35
9	12	6	2	1	3	20	16	21	24	33	10	15	21	27	17	34	22	17	27	18	20	12
10				1	2	13	12	15	26	16	9	28	33	39	28	44	36	32	35	27	38	20
11	18	2	9	1	6	26	22	30	24	47	19	16	42	30	54	46	30	40	19	36	28	40
12				1	5	27	27	42	30	51	30	24	47	38	53	52	38	45	22	48	41	45

20% ≤ t.i.p. &lt; 30%

30% ≤ t.i.p. &lt; 40%

t.i.p. ≥ 40%

## 5.2 Corrosion rate evaluation models

### 5.2.1 Experimental corrosion rate (mass loss rate)

For a sake of clarity, we report once more the Table 4.2 (Chapter 4), which reports the experimental corrosion rate, by means of mass loss measurements, of the tested samples. The accuracy of the measurement is  $\pm 10 \mu\text{m}/\text{year}$ .

**Table 5.2 (as Table 4.2)** – Corrosion rate values obtained from mass loss measures

Specimens	on period (hours/cycle)	off period (hours/cycle)	On/off time ratio	CR <sub>exp</sub> ( $\mu\text{m}/\text{year}$ )
<b>1</b>	2	2	1	<b>12</b>
<b>2</b>				<b>43</b>
<b>3</b>	6	2	3	<b>6</b>
<b>4</b>				<b>15</b>
<b>5</b>	6	6	1	<b>64</b>
<b>6</b>				<b>116</b>
<b>7</b>	12	2	6	<b>20</b>
<b>8</b>				<b>18</b>
<b>9</b>	12	6	2	<b>143</b>
<b>10</b>				<b>137</b>
<b>11</b>	18	2	9	<b>16</b>
<b>12</b>				<b>21</b>
<b>13 (CP)</b>	24	0	--	--
<b>14 (free corr.)</b>	0	24	--	<b>150</b>

The corrosion rate calculated as mass loss rate has the following meaning: it is the mean corrosion rate (mass loss divided for unit time and surface) without considering any OFF or ON period. The considered time is the total test-time (147 days of test). Nevertheless, each sample does not corrode uniformly during this time, because when CP is applied corrosion is impossible ( $E < E_{\text{eq}}$ ) or negligible ( $E < -0.85 \text{ V CSE}$ ). It follows that corrosion can take place only during the OFF period, when the potential does not match the protection criteria defined by the  $-0.85 \text{ V CSE}$  limit. Three models of interpretation are discussed in the following:

- Base model of corrosion rate evaluation;
- Corrected model which takes into account the t.i.p. contribution;
- Theoretical model based on the Tafel's equation.

## 5.2.2 Base model for corrosion rate evaluation

This model of interpretation is based on a very simple assumption:

- Corrosion rate = 0  $\mu\text{m}/\text{year}$  during the ON period, when CP is applied (in all the cases, the measured potential during this period is lower than -0.92 V CSE, that is the equilibrium potential of iron considering a  $10^{-6}$  M concentration of iron ions, according to Pourbaix assumption);
- Corrosion rate = 150  $\mu\text{m}/\text{year}$  during the OFF period, that is the corrosion rate measured for the Sample 14 in free corrosion condition (Table 5.2).

In other words, the model does not consider any gradual depolarization of the metal during the OFF period. The metal is considered in a binary condition: completely protected (ON period) or in fully corrosion condition (OFF period). Figure 5.8 shows schematically the model.

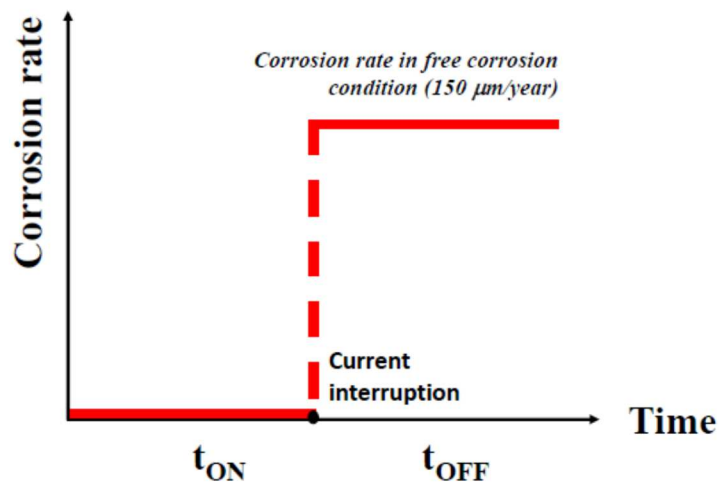


Fig 5.8 – Scheme of the base model for corrosion rate evaluation during intermittent cathodic protection

According to the proposed scheme, it is possible to calculate the corrosion rate provided by the model by this equation:

$$(5.3) \quad CR_{base} = \frac{t_{OFF}}{t_{ON} + t_{OFF}} \cdot CR_{FC}$$

Where  $CR_{FC}$  is the corrosion rate of the sample in free corrosion condition (150  $\mu\text{m}/\text{year}$ ) and the meaning of other symbols is known. Table 5.3 reports the comparison between experimental corrosion rate (mass loss rate) and the corrosion rate provided by the base model.

**Table 5.3** – Samples corrosion rate calculated with base model

<b>Samples</b>	<b>(t<sub>OFF</sub>/t<sub>ON</sub> + t<sub>OFF</sub>)</b>	<b>CR<sub>base</sub> (µm/year)</b>	<b>CR<sub>exp</sub> (µm/year)</b>
<b>14</b>	-	-	<b>150 (CR<sub>FC</sub>)</b>
<b>1</b>	0,5	<b>75</b>	<b>12</b>
<b>2</b>	0,5	<b>75</b>	<b>43</b>
<b>3</b>	0,25	<b>37</b>	<b>6</b>
<b>4</b>	0,25	<b>37</b>	<b>15</b>
<b>5</b>	0,5	<b>75</b>	<b>64</b>
<b>6</b>	0,5	<b>75</b>	<b>116</b>
<b>7</b>	0,14	<b>21</b>	<b>20</b>
<b>8</b>	0,14	<b>21</b>	<b>18</b>
<b>9</b>	0,33	<b>49</b>	<b>143</b>
<b>10</b>	0,33	<b>49</b>	<b>137</b>
<b>11</b>	0,1	<b>15</b>	<b>16</b>
<b>12</b>	0,1	<b>15</b>	<b>21</b>

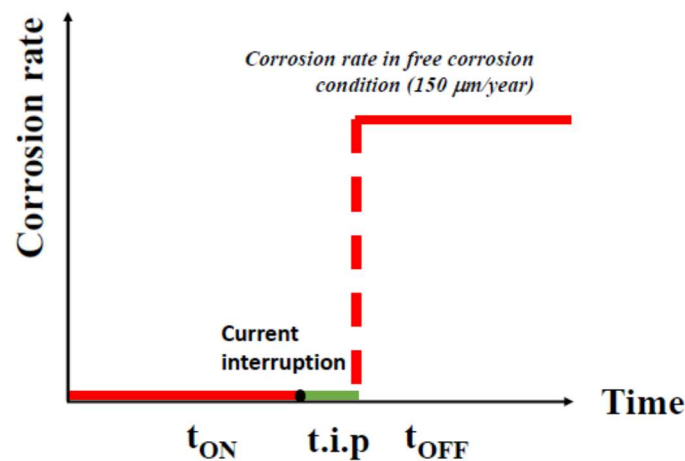
The corrosion rate defined by the base model is the maximum expected corrosion rate according to the theory. In three cases of 12, the experimental corrosion rate is higher than the theoretical one (highlighted in red in Table 5.3). These values have no meaning, especially for Samples 9 and 10. This is probably due to the mass loss of the metal that occurred on the back surface of the specimen due to a water leak in the sample holder. Due to the long-time of testing, about 4 months, this leak produced corrosion on the back surface that affected strongly the mass loss measurement. In the other cases, corrosion rate is lower or approximately equals to the corrosion rate of the base model. The lower corrosion rate with respect the theoretical model is due to a too conservative approach of this model: corrosion during the OFF period cannot be considered equals to the free corrosion rate because a depolarization of the metal occurs and the potential is not always equals to -0.68 V CSE (free corrosion potential of Sample 14). The corrected model described in the following is an effort to interpret corrosion rate data in this direction.

### 5.2.3 Corrected model which takes into account the t.i.p. contribution

This model is based on these assumptions:

- Corrosion rate = 0  $\mu\text{m}/\text{year}$  during the ON period, when CP is applied (in all the cases, the measured potential during this period is lower than -0.92 V CSE, that is the equilibrium potential of iron considering a  $10^{-6}$  M concentration of iron ions, according to Pourbaix assumption);
- Corrosion rate = 0  $\mu\text{m}/\text{year}$  during the OFF period if the potential, E, is lower (more negative) than -0.85 V CSE, namely during the *t.i.p.* period;
- Corrosion rate = 150  $\mu\text{m}/\text{year}$  during the OFF period if the potential, E, is higher (more positive) than -0.85 V CSE.

Figure 5.9 shows schematically the model.



**Fig 5.9** – Scheme of the corrected model for corrosion rate evaluation during intermittent cathodic protection

According to the proposed scheme, it is possible to calculate the corrosion rate provided by the corrected model by this equation:

$$(5.4) \quad CR_{corrected} = \frac{t_{OFF} - t.i.p.}{t_{ON} + t_{OFF}} \cdot CR_{FC}$$

Where the meaning of symbols is known. The considered t.i.p. is the mean value during all the test time. In other words, corrosion takes place only during the OFF period when the potential

is out of protection ( $E > -0.85$  V CSE). Table 5.4 reports the comparison between experimental corrosion rate (mass loss rate) and the corrosion rate provided by the corrected model.

**Table 5.4** – Samples corrosion rate calculated with the corrected model

<b>Samples</b>	<b>(<math>t_{OFF} - t.i.p.</math>) / (<math>t_{ON} + t_{OFF}</math>)</b>	<b>CR<sub>corrected</sub> (<math>\mu\text{m}/\text{year}</math>)</b>	<b>CR<sub>exp</sub> (<math>\mu\text{m}/\text{year}</math>)</b>
<b>14</b>	-	-	<b>150 (CR<sub>FC</sub>)</b>
<b>1</b>	0,4	<b>60</b>	<b>12</b>
<b>2</b>	0,46	<b>69</b>	<b>43</b>
<b>3</b>	0,17	<b>25</b>	<b>6</b>
<b>4</b>	0,19	<b>28</b>	<b>15</b>
<b>5</b>	0,46	<b>69</b>	<b>64</b>
<b>6</b>	0,33	<b>49</b>	---
<b>7</b>	0,1	<b>15</b>	<b>20</b>
<b>8</b>	0,1	<b>15</b>	<b>18</b>
<b>9</b>	0,27	<b>40</b>	---
<b>10</b>	0,27	<b>37</b>	---
<b>11</b>	0,07	<b>10</b>	<b>16</b>
<b>12</b>	0,07	<b>10</b>	<b>21</b>

As expected, the corrosion rate provide by the corrected model are lower than the corrosion rate of the base model, because the corrected one contains the t.i.p. effect.

For Samples 5-7-8-11-12, the corrosion rate calculated by the model is very close to the experimental corrosion rate. An important aspect must be point out: the accuracy of mass loss corrosion rate is in the order of 10  $\mu\text{m}/\text{year}$  so that, for example, corrosion rates of 15 and 20  $\mu\text{m}/\text{year}$  (Sample 7) can be considered comparable. This model seems to fit better in several conditions with respect to the previous one due to the consideration of the t.i.p. during which corrosion rate is very low.

## 5.2.4 Theoretical model based on Tafel's equation

The protection potential of -0.85 V CSE corresponds to a corrosion rate lower than 10  $\mu\text{m}/\text{y}$  (ISO 15589-1), which can be considered negligible from an engineering point of view in several applications. Considering the potential profile reported in Figure 5.1, it is possible to propose some further considerations related to the calculation of the instantaneous corrosion rate during the OFF period.

In particular, an instantaneous corrosion rate of 10  $\mu\text{m}/\text{y}$  or less can be considered for the entire ON period and for the OFF period segment in which the potential remains below -0.85 V CSE (t.i.p.). For potential more positive than -0.85 V CSE, corrosion rate increases accordingly to the potential, following the well-known Tafel's equation, which correlates the potential of the active metal (as carbon steel) to current density. In other words, the potential in the OFF period increase following Tafel's law up to the free corrosion potential (-0.68 V CSE), corresponding to which corrosion rate is equals to the oxygen limiting current density

It is therefore possible to propose a simple electrochemical model for calculating the corrosion rate based on the Tafel's law during the OFF period:

$$(5.5) \quad E = E_{eq} + b \log \frac{i}{i_0}$$

Where  $i_0$  is the exchanged current density of iron dissolution,  $E_{eq}$  is the equilibrium potential, and  $b$  is the Tafel's slope of the anodic process. At the protection potential ( $E_{prot}$ ), namely -0.85 V CSE, the following equation is valid:

$$(5.6) \quad E_{prot} = E_{eq} + b \log \frac{i_{prot}}{i_0}$$

Where  $i_{prot}$  is the residual anodic current density at the protection potential (10  $\mu\text{m}/\text{y}$ ). For convenience, it is possible to express the potential of the metal in terms of *overvoltage*, i.e. the difference between the potential of the metal,  $E$ , and the protection potential,  $E_{prot}$ :

$$(5.7) \quad \eta = E - E_{prot}$$

Combining Eq. 5.5, 5.6 and 5.7, the following equation can be obtained:



$$(5.8) \quad \eta = \left( E_{eq} + b \log \frac{i}{i_0} \right) - \left( E_{eq} + b \log \frac{i_{prot}}{i_0} \right) = +b \log \frac{i}{i_{prot}}$$

Corrosion rate, in  $\mu\text{m}/\text{year}$ , is proportional to the anodic current density,  $i$ , in  $\text{mA}/\text{m}^2$ :

$$(5.9) \quad CR_{Tafel} = 1.17 \cdot i = 1.17 \cdot i_{prot} \cdot 10^{\frac{\eta}{b}}$$

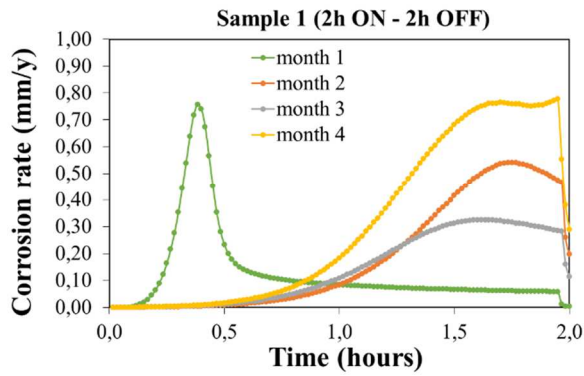
Tafel's slope,  $b$ , is a positive constant with the meaning of slope of the Tafel's line in a potential –  $\log i$  diagram. This constant assumes a value of 60 mV/decade for bivalent reactions as in the case of iron, and 120 mV/decade for monovalent reactions such as hydrogen evolution.

In the theoretical electrochemical model used, the parameter  $b$  is obtained from the experimental data of specimen N°14 in free corrosion conditions. For this test, the mean value of the free corrosion potential is -0.68 V CSE and the corrosion rate (mass loss rate) measured at the end of the test is 0.15 mm/y. Tafel's slope is so calculated:

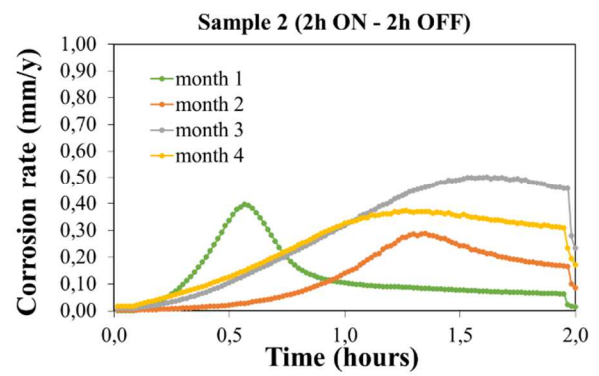
$$(5.10) \quad b = \frac{\eta}{\log\left(\frac{i}{i_{prot}}\right)} = \frac{-0.68 + 0.85}{\log\left(\frac{0.15}{0.01}\right)} = 0.144 \text{ V / decade}$$

This value is higher than the one predicted by the theory (Butler-Volmer equation), which hypothesizes a reaction exchange coefficient of 0.5 and does not take into account any overvoltage increase due to the formation of corrosion products and oxides.

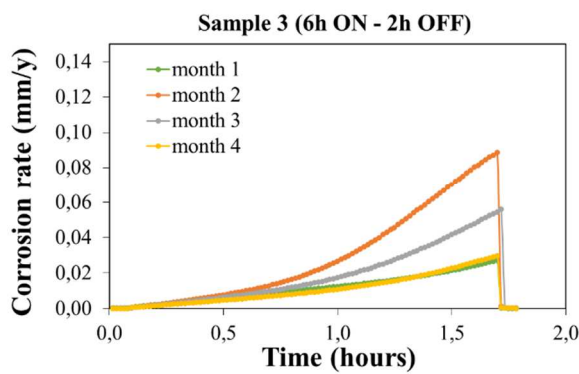
Tafel's equation (Eq. 5.9) was applied to the potential profiles measured during the OFF period for all the samples. Corrosion rate was calculated considering the measured potential (profiles reported in Chapter 4) and a constant Tafel's slope of 0.144 V/decade. Figures from 5.10 to 5.15 report the instantaneous corrosion rate for each sample (one profile for month is reported) during the OFF period. Each value represents the instantaneous corrosion rate of the metal.



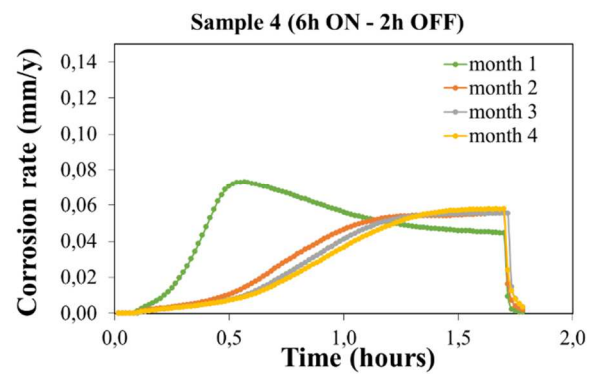
**Fig 5.10a** – Instant corrosion rate during the OFF period for Sample 1



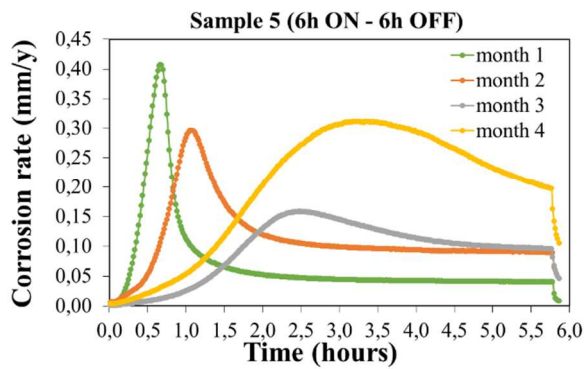
**Fig 5.10b** – Instant corrosion rate during the OFF period for Sample 2



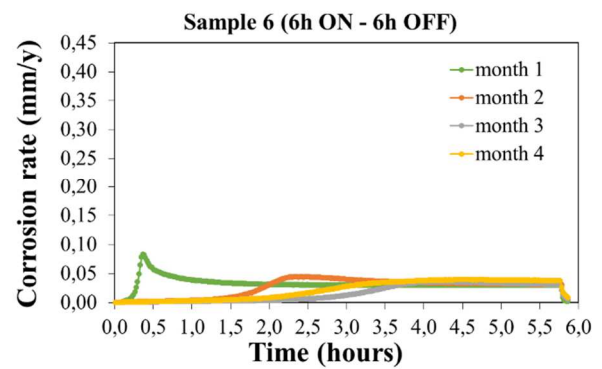
**Fig 5.11a** – Instant corrosion rate during the OFF period for Sample 3



**Fig 5.11b** – Instant corrosion rate during the OFF period for Sample 4



**Fig 5.12a** – Instant corrosion rate during the OFF period for Sample 5



**Fig 5.12b** – Instant corrosion rate during the OFF period for Sample 6

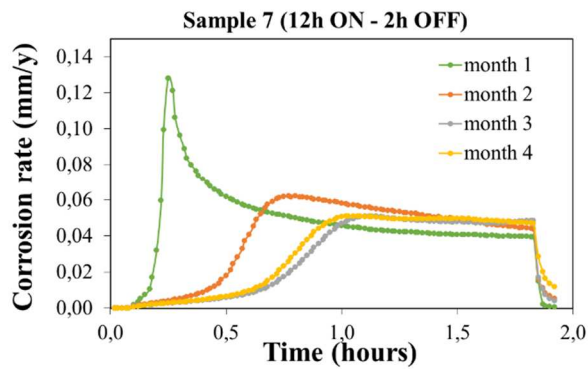


Fig 5.13a – Instant corrosion rate during the OFF period for Sample 7

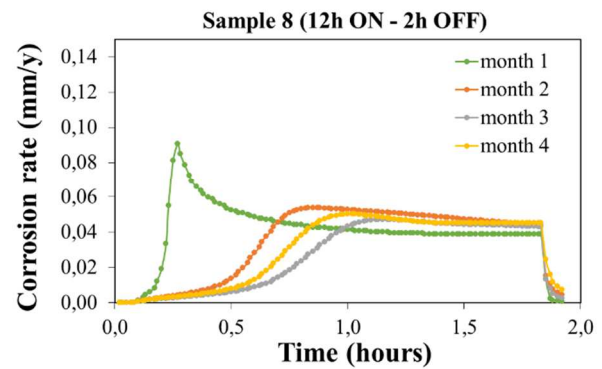


Fig 5.13b – Instant corrosion rate during the OFF period for Sample 8

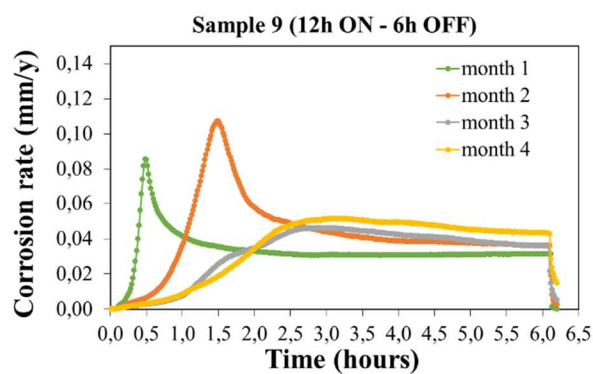


Fig 5.14a – Instant corrosion rate during the OFF period for Sample 9

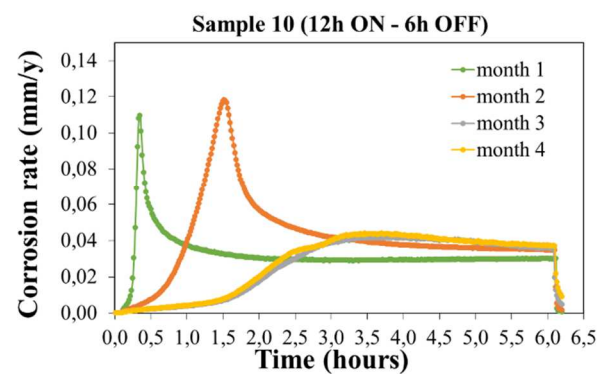


Fig 5.14b – Instant corrosion rate during the OFF period for Sample 10

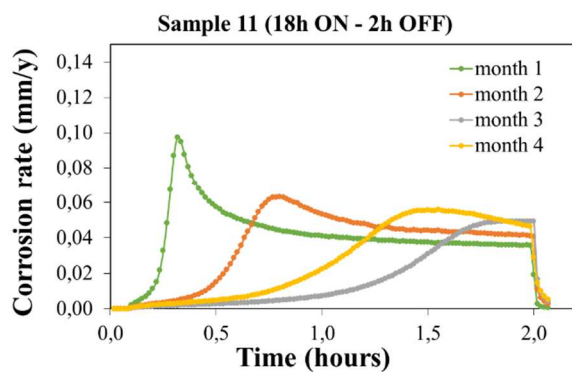


Fig 5.15a – Instant corrosion rate during the OFF period for Sample 11

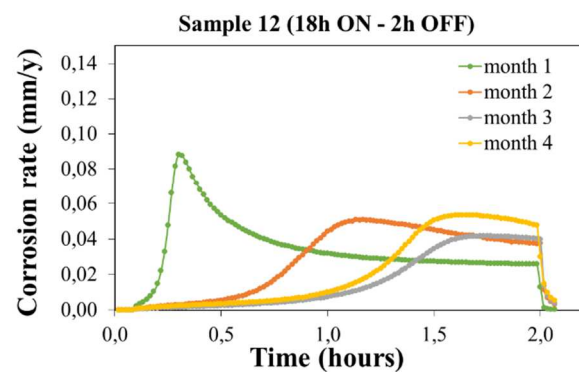


Fig 5.15b – Instant corrosion rate during the OFF period for Sample 12

As anticipated, for the specimen 14 in free corrosion condition, the free corrosion potential is -0.680 V CSE and the corrosion rate is equal to 0.150 mm/year. With the exception of Samples 1 and 2, in all the other conditions (Figures from 5.11 to 5.15), the instantaneous corrosion rate at the end of the OFF period never reaches this value. Moreover, a gradual increase of corrosion

rate is measured, differently from the first two interpretation models. The corrosion rate at the end of the period is generally in the range from 0.030 to 0.100 mm/year. In most of the cases, namely for Samples 3-4-6-7-8-9-10-11-12, the corrosion rate is about 0.050 mm/year and no great differences were shown considering the profiles during the test time (from month 1 to month 4). In other words, the potential seems to tend to an asymptotic value, lower than the free corrosion rate of Sample 14.

Nevertheless, it is also interesting to observe and comment the corrosion rate profile during the OFF period, not only the final value calculated. For most of the specimens, during the first month of testing, the corrosion sharply increases after the interruption of the cathodic current and then it stabilized to a constant value of about 0.050 mm/year. In the other cases, in particular from the third month, the corrosion rate increases very slowly (due to the slow potential increase already commented in Chapter 4) at it remains very low (namely lower than 10  $\mu\text{m}/\text{year}$ ) after 30 minutes – 1 hour from the interruption of CP. This can be interpreted considering oxygen diffusion in the solution in contact with the metal. During the ON period, oxygen is consumed ( $\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^-$ ) by the cathodic current, being the prevalent cathodic reaction at potential of about -1.0 V CSE. When the cathodic current is interrupted, oxygen is slowly replaced by diffusion from the bulk of the solution to the metal interface. This process takes time so that the potential (and consequently the corrosion rate) increases very slowly.

A second behavior observed is the corrosion rate decrease after reaching a peak. In other words, it seems that corrosion rate firstly increases and then decreases. In truth, this behavior is not simple, at least at a first view, to understand because oxygen gradually populated the metal-to-electrolyte interface so that corrosion rate is expected only to increase.

Nevertheless, it is important to remind that corrosion rate is calculated considering Eq. 5.9 with a constant Tafel slope experimentally evaluated (0.144 V/decade). This preliminary model does not take into account any modification of the electrochemical behavior of the metal due to the presence of a previous ON period of cathodic protection. Nevertheless, as already commented, CP creates alkalinity on the metal surface and the pH can increase up to 10 or higher. Alkalinity can promote the formation of a passive condition on the metal surface, in agreement with the passive region stability at high pH in the Pourbaix diagram of the system iron-water at 25°C. It follows that the assumption of a constant Tafel slope during the off period can be too restrictive, because the electrochemical condition of the metal is evolving during the OFF period.

In particular, and thanks to the scheme reported in Figure 5.16, three conditions can be distinguished:

- Free corrosion condition (Figure 5.16a): the metal in free corrosion condition (without intermittent CP) has the typical electrochemical behavior of an active metal with constant Tafel's slope;
- Immediately after the interruption of CP current (Figure 5.16b): during the previous ON period, the metal formed a passive film due to the local alkalinity promoted by the cathodic reactions occurring on the metal surface. The Tafel's slope of the anodic curve increases;
- During OFF period (Figure 5.16c): as soon as the current is interrupted, the passive condition gradually tends to dissolve because the source of alkalinity is interrupted. The diffusion mechanisms tends to neutralize the pH so that the metal comes back to the pristine active behavior.

This interpretation can explain the presence of potential (and corrosion rate) peaks during the OFF period. Initially the potential increases sharply because the metal is following the Tafel's curve with higher slope (blue curve in Figure 5.16b). The higher slope is due to the formation of a passive layer in the previous ON condition. Then, the potential (and corrosion rate) gradually decreases because the anodic curve change from passive to active, coming back to the previous electrochemical condition.

In conclusion, the effect of alkalinity is not considered in this simplified calculation even though potential measurements show that the metal tends to passivate thanks to the alkalinity produced in CP condition. It is reasonable to think that alkalinity promotes an increase in anodic overvoltage with two consequences: on the one hand, the value of Tafel's slope should be revised ( $b$  in Equation 5.9); on the other hand, the potential measurement would assume a new and different interpretation. For instance, at the free corrosion potential, the depolarization  $\eta$  is 0.17 V and the corrosion rate results:

- 150  $\mu\text{m}/\text{year}$ , considering a Tafel's slope of 0.144 V/decade;
- 70  $\mu\text{m}/\text{year}$ , considering a Tafel's slope of 0.200 V/decade;
- 20  $\mu\text{m}/\text{year}$ , considering a Tafel's slope of 0.500 V/decade;
- 1  $\mu\text{m}/\text{year}$ , considering a Tafel's slope of 1 V/decade (or higher, as in case of passive metal as stainless steel).

It follows that the corrosion rate calculated by a constant Tafel's slope can be misleading; the higher potential recorded does not correspond to high corrosion rate but, conversely, to a low corrosion rate because the metal has a different electrochemical behavior. In other words, a higher potential does not always corresponds to a high corrosion rate.

Figure 5.17 shows corrosion rate for different value of potential (i.e. overvoltage  $\eta$ ) with respect to Tafel's slope ( $b$ ), calculated by Equation 5.9. According to the described mechanism, the increasing of Tafel's slope of carbon steel promotes a decrease of corrosion rate, even if the overvoltage is higher. In conclusion, the potential measurement can be misleading if it not related to the proper electrochemical behavior of the metal.

It is important to precise that the passivity promoted by alkalinity does not seem strong as the passivity promoted by chemical alloying for example of a stainless steel. In this last case, the anodic slope is in the order of a few volts per decade.

A more detailed and sophisticated model could consider the Tafel slope variation during the OFF period: higher at the beginning and lower after the dissolution of the passive film. This model asks more detailed investigations and detailed tests are needed.

A strange behavior is observed for Sample 1 and Sample 2. Corrosion rate during the OFF period is very high, up to 0.7 mm/year. This corrosion rate is of course impossible because corrosion rate is limited to the maximum oxygen limiting current density (0.15 mm/year). A possible explanation is the "alkalization effect" described previously so that the calculated corrosion rate is misleading because it considers a constant and low Tafel's slope. Actually, it is not easy to interpret why the behavior is so prominent for these two Samples (2 hours ON – 2 hours OFF). Indeed, this effect can be expected in particular for specimens which have high ON period and low OFF period, as Samples 7-8-11-12, because of the higher alkalinity produced during the longer ON period. This aspect needs more investigations.

The electrochemical model discussed has allowed calculating the instant corrosion rate during the OFF period, starting from the experimental potential profiles.

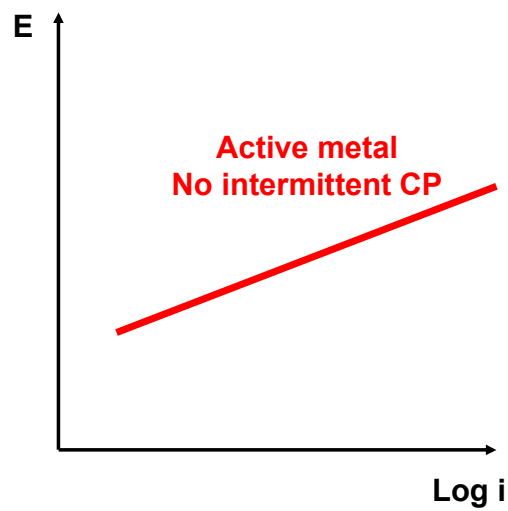


Fig 5.16a – Schematic representation of the anodic electrochemical curve of an active metal

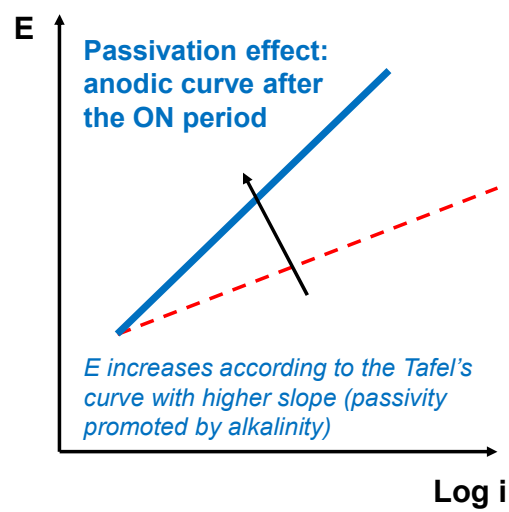


Fig 5.16b – Schematic representation of the anodic electrochemical curve immediately after the CP interruption of an intermittent CP system.

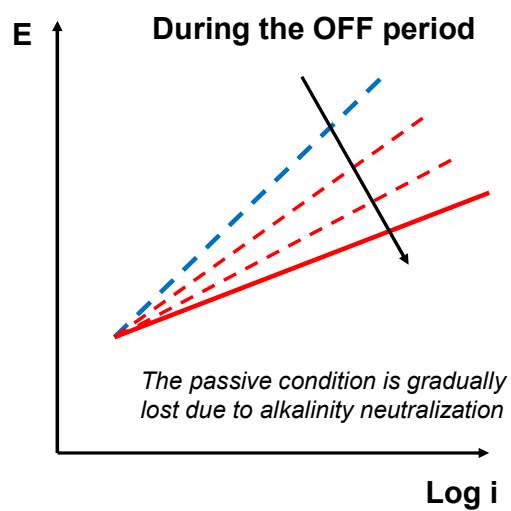


Fig 5.16c – Schematic representation of the anodic electrochemical curve during the OFF period of intermittent CP.

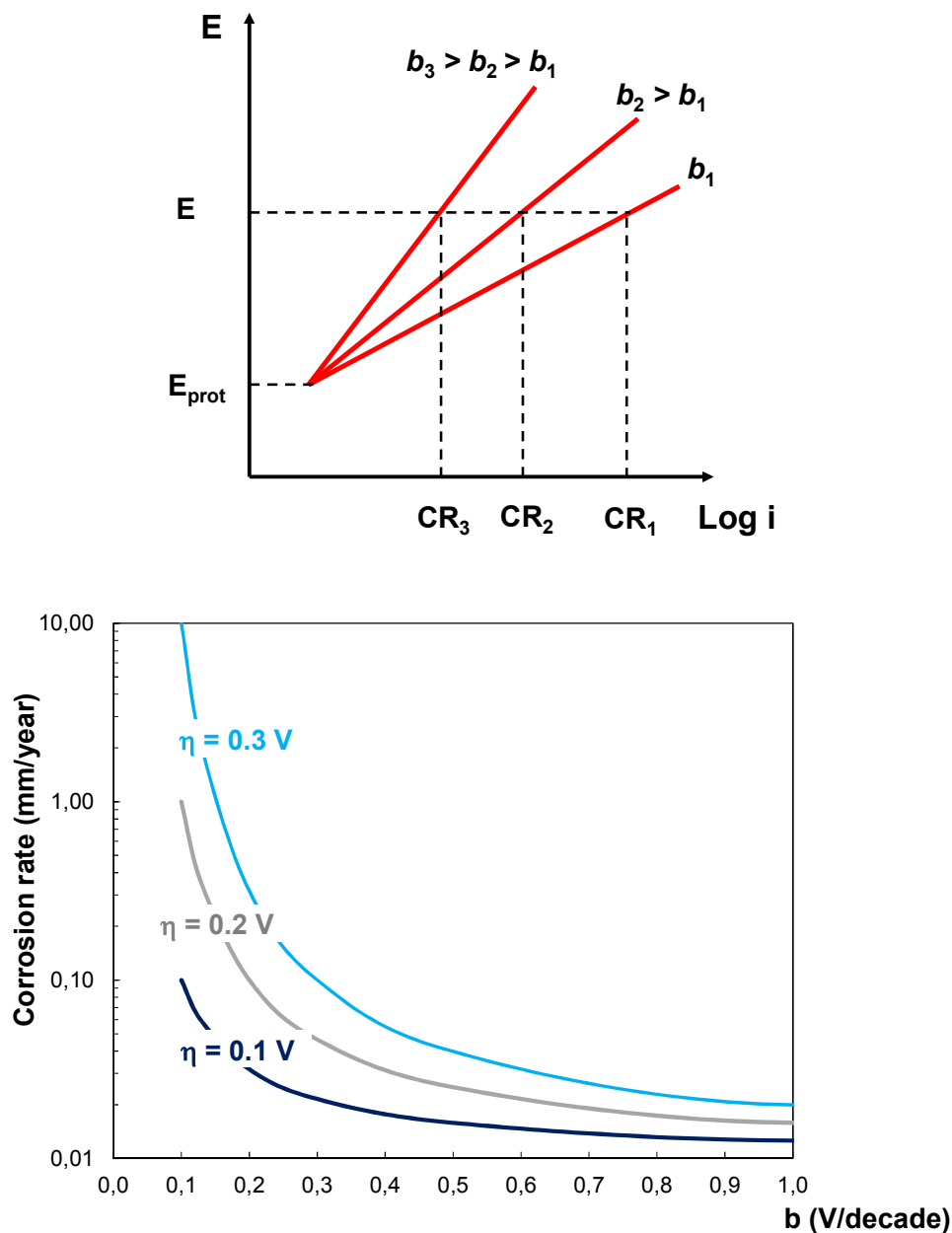


Fig 5.17 – Corrosion rate calculation (Eq. 5.9) by varying Tafel's slope and anodic overvoltage ( $\eta = E - E_{prot}$ ).

Obviously, the mean corrosion rate in the presence of intermittent CP (considering both the ON and the OFF period) depends on the ratio between the OFF and ON time. Mean corrosion rate during the OFF period (given by the mean integral theorem) is “spread” on all the exposition time. Effective corrosion rate,  $C_{rate}$ , can be written as:

$$(5.11) \quad C_{rate} = \frac{t_{OFF}}{t_{OFF} + t_{ON}} \cdot \bar{i}_{corr} = \frac{1}{t_{OFF} + t_{ON}} \cdot \int_{t=0}^{t=t_{OFF}} i_{E=E_{prot}} \cdot 10^{\frac{E(t)-E_{prot}}{b}} dt$$



where the meaning of the symbols is known. With a simplified approach, the effective corrosion rate can be estimated by calculating the mean corrosion rate during the OFF period, considering four potential profiles for each specimens (one profile per month, Table 5.5). The reported corrosion rate is then the average between the four mean values (one per month) corrected by the time factor taking into account that corrosion is not taking place during the ON period.

For instance, considering Sample 5, the mean value of corrosion rate during the OFF period in the four months testing are:

- *Month 1*: 71  $\mu\text{m}/\text{year}$ ;
- *Month 2*: 113  $\mu\text{m}/\text{year}$ ;
- *Month 3*: 95  $\mu\text{m}/\text{year}$ ;
- *Month 4*: 200  $\mu\text{m}/\text{year}$ .

The average corrosion rate is:

$$(5.12) \quad C_{rate,avr} = \frac{71+113+95+200}{4} = 120 \frac{\mu\text{m}}{\text{year}}$$

This value is finally multiplied by the time ratio. For Sample 5, OFF and ON periods are 6 hours, so that the time ratio is 0.5. The final corrosion rate provided by the third interpretation model is:

$$(5.13) \quad C_{th} = C_{rate,avr} \cdot \frac{t_{OFF}}{t_{OFF} + t_{ON}} = 60 \frac{\mu\text{m}}{\text{year}}$$

From Table 5.5, it emerges that, with the exception of the first two samples, the other values of corrosion rate calculated by Tafel's law can be compared with the experimental corrosion rates. In particular, Samples 3, 4 and 5 show corrosion rates very similar to the mass loss rate; good agreement is observed also for Sample 7, 8, 11, 12 (in both cases – theoretical and experimental – corrosion rate can be considered very low, namely below 20  $\mu\text{m}/\text{y}$ ). From this preliminary analysis, it seems that the study of the potential profiles during the OFF period with the Tafel's equation, even if with a constant  $b$  slope, can be an adequate method to predict the corrosion rate of the carbon steel in soil.

**Table 5.5** – Samples corrosion rate calculated with the model based on Tafel's law.

Samples	( $t_{OFF}/t_{ON} + t_{OFF}$ )	$CR_{th}$ ( $\mu\text{m}/\text{year}$ )	$CR_{exp}$ ( $\mu\text{m}/\text{year}$ )
14	-	150	150 ( $CR_{FC}$ )
1	0,5	99	12
2	0,5	101	43
3	0,25	5	6
4	0,25	9	15
5	0,5	60	64
6	0,5	13	---
7	0,14	5	20
8	0,14	5	18
9	0,33	12	---
10	0,33	11	---
11	0,1	3	16
12	0,1	3	21

### 5.3 FINAL CONSIDERATIONS

In order to compare the mass loss rate measurements with the corrosion rate provided by the three interpretation models considered, the following Table 5.6 is proposed. In this table, the average corrosion rate for each condition is reported (average between the two samples in the same condition). In case of only one value available (as for the mass loss rate of Sample 5 and 6 where corrosion rate of Sample 6 is meaningless), only one value is reported.

Corrosion rate values are divided in three groups:

- **Green:**  $CR < 20 \mu\text{m}/\text{y}$ , the corrosion rate is considered acceptable from an engineering point of view, so the mass loss is negligible for the safety of the metal;
- **Yellow:**  $20 \mu\text{m}/\text{y} < CR < 50 \mu\text{m}/\text{y}$ , the corrosion rate is not negligible but corrosion is not particularly severe;
- **Red:**  $CR > 50 \mu\text{m}/\text{y}$ , very high corrosion rate.

Table 5.6 reports the comparison of mass loss rate ( $CR_{exp}$ ) with the corrosion rate provided by the three models:

- Base model of corrosion rate evaluation ( $CR_{base}$ );
- Corrected model which takes into account the t.i.p. contribution ( $CR_{corrected}$ );

- Theoretical model based on the Tafel's equation ( $CR_{th}$ ).

It is important to highlight that the mass loss rate accuracy is in the order of  $10 \mu\text{m}/\text{year}$  so that this kind of comparison is considered more significant than the comparison of single values.

**Table 5.6** – Comparison between the experimental results and the theoretical models corrosion rates.

Sample	ON period (hours/cycle)	OFF period (hours/cycle)	$t_{OFF}/$ ( $t_{ON} + t_{OFF}$ )	Corrosion rate ( $\mu\text{m}/\text{year}$ )			
				$CR_{base}$	$CR_{corrected}$	$CR_{th}$	$CR_{exp}$
1-2	2	2	0,5	> 50	> 50	> 50	20 <> 50
3-4	6	2	0,25	20 <> 50	20 <> 50	< 20	< 20
5-6	6	6	0,5	> 50	> 50	20 <> 50	> 50
7-8	12	2	0,14	< 20	< 20	< 20	< 20
9-10	12	6	0,33	20 <> 50	20 <> 50	< 20	---
11-12	18	2	0,1	< 20	< 20	< 20	< 20

It is possible to observe that the model based on Tafel's law ( $CR_{th}$ ) better fits with the experimental data of corrosion rate ( $CR_{exp}$ ). For instance, for Samples 3-4 and 5-6 the base and corrected models seem too restrictive and provide a corrosion rate that is higher than the corrosion rate provided by testing. Indeed, these two models do not consider the depolarization during the OFF period, so that the calculated corrosion rate is too high.

The best operating intermittent CP conditions are characterized by a low *time ratio*, namely the ratio between the OFF period and the duration of the intermittent CP cycle (ON + OFF). This is an expected effect, because longer ON period favours the alkalisation and the oxygen consumption that are maintained during the following OFF period, according to the mechanism previously described. In particular, the lowest corrosion rates were measured for specimens that show a longer period than the OFF period:

- Samples 3-4: 6 hours ON; 2 hours OFF;
- Samples 7-8: 12 hours ON; 2 hours OFF;
- Samples 9-10: 12 hours ON; 6 hours OFF;
- Samples 11-12: 18 hours ON; 2 hours OFF.

Samples 7-8 and 11-12 always show acceptable values, both theoretical and experimental. It follows that the time ratio seems to have a very important effect: corrosion can be considered negligible below a critical time ratio. Figure 5.18 reports the corrosion rate provided by the Tafel-based model ( $CR_{th}$ ) as a function of the time ratio.

The dotted black lines refer to a corrosion rate of  $10 \mu\text{m}/\text{y}$  (negligible corrosion rate according to the  $-0.85 \text{ V CSE}$  criterion reported on ISO 15589-1 standard) and to  $20 \mu\text{m}/\text{y}$ , which is the

threshold value considered in this analysis (it is remembered that the accuracy of corrosion rate measurement is in the order of  $10 \mu\text{m}/\text{y}$ ).

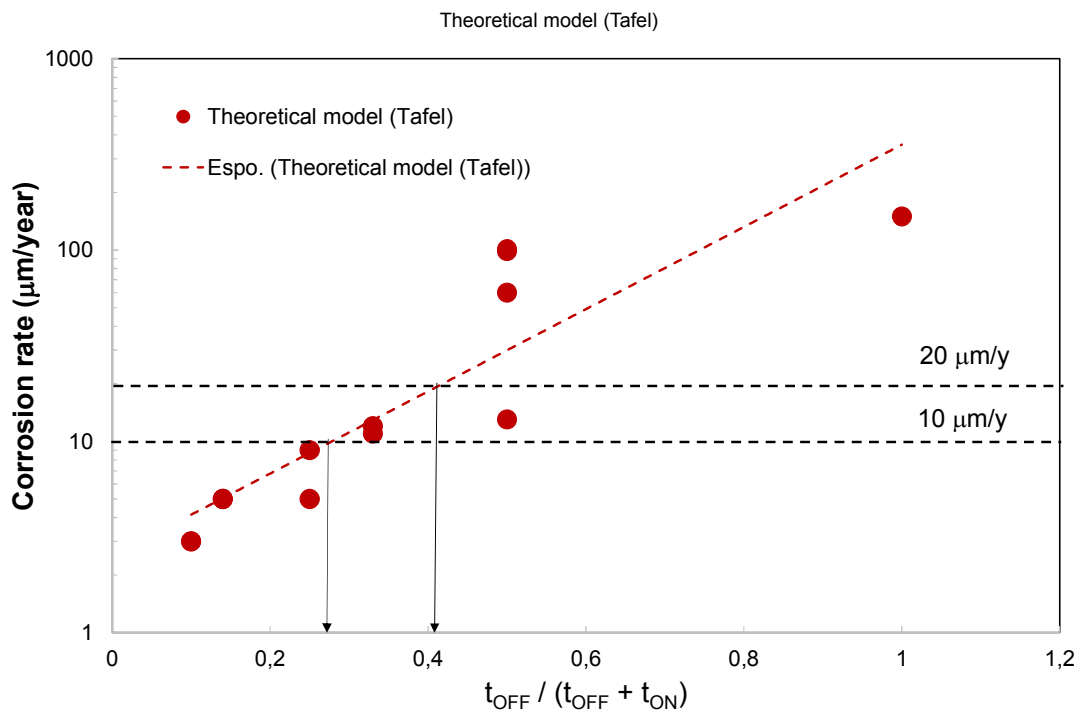


Fig 5.18 – Samples corrosion rate in function of the  $\frac{t_{OFF}}{t_{OFF} + t_{ON}}$  ratio.

The red line is the exponential trend line of the theoretical values obtained by the Tafel's equation. It intersects the  $10 \mu\text{m}/\text{y}$  value at about a time ratio of 0.3, while the  $20 \mu\text{m}/\text{y}$  intersects at about 0.4. It follows that, according to the corrosion rate provided by the model, a maximum time ratio between 0.3 and 0.4 is accepted, in order to guarantee negligible corrosion rate in intermittent CP condition:

$$(5.14) \quad \frac{t_{OFF}}{t_{OFF} + t_{ON}} < 0.3$$

Nevertheless, even if the time ratio is an important and useful parameter to consider, this condition is NECESSARY but not SUFFICIENT to have a negligible corrosion rate in intermittent condition. Indeed, considering for instance a time ratio of 0.3, this ratio can be obtained in different conditions, for examples:

- 2 hours OFF, 5 hours ON,
- 5 hours OFF, 12 hours ON,

- 12 hours OFF, 28 hours ON.

All these conditions respect the criterion of Eq. 5.14. Nevertheless, it is easy to understand that corrosion severity can be different even if the time ratio is the same. For example, the first and the last conditions cannot be considered similar, because the corrosion rate during an OFF period of 28 hours cannot be considered negligible at all.

In order to understand this behaviour, Figures from 5.2 to 5.7 are referred. These figures report the immunity time during the OFF period (*t.i.p.*) for all the tested conditions. This time varies according to the OFF and ON time but it is never higher than about 2 hours. It follows that, while an OFF period of 2 hours can be considered acceptable, an OFF period of 28 hours is too high, although the time ratio is the same. In other words, the OFF period should be limited even if the time ratio respect the criterion proposed in Eq. 5.14.

Table 5.7 reports the average *time-in-protection* (values reported in Figures from 5.2 to 5.7) for all the tested conditions. This value is the mean of two samples. In yellow, the conditions that respect the time ratio criterion (Eq. 5.14) are highlighted.

**Table 5.7** – Average time-in-protection (t.i.p.) value for every sample pair.

Sample	ON period (hours/cycle)	OFF period (hours/cycle)	t.i.p. (minutes)
1-2	2	2	17
3-4	6	2	33
5-6	6	6	71
7-8	12	2	33
9-10	12	6	77
11-12	18	2	39

The contribution is between 20 minutes and about 80 minutes. It follows that the maximum OFF period in an intermittent CP condition should be in the same order of magnitude (from 1 to 2 hours/cycle) and extended OFF period are not acceptable.

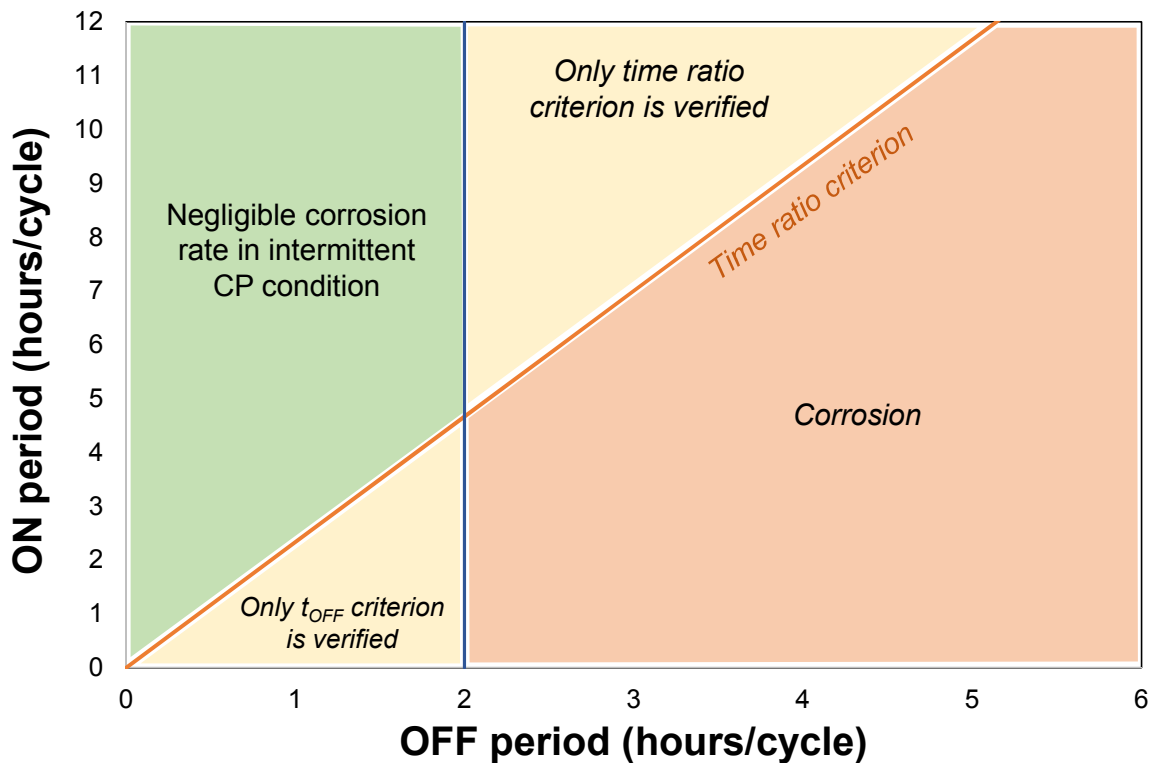
Three conditions can be distinguished (the condition based on the time ratio is considered respected):

1.  $t_{OFF} < t.i.p.$ : no corrosion is expected during intermittent CP. The potential of the metal is always below -0.85V CSE, so that corrosion is negligible;
2.  $t_{OFF} \approx t.i.p.$ : corrosion rate can be higher than 10 mm/year but only for very short periods, namely when  $t_{off}$  is higher than  $t.i.p.$ ;
3.  $t_{OFF} > t.i.p.$ : corrosion is not negligible, because the OFF period is too long and the beneficial effects of the ON period are lost during the  $t.i.p.$  period.

Thus, in addition to the time ratio criterion (Eq. 5.14), a further criterion is needed, based on the maximum length of the OFF period:

$$(5.15) \quad \frac{t_{OFF}}{t_{OFF} + t_{ON}} < 0.3 \quad \text{and} \quad t_{OFF} \leq t.i.p. \cong 2 \text{ hours / cycle}$$

The Figure 5.19 reports a corrosion intermittent CP map based on the results obtained in this thesis work. The orange line refers to the time ratio criterion (Eq. 5.14); the blue line refers to the maximum acceptable OFF period, based on *t.i.p.* measurements. The green zone is the domain where both criteria are verified: high ON period and a maximum OFF period of 2 hours/cycle are acceptable. Red zone corresponds to severe corrosion; yellow domains correspond to the conditions where only one criterion is respected.



**Fig 5.19** – Corrosion rate map in intermittent CP conditions.

## Conclusions

In this work, the effects of the interruption of cathodic protection (CP) on potential monitoring and corrosion rate of carbon steel were evaluated. Long-term tests (about four months) on carbon steel specimens in soil simulating condition under intermittent CP condition were carried out, varying the ON period (i.e. when the CP current is applied) and the OFF period (without cathodic protection). Main conclusions are:

- During the OFF period of the intermittent CP cycle, the potential gradually increases up to the free corrosion potential. During the first month, this time is in the order of a few minutes, while after four months testing, a few hours are needed to come back to the free corrosion condition;
- During the OFF period, the potential remains lower than -0.85 V CSE (protection potential according to ISO 15589-1 standard) for a time that varies from 30 to 120 minutes. The length of this time depends on the duration of the ON and OFF periods (generally it increases as the ON period increases); it follows that CP condition (negligible corrosion rate) is extended also during the OFF period for a time which depends on the intermittent CP condition;
- During the ON period, CP is beneficial because of the alkalization at the cathode and the oxygen consumption. These effects are not immediately lost during the OFF period but are maintained for a short period during which protection is guaranteed;
- Three interpretation models of corrosion rate data were proposed. The model based on Tafel's law, which takes into account the slow depolarization during the OFF period is the most appropriate and it provides values comparable to the mass loss rate results experimentally obtained;
- Based on this experimental work, the safe intermittent CP condition can be summarized as follows:

$$\frac{t_{OFF}}{t_{OFF} + t_{ON}} < 0.3 \quad \text{And} \quad t_{OFF} \leq t.i.p \cong 2 \text{hours} / \text{cycle}$$

- Further investigations and testing are needed to confirm the proposed intermittent CP criterion.





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