Corrosion inhibition of copper, zinc and copper-zinc alloys using azole-based organic compounds

Supervisors:
Prof. Marco Ormellese
Prof. Arjan Mol

Author:
Olmo Bottazzi – 853391
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English Abstract

Copper and its alloys are widely employed in the most different fields of applications, e.g. electronics, architecture and industries like marine and Oil&Gas. This is possible thanks to their mechanical, electrical and corrosion-resistance properties. However, they are susceptible to particular selective corrosion attacks such as Stress Corrosion Cracking, pitting, erosion-corrosion or de-alloying phenomena. In this regard, corrosion inhibitors are generally used to protect copper and its alloys from corrosion.

This thesis project aims to investigate how corrosion inhibitors belonging to theazole family and metal surfaces interact and so enlarge the, still very limited, knowledge about their interaction mechanisms.

To do so, various experimental techniques were used. Initially the best corrosion inhibitors among those ones proposed were selected using Linear Polarization Resistance (LPR) and Electrochemical Impedance Spectroscopy (EIS) techniques. The chosen inhibitors are: Benzimidazole, Benzotriazole, 1-methylbenzimidazole, 1-methylbenzotriazole and Indazole.

Subsequently the interactions between inhibitors and copper surface were investigated performing Fourier Transform InfraRed (FTIR) tests and correlating the results to Density Functional Theory (DFT) simulation performed by the team partner (Jožef Stefan Institute, Department of Physical and Organic Chemistry, Ljubljana, Slovenia).

It was found that molecular structure and in particular the substituents, not only modify the way the inhibitors interact with the surface, but also influence the corrosion protection effectiveness. Furthermore these compounds interact better with copper than with zinc as demonstrated by LPR measurements.
Italian Abstract

Il rame e le sue leghe sono largamente impiegate nei più disparati campi, come per esempio: elettronica, architettura, industria marina e quella Oil&Gas. Questo è possibile grazie alle loro ottimi proprietà meccaniche, elettriche e di resistenza a corrosione. Comunque, queste leghe sono suscettibili a particolari attacchi di corrosione come Stress Corrosion Cracking, pitting, erosione-corrosione e fenomeni di de-alloying. A questo scopo gli inibitori di corrosione sono comunemente usati per proteggere il rame e le sue leghe dalla corrosione.

Questo progetto di tesi ha come obiettivo quello di indagare come gli inibitori di corrosione appartenenti alla famiglia degli azoli e la superficie metallica interagiscono e incrementare in questo modo la, ancora piuttosto limitata, conoscenza dei loro meccanismi di interazione. Per ottenere questo, diversi tecniche sperimentali sono state impiegate. Inizialmente sono stati selezionati i migliori inibitori di corrosione in termini di protezione dalla corrosione utilizzando tecniche di polarizzazione lineare e spettroscopia a impedenza elettrochimica. Gli inibitori selezionati sono: Benzimidazolo, Benzotriazolo, 1-metilbenzimidazolo, 1-metilbenzotriazolo, Indazolo. Successivamente sono state studiate le interazioni tra gli inibitori e la superficie del campione di rame, eseguendo FTIR test e correlando poi i risultati con le simulazioni DFT (Density Functional Theory) effettuate dal team partner (Jožef Stefan Institute, Department of Physical and Organic Chemistry, Ljubljana, Slovenia).

E’ stato riscontrato che la struttura molecolare delle molecole e in particolare i suoi sostituenti, non solo modificano il modo in cui avviene l’interazione con la superficie metallica, ma influenzano anche l’efficacia del meccanismo di protezione dalla corrosione. Inoltre questi composti interagiscono meglio col rame che con lo zinco, come dimostrato dalla più elevata velocità di corrosione osservate nei campioni di zinco, registrata con la tecnica di polarizzazione lineare.
Introduction

Corrosion plays a very important role in several industrial fields and has a non-negligible impact on countries’ economies. The global costs of corrosion are estimated at 2.5 trillion US dollars, the equivalent of 3.4% of the global GDP (2013). Using modern corrosion control methods, it is estimated that is possible to reduce the costs of corrosion by 15% to 35%. Furthermore, these costs usually do not consider individual safety, environmental consequences, missed incidents or forced shutdowns. Therefore, a proper corrosion management is of paramount importance in all the industrial aspects. [1][2]

Corrosion can be defined as the deterioration of a material’s properties due to its physical-chemical interaction with the environment. [3]

The goal of studying its processes is to find ways of minimizing corrosion or preventing it from occurring. [1]

Since the corrosion phenomena is almost always a thermodynamically favoured process it never stops, but its extent and severity can be lessened. For this purpose several methods of corrosion control were developed. These methods mainly consists in technological approaches with the purpose of fight corrosion. Some of the most known methods of corrosion control are:

- Cathodic and anodic protection
- Inhibitors
- Coatings
- Material selection
- Appropriate design

All these methods applied alone or together allow to reduce the corrosion rate to negligible value from the engineering point of view.

All the corrosion protection methods based on corrosion engineering are then applied in accordance with the basis of corrosion management which is concerned with the development, implementation, review and maintenance of the corrosion policy. [4][5]
Chapter 1 – Wet corrosion

1.1 Corrosion of metals

Corrosion is a chemical-physical interaction between a metal or a metal alloy and its environment, resulting in a change of material’s properties.

Corrosion is a natural phenomenon due to the tendency of metallic material to return to its original oxidized state. For this reason, corrosion is also called extractive metallurgy in reverse. Corrosion can be distinguished into two categories:

- Wet corrosion that occurs when the material is exposed to an electrolytic solution and an oxidant;
- Dry corrosion occurring at high temperatures (T > 400°C) usually when the material is exposed to hot gasses.

Wet corrosion is an electrochemical process in which the metal, water and an oxidant react forming corrosion products. Thus, this system, is represented as an electrochemical cell that can, in turn, be divided into two half-cell reactions: the anodic reaction and the cathodic reaction. [6][7]

The anodic reaction corresponds to an oxidation process in which the metal valence increases, liberating electrons. For example, considering iron corrosion in water, the corresponding anodic reaction is given by:

\[ \text{Fe} \rightarrow \text{Fe}^{2+} + 2\text{e}^- \]

![Fig. 1.1 - Anodic reaction for iron corrosion in water [7]](image-url)
Or more in general:

\[ M \rightarrow M^{n+} + ne^- \]

By contrast, the cathodic reaction is a reduction in which the oxidation state of the reductive species decreases, consuming the electrons produced by the anodic process. Two are the main cathodic reactions:

- Oxygen reduction
  \[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]
- Hydrogen evolution
  \[ 2H^+ + 2e^- \rightarrow H_2 \]

In the end, in order to complete the circuit, two other processes should be taken in account. The first consists in electrons transport within the bulk metal, moving from the anodic site, where they are produced, to the cathodic site, where they are consumed. The second is the current flow through the electrolyte by means of ions transfer. [7][8]

Although the two half-cell reactions, both anodic and cathodic reactions, occur at different sites, they can take place on the same surface. This is possible because the surface of a metal is never completely homogeneous and is full of lattice defects (dislocations, vacancies, etc...) and flaws in chemical composition. Due to this lack of homogeneity it is possible that sites with different potentials emerge,
thus forming the anode and the cathode. This difference in potential represents the driving force for the corrosion process. [9]

1.2 Thermodynamic of corrosion

In order to achieve a complete understanding of the energy changes involved in the electrochemical reactions occurring during corrosion, thermodynamic has to be considered. [6]

The change of system energy can be described using the free Enthalpy or Gibbs energy (G) which is dependent on pressure (P) and temperature (T). Consequently it is possible to associate the electrochemical process with the Gibbs energy and understand when the process is spontaneous (ΔG < 0) or not (ΔG > 0). Coupling the two half-cells and the respective potential, e_A for the anode and e_C for the cathode, the overall potential of the electrochemical cell can be determined.

\[ E = e_A + e_C \]

The free energy change (ΔG) and the potential of the cell (E) could be related as follow, according to the fundamental relationship

\[ \Delta G = -nF \Delta E \]

where \( n \) represents the number of electrons exchanged in the reaction and \( F \) is Faraday’s constant, 96500 Coulombs.

The fundamental equation mentioned above clearly shows that in order to have a spontaneous reaction, the potential of the cell (E) has to be positive and consequently so should the difference between the cathode potential and the anode potential (ΔE). [10][6]

Being

\[ \Delta E = e_C - e_A \]

The final condition to have a spontaneous reaction is:

\[ e_C > e_A. \]
1.3 Kinetic of corrosion

Although corrosion in aqueous systems is mainly governed by electrochemical reactions, a complete understanding of the fundamental principles of electrochemical reactions kinetics is of paramount importance to determine and predict the rate of corrosion and improve methods of protection against it. [11][6]

A metal containing mobile electrons, when in contact with an aqueous solution, forms a complex boundary layer separating the solid from the liquid phase, called electrical double layer. It consists of an array of charged species, which are negative underneath the electrode surface and positive in the solution (or vice-versa depending if the surface’s behaviours is anodic or cathodic) which experimentally behaves like a charged capacitor. As the surface of the metal undergoing corrosion is neither chemically nor geometrically homogeneous, it allows both local anodic and cathodic processes.

Asymmetrical polar H₂O molecules are attracted to the conductive surface forming the above mentioned double layer, hindering in this way the approach of charged species (ions) from the solution and consequently limiting electrochemical reactions at the surface. [6][7][10]

![Electrical double layer representation according to Helmholtz model](image)

Since the corrosion process requires a charge and mass transfer throughout the solution-metal interface, the properties of the electrical double layer play a fundamental role in the kinetic of the corrosion process.
The electrons flow is measured as current (I) in amperes. The relation between I and the mass reacted (m) in electrochemical reaction is given by Faraday’s Law:

\[ m = \frac{Ita}{nF} \]

Where \( F \) is Faraday’s constant, \( n \) the number of equivalent electrons exchanged, \( a \) the atomic weight and \( t \) the time.

From this, the corrosion rate (CR) can be obtained dividing by time (t) and surface area (A):

\[ CR = \frac{m}{tA} = \frac{iA}{nF} \]

Where \( i \) is defined as current density. Therefore the equation above expresses the mass loss per unit area per unit time (e.g. mg/dm²/day). [6]

Current density measured at the electrode is the difference between the current densities of the anodic and cathodic reactions. [11] In the same way the net potential is the result of the coupled half-cell reactions and is called standard potential.

Measuring of the current density exchanged at the standard potential is a useful method to study the corrosion behaviour of a material exposed to an electrolytic solution. Furthermore, considering that in this condition no extra-potential is applied to the electrochemical cell, it is common to refer to standard potential as corrosion potential (E\text{CORR}) or Open Circuit Potential (OCP). If the electrons are easily available the potential at the metal surface (OCP or E\text{CORR}) becomes more negative, due to the accumulation of electrons at the metal/solution interface waiting for reaction.

This means that the cathodic reaction is not sufficiently fast to consume all the electrons released during the anodic process. This phenomenon is called cathodic polarization (\( \eta_c \)), because the predominant reaction limiting the corrosion process is the cathodic one and since it represents a negative potential change, it can only be negative.

Similarly, a positive potential change at the metal surface is observed when the electrons liberated from the metal are not supplied fast enough to accommodate the cathodic reaction. In this case, the surface is depleted of electrons and the anodic reaction limits the process, hence the
name anodic polarization ($\eta_a$). Since it is related to a positive change of potential it must be positive. [11][6][8]

Polarization can be classified into two types: activation polarization and concentration polarization.

A reaction is said to be under activation polarization control when one of the steps in the half-cell controls the electrons flow.

It is possible to establish a relationship between the activation polarization or overpotential ($\eta$) and the rate of the corrosion reaction represented by current density ($i$), as follow.

For anodic polarization:

$$\eta_a = \beta_a \log \frac{i_a}{i_o}$$

For cathodic polarization:

$$\eta_c = \beta_c \log \frac{i_c}{i_o}$$

where $\beta_c$ and $\beta_a$ are known as Tafel constants for the half-cell reaction, $i_o$ is the exchange current density equivalent to the rate at equilibrium.

The presence of overpotential can be related to the presence of energy barriers. When a cathodic overpotential $\eta_c$ is present, the discharge reaction rate is reduced (by decreasing of activation energy), whereas the rate of ionization is increased. [6][10]

Conversely the concentration polarization refers to a mechanism in which the factor that determines the corrosion rate is the mass transport within the solution. This means that the cathodic reactions deplete the adjacent solution of the species and therefore a shortage of reactants, to be reduced, occurs at the electrode surface. It is also possible that this mechanism is caused by an accumulation of reaction products on the electrode surface. [10]

Concentration polarization is significant only for cathodic reaction, whereas for anodic mechanism it can be usually neglected because there is an unlimited supply of electrons in the metal. [6] Consequently it is possible to determine the so called limit current density ($i_L$), namely the maximum current density that can be achieved in a corrosion process controlled by concentration polarization mechanism.
In the end, it is clear that kinetic of corrosion provides further information with respect to simply thermodynamic observations. It is indeed possible to obtain information regarding the rate of corrosion, something definitely more useful in engineering field.

All the half-cell reactions occurring on the conductive metal surface have to obey the principle of charge conservation, so that the sum of anodic currents must be equal to the sum of cathodic reduction currents.

Observing the intersection between the cathodic and the anodic curves it is possible to identify the exchanged current density or corrosion current density ($i_{corr}$) and the corrosion potential ($E_{corr}$). [6][10]
Cathodic reactions:

Oxygen reduction \[ O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \]

Hydrogen evolution \[ 2H^+ + 2e^- \rightarrow H_2 \]

Anodic reaction:

\[ M \rightarrow M^{n+} + ne^- \]

1.4 Copper and its alloys

Among all the metals and alloys employed in engineering field, this thesis looks into Cu and its zinc alloys, which are widely used for several different applications. Copper has been applied in several different environments and fields such as electronics, architecture and all its alloys have a long history of employment in marine environments in applications such as heat exchangers, water distribution systems and desalinization plants. All these fields of applications are possible thanks to the considerable different properties that copper possesses, e.g excellent electrical and heat conductivity, good machinability, resistance to corrosion and biofouling, nice colouration. [13][14]
As shown in Fig. 1.6 considering aqueous solution, the potential range of activity is sufficiently high to not allow hydrogen reduction as cathodic reaction. Therefore corrosion can occur only if other oxidizers are present.

![Pourbaix diagram for copper in aqueous environment](image)

**Fig. 1.6** – Pourbaix diagram for copper in aqueous environment [15]

It is clear that in the range of pH between 7 and 13 at every potential value copper shows excellent corrosive resistance properties. This explains the good performances of copper in neutral and alkaline environments, with exception of ammonia based solutions. [10] Indeed pure copper demonstrates excellent resistance in soil and atmospheric corrosion thanks to the formation of a protective oxide layer (CuSO₄), giving it the characteristic green colour. [6] Although it is well known that noble metal are able to withstand most rural, marine and industrial environments [16], copper and its alloys are susceptible to different selective corrosion attacks such as SCC, pitting and erosion corrosion. [10]

Considering copper alloys the most diffused is brass, it is produced adding zinc with a concentration varying from 10% to 40%, so increasing mechanical properties and reducing costs. However, zinc addition lowers the corrosion resistance of the alloy and promotes dezincification issues. [6]

Brasses are copper-zinc alloys with a wide range of engineering uses. Brasses are particularly susceptible to corrosion by solutions containing ammonia or amines. Furthermore Brass alloys containing more than 15% of zinc may experience dezincification. This type of corrosion phenomena is related to dealloying of zinc, that is preferentially removed from the
material. Since zinc and copper are not present in the alloy as separate different constituents, but as solid solution, it is not possible to have a selective leach out of zinc from copper. Therefore in the actual corrosion mechanism copper and zinc are removed together but, right after the solubilization, copper is almost instantaneously redeposited on the surface. [17]

The final effect is the zinc removal, leaving on the surface a porous and weak corrosion product of copper. [18]

When brass is exposed to the atmosphere, generally a superficial tarnish film appears, leading to formation of a stable protective green patina, that preserves the surface for long time. The possible applications of brass do not exclude seawater, indeed his attack can be held off selecting the proper alloy. [19]

Another widely spread copper alloy is Bronze, obtained adding 8-10% tin and often also small amounts of phosphorus to enhance impingement attack resistance. Adding aluminium between 5% and 12% to Bronze, Aluminium-Bronzes are obtained. This addition improves the corrosion resistance with respect to standard Bronzes, but does not change the typical copper susceptibility to oxidizing salts, ammonia and SCC. [6]

The last category of copper alloys is represented by Copper-Nickel alloys. These are the most corrosion resistant among the commercial copper alloys, when the maximum amount (45%) [20] of Nickel is reached. They are mainly employed in recirculating steam systems for condensers and heat exchangers. [6]

Depending on the specific conditions of each environment, a different degree of corrosion attack can be detected on copper and its alloys. Usually oxygen and aggressive ions such as chlorides and sulphates are responsible for this. An example of copper suffering corrosion takes place in heat exchangers, since tubes are usually working in contact with aggressive fluids such as saline water in desalination systems. [16][14]

Pitting corrosion is another example and will most likely occur during shutdown periods, in those zones where stagnation of solution promotes accumulation of aggressive species, then increasing the probability of corrosive attack. [21]

Therefore, for this and most other applications, corrosion protection of copper remains of utmost importance.
In this regard an ample amount of different corrosion inhibitors have been used in order to limit corrosion damages and control corrosion rate. [16]
Chapter 2 – Corrosion inhibitors

A corrosion inhibitor is a substance that, added in a small amount, allows to inhibit, reduce or prevent corrosion. The employment of corrosion inhibitors is one of the most applied methods to control corrosion in case of Cu alloys. [1][22]

There are several ways to classify inhibitors. One of the most popular is to divide inhibitors into inorganic inhibitors and organic inhibitors. [22]

2.1 Inorganic inhibitors

Anodic inhibitors: also called passivation inhibitors, promote a large anodic shift of the corrosion potential supporting passivation reaction on the metal surface. Anodic inhibitors usually works reacting with metallic ions (Me\\(n^+\)), produced by corrosion, forming a insoluble compounds which is then deposited on the metal (Me) surface forming the so called passive layer (MeO). The occurring reaction typically consists in hydrolysis forming, as by-product, OH⁻ ions.

As shown in Fig. 2.1 the presence of an anodic inhibitor promotes a shift of the potential to more positive values. Simultaneously the value of the current decreases, corresponding to a lowering in the corrosion rate.

![Anodic Inorganic Inhibitor](image)

Fig. 2.1 - Example of potentiostatic polarization curve for a metal exposed to a solution containing an inorganic anodic inhibitor
The concentration of the anodic inhibitor has a primary importance because if it is lower than its characteristic critical threshold the film does not fully cover the surface, consequently it enhances the corrosion phenomena, promoting localized corrosion. Examples of anodic inorganic inhibitors are chromates, molybdates, nitrates and orthophosphates. [22][23][10][24]

**Cathodic inhibitors:** this type of inhibitors reduce the corrosion rate directly slowing down the cathodic reaction or forming a film on the cathode surface.

Fig. 2.2 shows that under influence of the inhibitor a cathodic shift of the potential takes place, with the consequent lowering of the current and in turn of the corrosion rate.

![Cathodic Inorganic Inhibitor](image)

**Fig. 2.2** - Example of potentiostatic polarization curve for a metal exposed to a solution containing an inorganic cathodic inhibitor

Cathodic inhibitors can slow down the corrosion process by means of three different mechanisms:

- **Cathodic poisons:** such as sulphides and selenides. They work hindering the recombination and discharge of hydrogen, so slowing down the cathodic reaction. However this type of mechanism can also promote hydrogen induced cracking since hydrogen, kept in atomic state, can penetrate the metal;
- Cathodic precipitates: such as carbonates of calcium and magnesium, they increase the alkalinity at cathodic sites and forms insoluble compounds precipitating on the cathode surface. Furthermore, by film formation these type of inhibitors both reduce the diffusion rate of species and increase surface impedance;
- Oxygen scavengers: the inhibitor reacts with oxygen dissolving it. E.g. sulphite or bisulphite ions that react with oxygen forming sulphate. [23][24][25][26][27]

2.2 Organic inhibitors

Though inorganic inhibitors often show good anticorrosive performances, most of them are highly toxic to both human beings and the environment. Awareness of the safety issue of corrosion inhibitors has always been a global concern. Since these inhibitors may cause temporary or permanent damages and the toxicity may manifest itself either during the synthesis or during the application, new eco-friendly and harmless compounds were developed. [28]
Furthermore nowadays due to environmental laws, inorganic inhibitors such as chromate or nitrites have been banned and replaced by the safer organic inhibitors. [29]

In the presence of organic inhibitors, both anodic and cathodic effects can sometimes be observed, but in general they build up a protective hydrophobic film on the metal surface, providing a barrier to aggressive ions and hindering the dissolution of the metal in the electrolyte. [30][23]
Fig. 2.3 below, shows the effect of the solution containing organic inhibitor: the corrosion potential remains constant, while the current decreases.
The effectiveness of the protective layer is mainly related to the strength of the metal-inhibitor bonds, [31][32] but other parameters also contribute to its effectiveness:

- Size of the organic molecule;
- Aromaticity and/or presence of conjugated bonds;
- Carbon chain length;
- Ability for the layer to become compact or cross-linked;
- Capability to form a complex with the atom as a solid within the metal lattice;
- Adequate solubility of the inhibitor in the electrolyte solution [33]

Considering copper, in general its corrosion inhibitors contain polar groups including nitrogen, sulphur, oxygen and heterocyclic compounds with polar functional groups and conjugated double bonds. An example of such corrosion inhibitors are azole derivatives like benzotriazole, mercapto-benzothiazole, benzimidazole and imidazole. [30]
2.2.1 Azole compounds

Azole compounds, employed in medicine since 1944 for their antifungal activity [34], are also well known as precursor for high performances corrosion inhibitors. They are organic compounds characterized by the presence of nitrogen atoms with free electrons pairs. These lone pairs can be either used as interaction site with the metallic surface to be protected or employed to coordinate the compound with other heteroatoms and molecules, producing in this way a wide range of derivatives of the original formula, exhibiting good inhibition properties. [35]

The two main types of azole compounds studied in this thesis are imidazoles and triazoles, so called according to the number of nitrogen atoms in the organic ring structure, respectively two and three. [36]

Among all the possible molecules benzimidazole, benzotriazole, 1-Methylbenzimidazole, 1-Methylbenzotriazole and indazole, shown in Fig.2.4, are considered.

![Fig. 2.4 - a) Benzimidazole (C7H8N2), b) Benzotriazole (C6H5N3), c) 1-methyl-benzimidazole (C8H8N2), d) 1-methyl-benzotriazole (C7H7N3), e) Indazole (C7H5N2)](image_url)
1-methyl-benzimidazole and 1-methyl-benzotriazole molecules are characterized by the coordination of the methyl group to the amine type nitrogen (therefore in position 1). From this point it will be referred to 1-methyl-benzimidazole as methyl-benzimidazole and to 1-methyl-benzotriazole as methyl-benzotriazole.

Benzotriazole in particular has been recognized as excellent corrosion inhibitor since 1947 [37] and it is one of the most commonly employed inhibitor in protection of copper and its alloys in several different environments, [13] particularly in chlorides-containing environments. [16] Benzotriazole and its derivatives are unanimously considered efficient and stable corrosion inhibitors, with a strong persistence in time and properties that allow their employment in both stagnant and flow conditions. [16]

Benzotriazole is obtained starting from triazole structure and then adding a benzene ring. As mentioned earlier, the molecular structure of the inhibitors is of paramount importance and plays a key role in the type of interactions with the metallic surface. [38] In order to interact with the surface and form a metallic complex the inhibitors molecule should show specific features. [16]

The way inhibitor’s molecules interact with the surface determine their anti-corrosion effectiveness. Two types of absorption are possible: chemisorption and physisorption. Chemisorption can be defined as an interaction leading to the formation of chemical bonds. With this mechanism new molecules or complexes can be formed. [1]

On the contrary, physisorption is the adsorption mechanism where intermolecular forces are involved. This type of interaction does not involve considerable variations in the electronic orbital patterns of the species participating in. [39]

Usually neutral molecules show a weak interaction to the surface, whereas compounds exhibiting charges, as in case of deprotonated molecules, are definitely more prone to create strong chemical bonds. [1]

In particular deprotonation (almost the same reaction of dehydrogenation, with the only difference that in dehydrogenation, radicals are preferentially formed, whereas in deprotonation ions are produced) is common in azole molecules and plays an important role in the mechanism of interaction with the sample’s surface. Indeed, deprotonation molecules not only tend to form stronger bonds, but also promote formation of dipole momentum. The presence of a dipole allows the molecule to interact with the others along the axis perpendicular to the metallic surface. [40][41]
The importance of these intermolecular interactions is related to the common assumption that good corrosion inhibition is achieved when a protective layer is built up, consequently hindering the approach of aggressive species to the surface. [1]

Focusing now on chemical adsorption, electronic properties play a critical role in the definition how the inhibitor molecule will interact with the surface. The main electronic structure parameters are: position of HOMO and LUMO, HOMO-LUMO gap, chemical hardness, electronegativity, dipole moments.

As already stated the dipole moment is important in the interaction mechanism. In order to derive the dipole moment, molecular structure and charges distribution inside the molecule should be taken in account. For instance, either imidazole, benzimidazole and their methyl derivatives show a dipole moment. Furthermore for all of them the negative charge results concentrated on the third nitrogen atom of the imidazole ring, that can be then pointed out as possible reaction site, feasible for bonding with the surface. [42] [41]

Although the relation of dipole moment and actual inhibition effectiveness is not undoubtedly established, it has been demonstrated in [43] that:

- When dipoles are directed parallel with respect to the surface an accumulation of molecules is observed;
- When dipoles are perpendicular with respect to the surface, molecules are subjected to repulsive forces, so their relative distance increases. [42]

Considering now the influence of molecular orbitals, their position with respect to HOMO and LUMO is considered. Indeed, the closeness of lone pair orbitals to HOMO explains the tendency of azoles to create bonds with the metal’s surface through the lone electrons of nitrogen.

Regarding the HOMO-LUMO gap it can be related to the reactivity of the inhibitor molecule. [42] HOMO and LUMO energy can be helpful to assess the way the molecule interacts. The HOMO, being the outermost (namely with higher energy), is responsible for electron donor behaviour. By contrast, the LUMO is the innermost (namely with lowest energy) and it is therefore able to accept
electrons.

It is accepted that the HOMO-LUMO gap is good indicator of molecular stability. [44]

Similarly chemical hardness also gives practical information, which is useful to explain reactivity of molecules and consequently point out which molecule has more possibility to be adsorbed on the surface in efficient way. [42]

The chemical hardness can be defined as the ability of a chemical system to resist to changes of the electrons cloud density. It can be used as good indicator of molecule’s chemical stability. [45][46]

Therefore it is possible to derive the following general rules: the reduction of HOMO-LUMO gap and chemical hardness values is directly related to a higher reactivity of the molecule and consequently it leads to a higher probability to get adsorbed on metals’ surface. [42]

Also electronegativity can be taken in account. The difference between the electronegativity corresponding to the inhibitor molecule and that one of the metallic surface determines the amount of exchanged electrons and consequently the strength of the formed bond.

Considering now the effect of substituents (as methyl group), it does not provide strong changes in the electronic properties, whereas electronegativity is affected. Similarly, it has been experimentally observed a correlation between molecule’s size and chemical hardness: the bigger the molecule, the lower the chemical hardness, in turn leading to higher molecular reactivity. [42]

In any case, inhibition efficiency cannot be explained by only studying the bonds formed with the metallic surface.

Indeed two other properties be worth to be considered:

- Complex formation between Cu ions (mainly hydrated Cu$^{2+}$) and inhibitor molecules;
- Solubility of the inhibitor in water.

It is observed that inhibitor molecules with higher solubility show a lower inhibition effectiveness. This is due to the fact that when the molecules show a high stability in the aqueous environment they will also show a low propensity to form strong interaction with the surface. [41]
As shown in table 2.1 it is clear that the presence of substituents in the molecule can strongly modify its solubility. Considering for example Imidazole it is shown that the introduction a methyl group and then a benzene ring in the molecule greatly reduced its solubility.

**Table 2.1 - Inhibitor solubility in distilled water**

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>Substituent added</th>
<th>Solubility (mol/L)</th>
<th>Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Imidazole</td>
<td>none</td>
<td>11.18</td>
<td>25</td>
<td>[41]</td>
</tr>
<tr>
<td>1-methyl-imidazole</td>
<td>CH₃</td>
<td>1.77</td>
<td>25</td>
<td>[41]</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>Benzene ring</td>
<td>0.03</td>
<td>25</td>
<td>[41]</td>
</tr>
</tbody>
</table>
Chapter 3 – Methodology and techniques

This work aims to look into corrosion inhibition mechanisms in order to enlarge our, still limited, understanding of interaction mechanisms among azole-based corrosion inhibitors and copper. To do so various experimental techniques were used, testing different samples ranging from pure Cu to Cu alloys (10%Zn, 30%Zn) and pure Zn.

3.1 Sample preparation and experimental set-up

The material was supplied by Goodfellow in form of 4 mm thick square sheet for pure Cu and Cu-Zn alloys samples, and 1 mm for pure Zn samples. Each specimen was cut from the foil in squared pieces 30 mm x 30 mm.

In agreement with the partner from Ljubljana University, prior to the tests a surface finishing aimed to reduce the roughness was performed. Initially the sample was mechanically sanded using SiC papers mounted on a circulating device, under a stream of water. The papers’ roughness was step-by-step reduced, starting with 180 grade and then with 320, 800, 1200, 2400, 4000. Following wet polishing, using first “MD Mol” Cloth in combination with 3 μm slurry, then “MD Nap” cloth with 1 μm slurry.

The sample was then cleaned with ethanol in ultrasonic bath for 10 min, rinsed with ethanol and distilled water and finally dried with nitrogen gas.

Fig. 3.1 – Copper samples after sanding and wet polishing surface treatments

In order to test the corrosion performances of the material coupled with a specific inhibitor, a solution
composed by distilled water, NaCl 3%wt and 1mM organic inhibitor was used. The solution is then mechanically stirred by means of a magnetic stirrer until complete dissolution is achieved. Sometimes, in order to attain a complete dissolution, an alternation of mechanical stirring session and ultrasonic session was required.

Only in the case of measurements performed with Fourier Transform Infrared Spectroscopy (FTIR) a solution of 99,8% pure Tetrahydrofuran (THF) and 3mM organic inhibitor was used.

In agreement with the guidelines given by the project partner, before the exposure, the sample was covered with solution-resistant epoxy-tape leaving unprotected a defined circular area corresponding to $3,14\text{cm}^2$ (2 cm diameter). At the same time on the back of the sample a piece of copper tape was applied in order to allow electrical connection between the potentiostat and the reference electrode itself, as shown in Fig. 3.2.

![Zinc sample tape-covered, ready for exposure](image)

The sample was then dipped in the solution together with a graphite counter electrode and a reference electrode, Saturated Calomel Electrode (SCE) or Silver Chloride Electrode (Ag/AgCl sat.KCl). A three-electrodes set-up was used for all the electrochemical tests, as shown in Fig. 3.3. The beaker was covered with a plastic lead in order to hinder the solution evaporation.
3.2 Corrosion tests

3.2.1 Polarization methods

The first technique employed is the so called Linear Polarization Resistance (LPR). This type of electrochemical analysis examines the correlation between the degree of polarization at a given applied current and corrosion rate. [6]

A potential perturbation of ±10 mV was applied to the sample (working electrode) with a scan rate of 0.1 mV/s. Such a small potential perturbation was applied in order to keep the polarization curve in the linear region.

A graph with potential (E) as x-axis and current (I) as y-axis is obtained. Then the slope of the polarization curve is extrapolated and in turn related to the polarization resistance. Furthermore the polarization resistance is correlated to the corrosion current density $i_{corr}$ through Stern-Geary equation:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta_a \beta_c}{2.3 i_{corr}(\beta_a \beta_e)}$$
Where $\beta_a$ and $\beta_c$ are the Tafel slopes of the anodic and cathodic reactions, respectively, $\Delta E$ is the applied potential change, $\Delta i_{\text{app}}$ is the resultant current density change, and $i_{\text{corr}}$ is the corrosion current density at the free-corroding potential. [47]

The Stearn-Geary equation can be rephrased as follow:

$$i_{\text{corr}} = \frac{\beta_a \beta_c}{2,3(\beta_a + \beta_c)} \frac{1}{R_p}$$

where $R_p$ is the polarization resistance measured during the LPR test. It becomes then clear that exists a inverse proportionality between the measured polarization resistance ($R_p$) and the corrosion current density ($i_{\text{corr}}$). The calculation of the polarization resistance is therefore a useful method to quantitatively assess the corrosion resistance of a given material-environment couple. [48]

The evaluation of $R_p$ is performed as in Fig 3.4. The $R_p$ values, corresponding to the slope of the curve, at different times are plotted in order to easily monitor its trend and compare performances of different inhibitors.
3.2.2 Electrochemical Impedance Spectroscopy (EIS)

EIS is a technique used to characterize electrochemical systems. Its aim is to understand the physical and chemical phenomenon governing the analysed electrochemical system. EIS test consists in apply a small sinusoidal signal on the sample (working electrode) and measure the response. Applying a sinusoidal voltage, the output is a sinusoidal current signal with a phase shift ($\phi$) with respect to the input (see Fig. 3.5). In the same way when the input is a current the output signal is a voltage.

![Fig. 3.5 – Voltage and current as function of time](image)

The EIS instrument records the two components of the impedance response of the system: real (resistance) and imaginary (capacitance) components. [49]

Electrochemical impedance spectroscopy measurements were performed on polished samples exposed to the same water-based solution containing 3%wt NaCl and 1mM corrosion inhibitor and same three-electrode set up as shown in Fig. 3.3.

The frequency range used for the tests was: 0.01Hz – 100kHz with an AC amplitude of 10mV, 10 steps/decade. The perturbation was applied with respect to the OCP signal.

3.3 Fourier Transform InfraRed spectroscopy (FTIR)

FTIR spectroscopy exploits a light beam (IR) focused on the sample in order to obtain a spectra, representing absorption and transmission of molecules deposited on sample’s surface.
Each peak of the spectra is related to a particular vibrational mode of molecules analysed, so that each frequency can be associated to a type of bond. Therefore studying the spectra is possible to identify the type of components present on the sample and determine their relative amount. [50]

In-situ FTIR measurements were performed on copper samples using FTIR instrument model “NICOLET 6700”.

In order to perform in-situ tests a pure Ge crystal was used. As first step the Ge crystal was carefully cleaned by means of ultrasonic bath, first immersed in distilled water and then in pure ethanol. Then a layer of material was deposited on its flat surface using a Physical Vapour Deposition (PVD) machine model “BALZERS – BAE250 Coating system” with the following parameters:

- mass of material in the crucible: 0,17g;
- deposition time: 12-15s;
- chamber pressure: $10^{-5}$ mbar;
- current applied during evaporation: 100-125 mA.

These parameters were chosen in order to obtain a copper layer sufficiently thin to allow the light to interact with the inhibitor’s molecules on the surface and simultaneously sufficiently thick and homogeneous to guarantee that the only interactions possible were those ones between inhibitor and copper.

After the deposition the sample is mounted in the accessory (model: Seagull) as shown in Fig. 3.6. Before the actual test the background spectra of the sample exposed to pure THF was recorded. After that the sample is exposed to a 3mM inhibitor solution in THF and measurement starts. Thanks to this device it was possible to flow the solution through the tubes (marked as “B” in Fig. 3.6 and Fig. 3.7) reaching the sample surface and analysing in this way the in-situ interaction among inhibitor molecules and copper surface.

At the beginning only pure THF was poured in the syringe letting it flows through the “IN” tube (right) and then collecting it from tube “OUT” (left), as shown in Fig. 3.7. After some seconds the flow was stopped by closing the outlet and the background measurement was performed. Once the background was collected the outlet was opened again and the inhibitor solution was poured in the syringe.

The change of solution was performed right after the beginning of the actual test in order to be reasonably sure to collect all the possible interactions and changes from the very beginning of the
exposure.

The parameters used for spectra collection are the following:

N° of scans: 128

Interval time: 1

Fig. 3.6 – Top view (left) and side view (right) of in-situ accessory. A: mounted crystal, B: tubes in and out

Fig. 3.7 – Experimental set-up showing solution inlet and outlet
Chapter 4 – Results and discussion

4.1 Corrosion performances

Initially a first batch of 20 inhibitors was tested performing a 100 hours LPR measurement for each inhibitor on Cu samples, in order to point out the best corrosion protection performances.

The second step, described in this chapter, consisted of an in depth study of corrosion inhibition performances of the five shortlisted inhibitors applied on pure Cu, alloy 10% Zn, alloy 30% Zn and pure Zn. Initially all four materials were tested in order to assess their behaviour when exposed to the corrosive environments, but in the next phase only pure copper was considered, focusing on its behaviour.

These corrosion performances tests were performed with the aim to select the best inhibitor for copper-based materials, to show how the amount of zinc contained in the alloy influences the performances and to build a solid basis from which to start to study the corrosion protection mechanisms.

4.1.1 Linear polarization resistance

The plots of polarization resistance values for each inhibitor-material combination and with no inhibition are shown in order to have a quantitative rank of their performances. Furthermore also plots showing the related estimated corrosion rate are presented giving in this way an idea about the actual rate of corrosion that these samples suffered when exposed to the chosen environment.

In order to correlate $R_p$ values to corrosion rate as shown in paragraph 3.2.1 the Stearn-Geary equation is used. For this calculation the constant B is required:

$$i_{corr} = \frac{B}{R_p} \quad \text{with} \quad B = \frac{\beta_a\beta_c}{2.3(\beta_a+\beta_c)}$$

These Tafel constants may be assumed for quick calculations, considering that they are usually in the range of 0.1 V/decade. Indeed assuming this value for both the Tafel constants it is possible to calculate the corrosion current density ($i_{corr}$) with an error that at maximum can be 2.2. [51]
Therefore the proportionality constant used for the following calculation is \( B = 0.022 \).

In order to correlate the extrapolated corrosion current density \( (i_{corr}) \) with a corrosion rate (expressed in mm/years) the Faraday law is applied:

\[
\Delta M = \frac{M}{z \cdot F} \cdot I \cdot t
\]

Where \( \Delta M \) is the corroded mass, \( M \) atomic mass of the material, \( z \) valence of the ions produced during the oxidation process, \( F \) Faraday constant (here considered 96500 Coulombs), \( \rho \) the material’s density, \( t \) the time, \( I \) the corrosion current. Rephrasing the Faraday law the penetration rate expressed in mm/year is calculated with the following:

\[
CR = \frac{MW}{z \cdot F} \cdot \frac{i_{corr}}{\rho} \cdot t
\]

The equivalent weight, necessary to complete the calculation is obtained using the equation below:

\[
Equivalent \ weight = \frac{MW}{z} = N_{eq}^{-1} = \frac{1}{\sum \frac{Z_i f_i}{M_i}}
\]

[52] [8]

with \( f_i \) is the fraction of each alloying element.

The main variables employed for corrosion rate calculation are shown in table 4.1.

<table>
<thead>
<tr>
<th>Material composition</th>
<th>Equivalent weight</th>
<th>Density (g/cm(^3))</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure copper</td>
<td>31,77</td>
<td>8,96</td>
<td>[53]</td>
</tr>
<tr>
<td>10% Zn</td>
<td>31,84</td>
<td>8,80</td>
<td>[54]</td>
</tr>
<tr>
<td>30% Zn</td>
<td>32,03</td>
<td>8,52</td>
<td>[54]</td>
</tr>
<tr>
<td>Pure zinc</td>
<td>32,70</td>
<td>7,13</td>
<td>[55]</td>
</tr>
</tbody>
</table>

4.1.1.1 Inhibitors screening

In table 4.2 the average \( R_p \) values for the 20 inhibitors are shown. The three best performing inhibitors were selected for further studies, to those ones also two methyl-substituted version of benzimidazole and benzotriazole were added.
Table 4.2 – $R_p$ mean values for inhibitors screening

<table>
<thead>
<tr>
<th>Inhibitor</th>
<th>$R_p$ mean values (Ω·cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3H-Benzotriazole-5-carboxylic acid</td>
<td>1 069</td>
</tr>
<tr>
<td>5-Amino-2-mercaptobenzimidazole</td>
<td>3 469</td>
</tr>
<tr>
<td>1-(3-Hydroxypropyl)-imidazole</td>
<td>4 603</td>
</tr>
<tr>
<td>8-Hydroxyquinoline</td>
<td>5 961</td>
</tr>
<tr>
<td>7-Hydroxyindole</td>
<td>8 264</td>
</tr>
<tr>
<td>4-Phenylimidazole-2-thiol</td>
<td>8 863</td>
</tr>
<tr>
<td>1-methylBenzotriazole</td>
<td>9 139</td>
</tr>
<tr>
<td>1-Butylimidazole</td>
<td>10 531</td>
</tr>
<tr>
<td>2-Hydroxybenzimidazole</td>
<td>11 622</td>
</tr>
<tr>
<td>1- Decyl-2-methylimidazole</td>
<td>12 521</td>
</tr>
<tr>
<td>1-(3-aminopropyl)imidazole</td>
<td>20 314</td>
</tr>
<tr>
<td>1-methylBenzimidazole</td>
<td>21 392</td>
</tr>
<tr>
<td>2-Mercapo-1-methylimidazole</td>
<td>25 071</td>
</tr>
<tr>
<td>5-Methoxy-1H-benzo[d]imidazole</td>
<td>36 586</td>
</tr>
<tr>
<td>2-(Methylthio)benzimidazoel</td>
<td>44 193</td>
</tr>
<tr>
<td>1H-benzimidazole-2-methanol</td>
<td>75 930</td>
</tr>
<tr>
<td>5-Methoxy-2-benzimidazole-thiol</td>
<td>77 775</td>
</tr>
<tr>
<td>Benzimidazole</td>
<td>81 369</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>114 310</td>
</tr>
<tr>
<td>Indazole</td>
<td>157 295</td>
</tr>
</tbody>
</table>

$R_p$ values were extrapolated with the same method shown in paragraph 3.2.1 and then the average was calculated. As example Fig. 4.1 depicts the plot representing polarization resistance values for copper exposed to 1-(3-Aminopropyl)-imidazole and Table 4.3 shows the corresponding data points used to calculate $R_p$ mean value: 20 314 Ω·cm$^2$. 
Fig. 4.1 – Polarization resistance plot for Cu exposed to 1-(3-Aminopropyl)-imidazole water-based solution

Table 4.3 - $R_p$ values for Cu exposed to 1-(3-Aminopropyl)-imidazole water-based solution

<table>
<thead>
<tr>
<th>$R_p$(Ω·cm$^2$)</th>
<th>Time (hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>31 486.5</td>
<td>0</td>
</tr>
<tr>
<td>27 539</td>
<td>2</td>
</tr>
<tr>
<td>41 408</td>
<td>5</td>
</tr>
<tr>
<td>23 670</td>
<td>10</td>
</tr>
<tr>
<td>16 543</td>
<td>20</td>
</tr>
<tr>
<td>16 481.5</td>
<td>30</td>
</tr>
<tr>
<td>17 132.5</td>
<td>40</td>
</tr>
<tr>
<td>23 789</td>
<td>50</td>
</tr>
<tr>
<td>14 197.5</td>
<td>60</td>
</tr>
<tr>
<td>14 996</td>
<td>70</td>
</tr>
<tr>
<td>12 645.3</td>
<td>80</td>
</tr>
<tr>
<td>12 280.5</td>
<td>90</td>
</tr>
<tr>
<td>11 920.5</td>
<td>100</td>
</tr>
</tbody>
</table>
4.1.1.2 Inhibitors interacting with pure copper

Fig. 4.2 shows the linear polarization resistance values of Cu exposed to five different environments each containing a different inhibitor and an un-inhibited one. For a more intuitive and rapid analysis of inhibitor performances another graph showing the related corrosion rate is presented (Fig. 4.3).

![Polarization resistance plot](image1)

**Fig. 4.2** – Polarization resistance plot for Cu exposed to five inhibited environment and with no inhibition

![Corrosion rate plot](image2)

**Fig. 4.3** – Corrosion rate plot for Cu exposed to five inhibited environment and with no inhibition
Observing the two graphs, is clear that the best inhibitor for pure copper is indazole since it shows the highest polarization resistance characterized by a steadily increasing trend, and consequently a particularly low corrosion rate. In similar way also benzimidazole and benzotriazole demonstrate excellent corrosion resistance performances. The same trend can be noticed observing the inhibition efficiency (Table 4.4) that has been calculated as follow:

$$\eta = \frac{i_0 - i_i}{i_0} \cdot 100\%$$

Where \(i_i\) is the inhibited corrosion current density and \(i_0\) is the corrosion current density without inhibitor addition. The current density is calculated as average of the values considered in \(R_p\) calculation for each specific inhibitor.

**Table 4.4** – Inhibition efficiency for Cu samples exposed to five inhibited environment and with no inhibition

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Current density, (i) (A/cm(^2))</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzimidazole</td>
<td>6,12E-07</td>
<td>+84%</td>
</tr>
<tr>
<td>Methyl-benzimidazole</td>
<td>1,19E-06</td>
<td>+69%</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>2,69E-07</td>
<td>+93%</td>
</tr>
<tr>
<td>Methyl-benzotriazole</td>
<td>3,36E-06</td>
<td>+14%</td>
</tr>
<tr>
<td>Indazole</td>
<td>1,68E-07</td>
<td>+96%</td>
</tr>
<tr>
<td>No inhibitor ((i_0))</td>
<td>3,90E-06</td>
<td>/</td>
</tr>
</tbody>
</table>

On the other hand methyl-benzimidazole and methyl-benzotriazole show a linear polarization values an order of magnitude lower than those one measured for the other inhibitors. In particular, methyl-benzotriazole during the last 30 hours of exposure shows a corrosion rate higher than that one measured without inhibition. This clearly shows that is not always true that the addition of a corrosion inhibitor necessarily leads to a lowering of the corrosion rate, but sometimes small changes in the molecular structures can promote a detrimental behaviour.
4.1.1.3 Inhibitors interacting with Cu-Zn alloys

Also the corrosion rate for copper alloys with 10% Zn, 30% Zn and pure Zn were tested, as shown in Fig. 4.4 and Fig. 4.5.

Fig. 4.4 - Polarization resistance plot for Cu alloy with 10% Zn exposed to five inhibited environment and with no inhibition

Fig. 4.5 - Corrosion rate plot for Cu alloy with 10% Zn exposed to five inhibited environment and with no inhibition

Considering the first copper alloy containing 10% Zinc, it can be noticed a trend similar to that one
observed in case of copper. Indazole, benzimidazole and benzotriazole performed very well as for pure copper experiments, whereas the samples in presence of methy-benzotriazole and methyl-benzimidazole show a constant increment in corrosion rate, slightly lower than the corrosion rate recorded without inhibition.

A further increase of Zn concentration in the alloy leads on average to a lowering of polarization resistance and a consequently increase in corrosion rate, as shown in Fig. 4.6 and Fig. 4.7.

**Fig. 4.6** – Polarization resistance plot for Cu alloy with 30% Zn exposed to five inhibited environment and with no inhibition

**Fig. 4.7** – Corrosion rate plot for Cu alloy with 30% Zn exposed to five inhibited environment and with no inhibition
4.1.1.4 Inhibitors interacting with pure zinc

The previous observations also pointed out the performances registered during exposure of pure zinc samples. Indeed in this case, the polarization resistance is one order of magnitude smaller comparing the best inhibitors for copper and zinc, reaching sometimes two order of magnitude difference considering average performance inhibitors, as can be observed in Fig 4.8 and Fig 4.9.

Furthermore, we can observe from Table 4.5 that when these inhibitors are employed to protect zinc instead of copper, the inhibition efficiency is strongly reduced. Especially, in case of methyl-
benzotriazole, the efficiency assumes negative value, indicating that the corrosion rate observed without inhibitor is lower than that one measured with inhibition, a further demonstration of ineffectiveness of methyl-benzotriazole as corrosion inhibitor, for both copper and zinc.

**Table 4.5 - Inhibition efficiency for Zn samples exposed to five inhibited environment and with no inhibition**

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Current density, $i$ (A/cm$^2$)</th>
<th>Inhibition efficiency (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzimidazole</td>
<td>5.16E-06</td>
<td>+87%</td>
</tr>
<tr>
<td>Methyl-benzimidazole</td>
<td>3.45E-05</td>
<td>+10%</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>9.79E-06</td>
<td>+74%</td>
</tr>
<tr>
<td>Methyl-benzotriazole</td>
<td>4.78E-05</td>
<td>-24%</td>
</tr>
<tr>
<td>Indazole</td>
<td>2.26E-05</td>
<td>+41%</td>
</tr>
<tr>
<td>No inhibitor ($i_0$)</td>
<td>3.84E-05</td>
<td>/</td>
</tr>
</tbody>
</table>

Fig. 4.10 depicts the average corrosion rate for each material exposed to the five different inhibited environments and the not-inhibited one (see Table 4.6 for plotted values). It is possible to see that in general the corrosion rate measured for copper is lower than for the other materials and that with the increasing of zinc concentration also the corrosion rate is increased.
Fig. 4.10 – Average corrosion rate for pure Cu, 10% and 30% Zn alloys and pure zinc gathered according to inhibitor type

Table 4.6 – Calculated average corrosion rate data for pure Cu, 10% and 30% Zn alloys and pure zinc in mm/year

<table>
<thead>
<tr>
<th>Inhibitors</th>
<th>Pure copper</th>
<th>10% Zn alloy</th>
<th>30% Zn alloy</th>
<th>Pure zinc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzimidazole</td>
<td>0.0075</td>
<td>0.0080</td>
<td>0.0050</td>
<td>0.0773</td>
</tr>
<tr>
<td>Methyl-benzimidazole</td>
<td>0.0133</td>
<td>0.028</td>
<td>0.0626</td>
<td>0.5173</td>
</tr>
<tr>
<td>Benzotriazole</td>
<td>0.0032</td>
<td>0.0020</td>
<td>0.0061</td>
<td>0.1468</td>
</tr>
<tr>
<td>Methyl-benzotriazole</td>
<td>0.0389</td>
<td>0.0383</td>
<td>0.0256</td>
<td>0.7160</td>
</tr>
<tr>
<td>Indazole</td>
<td>0.0020</td>
<td>0.0012</td>
<td>0.0037</td>
<td>0.3389</td>
</tr>
<tr>
<td>No inhibitor</td>
<td>0.0452</td>
<td>0.0489</td>
<td>0.08720</td>
<td>0.5758</td>
</tr>
</tbody>
</table>
4.1.1.5 Experimental notes

Most of the linear polarization tests performed at the beginning are characterized by a highly noisy signal and sometimes a current intensity so low that was exceeding the maximum sensibility of the potentiostat. This condition, spotted more often in Cu samples and 10% Zn alloy, hindered the success of the measurements. After several attempts an almost definitive solution was find in three main setup changes:

- substitution of the counter electrode. Initially a Stainless Steel counter electrode with wire mesh structure was used. The electrical connection was established by a thin copper cable soldered on the top right corner. It was observed that even though the cable was not in contact with the solution after only one test the soldered part was presenting a layer of copper corrosion products in form of green oxide. This counter electrode was therefore substituted with a graphite stick, ensuring an higher liability, stability and life extent;

- increase of counter electrode/working electrode surface ratio and relocation of counter electrode as far as possible with respect to the working electrode. With the first improvement it was guaranteed that the counter electrode could provide whatever current the potentiostat demands avoiding to limit the cell current and with the latter was removed the interreference with the working electrode due to the possible pH change occurring at counter electrode surface. Furthermore the solution volume was increased to promote a higher electrode-solution contact area;

- In case of particularly low current, a potentiostat channel with low current cables was used.

Furthermore for all the samples and measurements the stability of reference electrodes was always checked, right before the test.

4.1.2 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy tests were performed with the aim to confirm the $R_p$ trend observed with Linear Polarization Resistance measurements and derive a possible overview of
inhibitor behaviour. In particular investigating the possibility of film formation on the surface, by the study of Nyquist plot.

In this chapter only analysis performed on copper samples are presented, since these inhibitors behave the best on pure copper and therefore it is easier and more probable to observe molecules-surface interactions and consequently film formation.

4.1.2 EIS analysis: benzimidazole on pure copper

In Fig 4.13 the Nyquist plots for copper sample exposed to the aggressive solution containing benzimidazole at 0, 2, 5, 10, 20, 30, 40, 50, 60, 70 hours are shown.

With the exception of the first curve representing the system at time 0h, all the others are fitted using an equivalent circuit based on that one characteristic of a metal substrate covered by a failed organic coating. Although this circuit can resemble the inhibitor-metal system considered here, it does not perfectly fit it, since the film formation (when occurs) takes some time and furthermore its compactness and density cannot be compare to that one obtained with a painted organic coating. In order to overcome this issue the simple capacitor is substituted with a Constant Phase Element (CPE) as shown in Fig 4.11. This circuit element better suits the non-homogeneity of the inhibitor layer formed on the surface, properly fitting the curves with a depressed semi-circular shape. [56]

![Fig. 4.11 – Equivalent circuit of inhibitor film on a metal substrate](image-url)
At the very beginning of the exposure only a first time constant is visible characterized by a diffusion tail, sign of presence of a diffusion controlled process. In this very first moment probably a not sufficient amount of inhibitor molecules are adsorbed on the surface therefore anodic dissolution is moderately fast. Since the charges have to be balanced, a cathodic reaction is required and therefore diffusion of oxygen to the surface occurs. The proposed equivalent circuit for the curve at time 0h is shown in Fig 4.12, but the relative errors for the most of the considered circuit elements were too high to be actually taken in account.

![Equivalent circuit of initial sample exposure to the solution](image)

**Fig. 4.12** – Equivalent circuit of initial sample exposure to the solution

Observing the Nyquist plots at different times, as shown in Fig. 4.13, it can be noticed that, already after 2h of exposure, a first and a second time constant are formed. The first semicircle, representing
the film resistance, increases with time until its maximum level is reached, after which it stays constant. The second time constant is dwarfed by the first semicircle, but it can be still seen.

Fig 4.13 – Nyquist plots of copper sample exposed to NaCl and benzimidazole water based solution

Table 4.7 – Electrolyte resistance, film resistance and polarization resistance for benzimidazole, with relative errors

<table>
<thead>
<tr>
<th></th>
<th>R_{elect}(Ohm)</th>
<th>%error</th>
<th>R_{film}(Ohm)</th>
<th>%error</th>
<th>R_{p}(Ohm)</th>
<th>%error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>~ 0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2h</td>
<td>~ 0</td>
<td>-</td>
<td>3 255</td>
<td>5,5</td>
<td>3 138</td>
<td>42,5</td>
</tr>
<tr>
<td>5h</td>
<td>~ 0</td>
<td>-</td>
<td>549</td>
<td>9,8</td>
<td>8 172</td>
<td>1,4</td>
</tr>
<tr>
<td>10h</td>
<td>~ 0</td>
<td>-</td>
<td>1 972</td>
<td>8,3</td>
<td>14 628</td>
<td>3,3</td>
</tr>
<tr>
<td>20h</td>
<td>~ 0</td>
<td>-</td>
<td>2 149</td>
<td>7,7</td>
<td>5 922</td>
<td>4,9</td>
</tr>
<tr>
<td>30h</td>
<td>~ 0</td>
<td>-</td>
<td>3 473</td>
<td>7,9</td>
<td>4 459</td>
<td>11,5</td>
</tr>
<tr>
<td>40h</td>
<td>~ 0</td>
<td>-</td>
<td>3 337</td>
<td>11,5</td>
<td>5 202</td>
<td>14,1</td>
</tr>
<tr>
<td>50h</td>
<td>~ 0</td>
<td>-</td>
<td>3 102</td>
<td>15,1</td>
<td>9 868</td>
<td>34,7</td>
</tr>
<tr>
<td>60h</td>
<td>~ 0</td>
<td>-</td>
<td>2 890</td>
<td>17,0</td>
<td>9 615</td>
<td>3,8</td>
</tr>
<tr>
<td>70h</td>
<td>~ 0</td>
<td>-</td>
<td>2 743</td>
<td>12,3</td>
<td>10 326</td>
<td>49,6</td>
</tr>
</tbody>
</table>
4.1.2.2 EIS analysis: methyl-benzimidazole on pure copper

Considering now the Nyquist plot for methyl-benzimidazole shown in Fig. 4.14 two main stages can be recognized. The first one starts with the initial measurement (0h) and ends with the curve corresponding to 20h of exposure, the second one lasts from that point until the end of the test.

During the first stage the formation of a second time constant in low frequency region, occurs. It can be considered as indicator of an initial adsorption of inhibitor molecules on the surface or more in general the partial covering of the surface. Considering this, the first four curves (0h, 2h, 5h, 10h) were fitted using the same equivalent circuit shown in Fig. 4.11.

![One time constant equivalent circuit](image)

The curves belonging to the second stage are characterized by a different fitting. In this case an equivalent circuit with one time constant was used, shown in Fig. 4.14. Fig. 4.15 shows that after 10h of exposure a change in shape occurs. A sudden increase of the semicircle is followed by a gradual shrinkage. In order to improve the understanding in this time frame two more measurements performed at 23h and 26h are added to the plot.

Furthermore it can be noticed that after 40h of exposure the system shows a $R_p$ smaller than that one observed at the beginning and that is gradually reduced. Fig 4.15 uses three red arrows to clarify the main trends.

Focusing on the 20h, 23h and 26h exposure curve and in particular to the right extreme, in the low frequency region, it can be noticed the onset of an inductive loop. This could be interpreted as signal of adsorption/desorption phenomena. It can be related to both dissolution of corrosion products formed on the surface or desorption of the inhibitor molecules that have interacted with the surface.
Probably weak interactions are present among inhibitor molecules and the surface, therefore the inhibitor is not able to form a compact and resistant film.

![Nyquist plots of copper sample exposed to NaCl and methyl-benzimidazole water based solution](image)

**Table 4.8** – Electrolyte resistance, film resistance and polarization resistance for methyl-benzimidazole, with relative errors

<table>
<thead>
<tr>
<th></th>
<th>% error</th>
<th>% error</th>
<th>% error</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{elect}} \ (\text{Ohm})$</td>
<td>0h</td>
<td>0</td>
<td>2 549</td>
</tr>
<tr>
<td></td>
<td>2h</td>
<td>0</td>
<td>2 855</td>
</tr>
<tr>
<td></td>
<td>5h</td>
<td>0</td>
<td>3 259</td>
</tr>
<tr>
<td></td>
<td>10h</td>
<td>0</td>
<td>3 159</td>
</tr>
<tr>
<td></td>
<td>20h</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>30h</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>40h</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>50h</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>60h</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>70h</td>
<td>0</td>
<td>-</td>
</tr>
</tbody>
</table>
4.1.2.3 EIS analysis: benzotriazole on pure copper

In Fig 4.16 the Nyquist plot at different exposure time of copper in benzotriazole solution is depicted. Two different circuits, shown in Fig. 4.17 and Fig. 4.18 were proposed to fit the impedance curves. The first one resembles a system characterized by 2 time constants: inhibitor film ($R_{\text{film}}$) and diffusion inside the inhibitor layer ($W_{\text{diff}}$) and a second one representing only one time constant, therefore without Warburg circuit element.

![Nyquist plots of copper sample exposed to NaCl and benzotriazole water-based solution](image)

**Fig 4.16** – Nyquist plots of copper sample exposed to NaCl and benzotriazole water-based solution

![Equivalent circuit with Warburg element](image)

**Fig. 4.17** – Equivalent circuit with Warburg element
Although some of the plotted curves show a diffusion behaviour the addition of a Warburg element to the equivalent circuit did not provide a proper fitting.

Observing the Nyquist plot two main trends can be highlighted. The first one, to which the curves from 0h to 10h belong, showing a slight increase in measured impedance, and the second one represented by all the other curves showing a slow but constant decline of impedance.

The lower of impedance may be related to the formation of a not so much lasting and stable inhibitor layer. As already stated, almost all the curves plotted show a sort of diffusion behaviour. The presence of diffusion may explain the development of a non-perfectly interacting layer. This behaviour is partially reflected by LPR measurements that show an initial increase in corrosion resistance and then a slight reduction.

4.1.2.4 EIS analysis: methyl-benzotriazole on pure copper

Fig. 4.20 shows the Nyquist plots for copper sample exposed to a methyl-benzotriazole solution. Since from the beginning two time constants can be observed, all the curves were fitted employing the same equivalent circuit, as shown in Fig. 4.19.

This circuit fits all the curves and it was proposed in [59] [60] [61] to describe a passive oxide layer or an inhibitor film presenting important inhomogeneities. From these considerations the equivalent circuit is proposed considering that LPR corrosion tests showed a poor protective behaviour and that according to DFT calculations is unlike that methyl-substituted azole compounds promote a strong protective layer. [41] [62]

During the first 10 hours of exposure mainly the first semicircle increases in size, then at 20h and 30h of exposure the shape changes showing a quick enlargement of the second semicircle and a slight shrinkage of the first one. During the last 40 hours the second semicircle strongly increases in size.
until the end of the test. Anyway it should be underlined that the trend occurring in the last 40 hours is not homogeneous since the measurement performed at 50h shows a much smaller semicircle for both the time constants.

This behaviour may be related, as already suggested, to the formation of an inhomogeneous layer, in particular large zones covered, alternated with others left uncovered. Therefore the film resistance and the polarization resistance values cannot be considered as real parameters of the system, since the inhibitor does not behave in homogeneous way on the surface.

![Fig. 4.19 - Two time-constants equivalent circuit in series](image1)

![Fig. 4.20 - Nyquist plots of copper sample exposed to NaCl and methyl-benzotriazole water based solution](image2)
### Table 4.9 – Electrolyte resistance, film resistance and polarization resistance for methyl-benzotriazole, with relative errors

<table>
<thead>
<tr>
<th>$R_{elec}$ (Ohm)</th>
<th>%error</th>
<th>$R_{film}$ (Ohm)</th>
<th>%error</th>
<th>$R_p$ (Ohm)</th>
<th>%error</th>
</tr>
</thead>
<tbody>
<tr>
<td>0h</td>
<td>~ 0</td>
<td>-</td>
<td>1 023</td>
<td>48,63</td>
<td>2 061</td>
</tr>
<tr>
<td>2h</td>
<td>~ 0</td>
<td>-</td>
<td>294</td>
<td>27,36</td>
<td>3 203</td>
</tr>
<tr>
<td>5h</td>
<td>~ 0</td>
<td>-</td>
<td>748</td>
<td>18,26</td>
<td>3 629</td>
</tr>
<tr>
<td>10h</td>
<td>~ 0</td>
<td>-</td>
<td>1 222</td>
<td>15,71</td>
<td>3 274</td>
</tr>
<tr>
<td>20h</td>
<td>~ 0</td>
<td>-</td>
<td>3 019</td>
<td>7,13</td>
<td>2 470</td>
</tr>
<tr>
<td>30h</td>
<td>~ 0</td>
<td>-</td>
<td>2 776</td>
<td>7,39</td>
<td>2 361</td>
</tr>
<tr>
<td>40h</td>
<td>~ 0</td>
<td>-</td>
<td>9 311</td>
<td>4,37</td>
<td>2 332</td>
</tr>
<tr>
<td>50h</td>
<td>~ 0</td>
<td>-</td>
<td>5 086</td>
<td>8,03</td>
<td>2 082</td>
</tr>
<tr>
<td>60h</td>
<td>~ 0</td>
<td>-</td>
<td>8 516</td>
<td>7,58</td>
<td>2 324</td>
</tr>
<tr>
<td>70h</td>
<td>~ 0</td>
<td>-</td>
<td>10 402</td>
<td>7,83</td>
<td>2 874</td>
</tr>
</tbody>
</table>

#### 4.1.2.5 EIS analysis: indazole on pure copper

Considering now the Nyquist plot for indazole (Fig. 4.22) two main trends can be observed. During the first 2 hours the semicircle size decreases and then suddenly starts to increase for the following 60 hours. The tails of the curves show a diffusion mechanism that is progressively reduced with increasing of exposure time. In particular the last three measurements (50h, 60h, 70h) show an almost disappeared diffusion tail. All the curves were fitted using the equivalent circuit shown in Fig. 4.21.

![Equivalent circuit](image)

**Fig. 4.21** – Equivalent circuit representing inhibitor film formation and diffusive behaviour

The equivalent circuit here employed was proposed in [63], where indazole is tested in similar circumstances. Although lower inhibitor concentration was used, similar shape of curves in Nyquist plot is observed and the proposed equivalent circuit well fits the plot.
The presence of diffusion tails, represented by the Warburg element, can be related to oxygen diffusing through the solution to the sample surface or it can be due to transport of Cu-Cl complexes to the bulk solution as consequence of corrosion. [63]

The increase of film resistance with time confirms the grow of the inhibitor film on the sample surface. Furthermore the diffusion is progressively reduced, sign that probably a compact and well-protecting layer is formed on the surface, hindering the diffusion of oxygen to the surface and/or the metal dissolution.

Fig. 4.22 - Nyquist plots of copper sample exposed to NaCl and Indazole water based solution
4.1.2.6 Experimental notes

In this paragraph some clarifications regarding the EIS data analysis are provided.

Confronting the $R_p$ values obtained from LPR and EIS measurements it may be noticed that sometimes they differ even of an order of magnitude. This was accepted considering the following observations:

- LPR and EIS techniques employ different types of current, respectively direct current (DC) and alternate current (AC);
- In case of LPR only processes that act as resistive element are considered. The actual resistance of the whole system (namely of any flow of current) is measured. In EIS spectra more complex information and processes are used. Some processes behave according Ohm law, whereas others behave like a capacitor, not responding as resistive element.

LPR is therefore considered more suitable to study overall corrosion behaviour of the system. EIS is more useful to go through singular elements. Anyway almost the same $R_p$ trends were observed in both the techniques.

Another necessary clarification is related to the fitting of the equivalent circuit. Since all the experiments were executed in the corrosion laboratories at TU Delft, shared with several other researchers, the possibility to perform the tests was subordinated to the availability of the machines. Consequently some measurements were performed with different machines and software. In particular CPE circuit element was expressed in two different ways depending on the
software used ZView or EC-Lab. Anyway the circuit element indicated as Q has the same meaning and function of that one indicated as CPE. It fits the same spectrum fitted by CPE element with the only difference that different parameters are used. Therefore, if necessary, the two parameters can be translated one in the other by means of a conversion formula. [64]

In the end, regarding the tables showing the fitted data, it can be pointed out that all the values of the resistive element representing the electrolyte resistance are approximated with ~0. Since the electrolyte resistance is particularly low, that element was kept constant equal to zero.

4.1.3 Data discussion and summary

The results obtained from Linear Polarization Resistance and Electrochemical Impedance Spectroscopy measurements are here summarized and discussed in order to depict an overview of the main conclusions that can be drawn from these data.

LPR

- The higher the zinc concentration the higher the corrosion rate. These inhibitors show a better behaviour with pure copper and more in general when the concentration of copper in the alloy is high;
- Methyl-substituted inhibitors do not performed well. The presence of a methyl substituent in the molecules strongly modifies the effectiveness of these inhibitors;
- Sometimes methyl-substituted inhibitors promote an increase in corrosion rate. In particular the corrosion rate measured for pure zinc exposed to methyl-benzotriazole solution is higher than that one observed with no-inhibited sample;
- Benzotriazole, benzimidazole and indazole are the best inhibitors. In particular indazole performs the best;
- Correlation between inhibitors effectiveness and type of material: inhibitors performing the best when coupled with copper, do not necessarily behave in the same way with zinc samples. This indicate a correlation between inhibition effectiveness and material type;
- The lowest corrosion rate is observed with the couple indazole – alloy 10% Zn. The fact that this is observed with a copper alloy and not with pure copper is probably related to several factors:
  1. The concentration of zinc in that alloy is still very low, therefore is reasonable that the behaviour is close to that one of pure copper;
  2. The approximation error introduced during the corrosion rate calculation could have created such erroneous situation;
  3. The values considered are averages.

In any case the increase of corrosion rate with the increasing of zinc concentration is clear and that one observed for pure zinc is one-two order of magnitude higher than that one measured with copper, for all the five inhibitors.

EIS
- Methyl-benzimidazole confirms its poor corrosion protection behaviour. As shown by EIS measurements a film is probably partially formed and then desorbed from the surface. The trend observed for LPR measurements is almost the same. Initially the $R_p$ slightly increases and then decreases after 20-30 hours of exposure;
- Indazole performs the best. EIS measurements confirm the excellent corrosion inhibition properties already shown by indazole during linear polarization resistance tests. $R_p$ increasing with time together with film resistance, showing the formation of an effective inhibitor layer;
- Methyl-benzotriazole shows an unclear behaviour. EIS study shows that at least a partial film formation occurs;
- Benzimidazole Nyquist plot depicts the formation of a film on the sample surface, however several values obtained from the fitting present a high error. Consequently it is not possible to draw a trend for $R_p$. On the other hand the film resistance, showing lower errors, seems to increase with time;
Benzotriazole demonstrates a not perfect protection behaviour, with presence of diffusion. Anyway the impossibility to properly fit the data hinders the interpretation of the graph. Only the main trends can be recognized: initially an increase and then a slight lowering of impedance.

4.2 Fourier Transform InfraRed Spectroscopy (FTIR)

In this section the results from FTIR spectroscopy are presented and discussed. The main purpose of this analysis is to investigate molecules-surface interactions and provide a possible mechanism by means the inhibitors work to protect the metal surface from corrosion.

The concentration of the species adsorbed on the sample surface can be related to the peak intensity by Beer-Lambert law. The Beer-Lambert law relates the amount of light absorbed by a sample to the concentration of absorbing species in the sample.

\[ A = \varepsilon \cdot c \cdot l \]

Where \( A \) is the absorbance, \( \varepsilon \) is a proportionality constant (absorptivity), \( c \) is the analyte concentration in the sample, \( l \) is the length of the light path.

4.2.1 Data analysis considerations

In order to investigate the inhibitors’ mechanism of interaction with the surface the analysis of FTIR spectra was focused on four points:

- \( I_s(CH_2) / I_s(CH_3) \): intensity ratio between symmetric \( CH_2 \) and \( CH_3 \) peaks, caused by resonance effect of benzene ring. This parameter can be correlated to the tilting of the molecule with respect to the surface. When it changes with time it means that also the inclination of the molecule on the surface is changing, on the contrary if it stays constant no sensible variation in inclination is present; [65]

- Benzene ring: the benzene peak area, related to benzene ring physisorption, was measured. Since each molecule is benzene-substituted the benzene peak intensity can be related to the
amount of the molecules adsorbed on the surface and their actual closeness (and possibly interaction) to the surface. Wavenumbers: 1450 cm\(^{-1}\) – 1600 cm\(^{-1}\) \[66\]

- Tertiary amine: based on DFT calculation these inhibitor molecules may strongly interact with the surface once deprotonated, then when they are in protonated or neutral state. Therefore the peak area related to tertiary amine was measured. An increase in this peak could mean that molecules deprotonation occurred and the nitrogen atom formed a new bond; \[1\] [40]
Wavenumbers: about 1200 cm\(^{-1}\) \[66\]

- N-O bond: the peak are related to this bond was calculated to investigate if chemical bonds are formed with the surface. Wavenumbers: 1250 cm\(^{-1}\) – 1265 cm\(^{-1}\) \[67\]

4.2.2 FTIR analysis: benzimidazole on pure copper

Looking at Fig. 4.23, the plot represents the tendency of the intensity ratio between symmetric CH\(_2\) and symmetric CH\(_3\) peaks. It is clear that their ratio is always almost constant and stays in a values range between 1 and 1,1. Considering its evolution in time, it can be noticed that with the increase of time the oscillations are progressively reduced. This shows an adjustment in the tilt angle of the molecule.

\[\text{Fig. 4.23} \quad \text{CH}_2 / \text{CH}_3 \text{ peak intensity ratio plot from benzimidazole FTIR spectrum}\]
Regarding the benzene ring signal, it was found in the spectrum, but since its intensity was partially masked by the baseline noise, it is not presented in the results to avoid evaluation errors.

Considering the tertiary amine peak, the trend of the related peak area is depicted in Fig. 4.24. After an initial constant oscillation around value 0.5 the calculated peak area starts to increase developing a clear up-trend.

![Fig. 4.24 – Tertiary amine peak area plot from Benzimidazole FTIR spectrum](image)

The peak area was calculated as Fig. 4.25 depicts. First all the spectra are brought in a common scale and then the tool “automatic baseline” is applied. After that, each spectra was vertically moved in order to obtain the best overlapping of the baselines. Finally, the peak area was calculated using the “peak area tool”, available in Omnic software.

Observing Fig. 4.25 it can be noticed that some peaks present multiple shoulders. This is probably due to different vibrational modes overlapping in that region.
In Fig. 4.26 is represented the trend of the peak area related to N-O bond. A clear up-trend can be observed. During the first 30 minutes no sensible variation is detected. After 40 min of exposure the amount of N-O bonds increases steadily until 110 min when it seems to reach a constant value.
4.2.3 FTIR analysis: methyl-benzimidazole on pure copper

The plot in Fig. 4.27 shows a steady line for methyl-benzimidazole, no clear trend can be recognized.

![Fig. 4.27 - CH₂ / CH₃ peak intensity ratio plot from methyl-benzimidazole FTIR spectrum](image)

Regarding benzene, tertiary amine and N-O bong signals no clear peaks are observed, as shown in Fig. 4.28, representing the FTIR spectrum in the wavenumbers range 1000 cm⁻¹ – 1600 cm⁻¹.

![Fig. 4.28 – FTIR spectrum for methyl-benzimidazole, range 1000 cm⁻¹ – 1600 cm⁻¹](image)
4.2.4 FTIR analysis: benzotriazole on pure copper

Considering the peak intensity ratio for benzotriazole (Fig. 4.29), even though also in this case the oscillation in values of the data points stays inside a quite narrow range, it can be noticed that with the increasing of the time also the amplitude of these oscillations increases. It can be observed that during the first 50 hours the calculated ratio is approximately constant and later it starts to move enlarging the oscillation range.

![Fig. 4.29 - CH₂ / CH₃ peak intensity ratio plot from benzotriazole FTIR spectrum](image)

Observing the FTIR spectrum depicted in Fig. 4.30 it is clear that the peaks corresponding to benzene ring, tertiary amine and N-O bond cannot be measured with sufficient accuracy. The strong noise registered indeed masks the first one. The tertiary amine, on the contrary, can be slightly observed due to its extremely low intensity and therefore it was not possible to measure its peak intensity or area without commits strong evaluation errors. Regarding the signal related to N-O bond it is cannot be detected since it is probably lower than the detection limit of the machine.

The noise clearly observed in Fig. 4.30 from 1900 cm⁻¹ and 1300 cm⁻¹ and slightly extending beyond these limits, it is probably related to oxide and hydrated oxide layers on the surface. [68]
4.2.5 FTIR analysis: methyl-benzotriazole on pure copper

A trend similar to that one already seen for methyl-benzimidazole is shown in Fig. 4.31. Except for the first data point in which the intensity calculated for both CH$_2$ and CH$_3$ symmetric peaks is the same, all the other values are particularly constant, oscillating inside the range 1.04 – 1.06.

![Fig. 4.31 - CH$_2$ / CH$_3$ peak intensity ratio plot from methyl-benzotriazole FTIR spectrum](image)

Regarding benzene, tertiary amine and N-O bond peaks their intensity is not sufficiently high to be considered (Fig. 4.32). Only two measurements (50 min and 60 min) show a peak intensity high...
enough to be distinguished with respect to the others. As consequence no clear trend was observed.

4.2.6 FTIR analysis: indazole on pure copper

Observing the plot shown in Fig. 4.33 it can be seen that the peak ratio measured for indazole is almost constant. Anyway looking carefully at the graph two clear changes can be seen. The first one occurs after 10 minutes of exposure when the line moves below 1,05 and stay steadily around 1,02 until 60 minutes. The second clear change occurs at 70 minutes of exposure. From that moment all the following data values lean in very narrow range around 1,06.

Although these changes are not particularly strong, they can indicate a slight change in tilt angle of the molecules.
In Fig. 4.34 the peak area related to benzene ring is plotted. During the first 50 minutes a steady increase can be observed followed by a spike at 70 minutes of exposure. After that the peak area slowly decreases and finally reaches a constant value, around 3, for the last 30 minutes.

Considering now the tertiary amine peak area plot (Fig. 4.35) and the N-O bond plot (in Fig. 4.36) a trend similar to that one already seen for benzene ring can be observed. Both plots constantly increase until 60 minutes of exposure are reached. They both reach their maximum values around 70-80 minutes and then they slightly decrease. Considering Fig. 4.35 during the last 20 minutes the
peak area is kept approximately constant at high values. On the contrary in the N-O bond plot a slight lowering is observed.

**Fig. 4.35** – Tertiary amine peak area plot from indazole FTIR spectrum

**Fig. 4.36** – N-O bond peak area plot from indazole FTIR spectrum
4.2.7 Experimental notes

Fringing effect

Analysing FTIR spectra of thin film on thick substrates it is possible to observe strong interference fringes that hinder the spectra reading covering the original peaks. The fringes can be recognised from their quasi-sinusoidal shape superimposed on the real spectrum. This phenomena, usually observed in Transmission-FTIR is generated by interferences of IR beams reflected at film surface and film-substrates interface or also by interferences of multiple beams reflected in the substrate. [69][70]

Although this phenomena is generally found in transmission FTIR measurement it was pointed out that it is possible to occur even in absorbance-type tests.

During ex-situ measurements fringing effect was observed in the range 3200 cm$^{-1}$ – 1000 cm$^{-1}$, therefore hindering the spectra analysis.

The ex-situ tests were performed exposing a polished copper sample (the same described at paragraph 3.1) for 30 minutes to THF solution containing inhibitor with 3mM concentration. After the exposure the sample was gently rinsed with pure THF for 3 seconds and then dried out using a soft flux of N$_2$ gas. Right after the exposure the sample was placed on the FTIR accessory and the experiment was started.

Aiming to remove the fringing effect the test was repeated in different ways. First it was performed again in the same condition, then increasing the exposure time to the solution and finally using a different accessory. In the end it was not possible to obtain a satisfying result and it was decided not to include the ex-situ results in this thesis work.

Since ex-situ tests were performed with the purpose to give an overview about how inhibitor molecules could interact with the sample surface and use them as basis for interpretation of in-situ results, the lack of information was partially covered using the several papers published in specific topic by A. Kokalj, I. Milošev et. altr, partner of this project, from Jožef Stefan Institute, Department of Physical and Organic Chemistry, Ljubljana, Slovenia. In this paper the interfacial bonding of these
inhibitors is investigated applying Density Functional Theory (DFT) simulation, providing an idea on how theses type of molecules could interact with the surface.

![Fig. 4.37 – Example of fringing effect](image)

**4.2.8 Data discussion and summary**

- $I_s(\text{CH}_2) / I_s(\text{CH}_3)$: The calculated ratio stays stable for almost all the inhibitors. Only considering benzotriazole it is seems that the oscillations of molecule angle increases with time;

- The tertiary amine peak can be clearly observed only for benzimidazole and indazole spectra. In case of methyl-benzotriazole, methyl-benzimidazole and benzotriazole they slightly appear or not at all. Some clarifications are required. Considering the first two inhibitors the baseline is clean and perfectly stable, whereas for benzotriazole a strong noise is present partially masking the signal;

- N-O bond peak is clearly present in benzimidazole and indazole spectra. As for amine peak, methyl-benzimidazole and methyl-benzotriazole do not show a strong clear peak. Benzotriazole spectrum does not show this peak;

- Benzene peak can be clearly observed only for indazole and partially for benzimidazole.
Chapter 5 – Conclusions

In this chapter main conclusions and hypothesis on how these inhibitors interact with the surface are drawn.

LPR results presented in chapter 4 clearly demonstrated that the five molecules performed the best when employed on pure copper and alloys containing a lower concentration of zinc. It is therefore assumed that molecules-surface interactions, providing corrosion protection, are mainly occurring on copper.

A first distinction should be introduced among those inhibitors that showed good corrosion protection performances and those characterized by a poor protection behaviour and slight or almost no interaction with the surface. Methyl-benzimidazole and methyl-benzotriazole are ascribed to this second category of inhibitors.

5.1 Poor corrosion inhibitors: methyl-benzimidazole and methyl-benzotriazole

These two molecules have as common feature the presence of a methyl group as substituent. Different studies have shown how the steric hinderance produced by the presence of such substituents in azole ring can hinder strong interaction with the surface.[41][62] The presence of methyl groups indeed blocks one of the possible coordination sites reducing the probability of the molecule to be deprotonated and chemisorbed on the surface. N. Kovačević et altri studied a methyl-substituted imidazole molecule. They observed that, although imidazole-based molecules in general behaved well as corrosion inhibitors, the effect on corrosion protection on copper of the methyl-substituted molecule was unfavourable, in all the possible concentrations. In particular when the inhibitor was added to a concentration lower than 1mM, a slightly disadvantageous effect was obtained, whereas when the concentration was higher than 10mM a strongly detrimental effect was recorded.[41] These results further confirm the negative effect of methyl substituents when added to the azole ring.

Therefore a fundamental factor able to promote a good corrosion protection behaviour or not can be found in the position of the methyl-group. It is shown that when the methyl group is bonded in position 1- or 2- in the azole ring, it prevents the formation of the protective layer, whereas when
substituted in the benzene ring, it promotes the formation of a stable layer on the surface (as shown in Fig. 5.1).[62] This further confirms the importance of azole ring on inhibition performances.

![Fig. 5.1 – A) 1-methyl-benzimidazole, B) 6-methyl-benzimidazole](image)

However when conditions are favourable, it is possible that these molecules are physiosorbed on the surface forming week interactions. Methyl-benzimidazole partially forms a layer on the surface, but it is probably quickly desorbed, since physisorption interactions can be ascribed as metastable condition.[1] In support of this argument FTIR data for this inhibitor does not show particular interactions, strengthening the hypothesis according to which the inhibitor only weakly interact with the surface (Fig 4.32, Fig. 4.28).

To methyl-benzotriazole can be ascribed a similar behaviour. EIS study displays a partial film formation (see paragraph 4.1.2.4) and FTIR results show weak peaks (Fig. 4.32). Although this seems in contrast with LPR measurements, this could actually explain its poor performances since the formation of an heterogeneous film could promote a localized corrosion attack with consequent boost of the corrosion rate. Furthermore N. Kovačević et al. showed that methyl groups favour complexation, forming cupric complexes with hydrated Cu$^{2+}$ ions. [41] This would promote dissolution of copper, consequently enhancing the corrosive behaviour.

All these effect combined explain the poor performances showed by these two inhibitors.

### 5.2 High performance corrosion inhibitors: benzimidazole, benzotriazole and indazole

All these three inhibitors showed good protection effectiveness and in particular indazole performed in excellent way. Several studies confirmed that benzimidazole and benzotriazole in deprotonated form have the tendency to form strong chemical bonds with copper surface. [40][1] It was also stated
that when these molecules are in neutral form they interact only in weak way (if compared to deprotonated state). They weakly adsorbed on the surface via pyridine type atom or, in case of benzimidazole, it can be physisorbed nearly parallel to the surface. [38]

Considering benzimidazole EIS data, it is shown the formation of a stable layer on the surface that increases with time (see paragraph 4.1.2.1). The interaction between this inhibitor and the surface is confirmed by FTIR spectrum showing a clear increase in tertiary amine and N-O bond peaks, Fig. 5.2.

![FTIR spectrum for benzimidazole](image)

**Fig. 5.2** - FTIR spectrum for benzimidazole, range 1120 cm\(^{-1}\) – 1260 cm\(^{-1}\)

Fig. 5.3 shows interactions of benzimidazole (A) and benzotriazole (B) molecules on copper simulated by DFT calculations, showing that these molecules are preferentially adsorbed perpendicularly. [40] Since benzotriazole interacts with two nitrogen atoms with the surface it results to be bonded in stronger way with respect to benzimidazole. As extension of this reasoning, it may considered that indazole behaves in similar way. Both indazole and benzotriazole have indeed consecutive nitrogen bonds that allow stronger interaction with the surface.
Indazole in particular shows the best corrosion protection effect and a constant build-up of the film on the surface as shown by EIS analysis (see paragraph 4.1.2.5). FTIR spectra shown in Fig 5.4 and Fig 5.5 demonstrate clear interactions. The progressive increase of benzene ring peak area can be related to the increase of the amount of molecules close to the surface. The actual presence of chemical interactions created by the inhibitor with the surface is confirmed by the clear peaks related to tertiary amine and N-O bond. The first one confirms the deprotonation of the molecule and the coordination of a different atom with the amine type nitrogen, the second one demonstrates the formation of bonds between the nitrogen and copper oxide present on the surface. Furthermore the constant peak intensity ratio (Fig.4.33), I₃(CH₂) / I₃(CH₃), strengthens the interpretation according to which indazole creates two bonds with the two consecutive nitrogen atoms, therefore strongly reducing the possibility of a change of angle.
Fig. 5.4 - FTIR spectrum for indazole, range 1140 cm$^{-1}$ – 1340 cm$^{-1}$

Fig. 5.5 - FTIR spectrum for indazole, range 1400 cm$^{-1}$ – 1540 cm$^{-1}$
In Fig. 5.6, 5.7 and 5.8 the proposed interaction reactions respectively for indazole, benzotriazole and benzimidazole are presented. The molecules first interact with the solvent undergoing to deprotonation reaction. Consequently the nitrogen atom interacts with the oxide on the surface. Also Cu-N bonds, with formation of organometallic complexes, were considered to occur but the only employment of in-situ FTIR technique does not allow their recognition.

![Fig. 5.6 – Deprotonation reaction and coordination with the surface for indazole](image)

The difference in corrosion protection performance observed during linear polarization tests between indazole and benzotriazole may be explained considering the amount of nitrogen atoms present in the azole ring. As stated above, thanks to their consecutive nitrogen atoms they are both able to form two bonds with the surface. Anyway in indazole the negative charges are fully localized at the bottom zone, represented by the two nitrogen atoms. In this way the charges are as close as possible to the surface generating a stronger interaction. On the contrary, benzotriazole structure allows delocalization of charges along the two bonds and therefore the third nitrogen atom may prevent the interaction disturbing the polarity of the molecule. Consequently the interaction with the surface results weaker, with respect to that one created by indazole. Furthermore DFT calculation demonstrated that, the higher the number of nitrogen atoms in the azole ring, the lower the magnitude of interaction energy. [71]

![Fig. 5.7 – Deprotonation reaction and coordination with the surface for benzotriazole](image)
Considering now benzimidazole, although the number of nitrogen atoms in the azole ring is the same of indazole their placing favour the formation of a single bond with the surface. This still allows the formation of a film, but with lower strength and therefore reduced protection performances.

![Fig. 5.8 – Deprotonation reaction and coordination with the surface for benzimidazole](image)

5.3 Future works

The main focus of this study was to investigate the corrosion protection performances and mechanism of interaction of azole-based corrosion inhibitors. For this work different techniques were applied on five different inhibitors (Benzimidazole, methyl-Benzimidazole, benzotriazole, methyl-benzotriazole, indazole) in combination with 4 different type of materials (pure Cu, Cu alloys 10% Zn, 30% Zn, pure Zn). The available time and work was therefore spread all over the several tests required, reducing the possibility to study more in depth the mechanisms occurring between molecules and surface.

From this thesis work clearly comes out the importance of the substituent type, coordinated with the azole molecule and its position in the molecule. An improvement in this field may be obtained studying the effects of different substituents and their position in a single azole molecules, as already partially done in [62] [38] [41].
A further step in this may be that one to take in consideration the different phases that can be formed at varying of Zn concentration. Different phases could lead to different interaction with the inhibitor molecules and therefore a better or worse corrosion protection effectiveness.

In addition to those ones already employed in this study different techniques able to investigate the composition of the compounds formed on the surface and quantify the interfaces, such as XPS or Auger spectroscopy, could be used. In this way more information could be provided regarding the formation of organometallic compounds and interaction between copper oxide and the inhibitor molecules.
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