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Chapter

Green Inhibitors to Reduce the Corrosion Damage

Said Abbout

Abstract

Over the last years, corrosion phenomenon is an important economical and lives lost, which calls in the last decades researches on its final resolution by various techniques. Through this book chapter, we present one of the most used methods to protect the metals: the corrosion inhibitor. We have presented the classification (liquid and gas phase), action mode (adsorption, barrier, reinforcing of the oxide layer, passivation, and formed insoluble complex), the application fields (water treatment, petroleum industry), and some particular inhibitors. In addition, we present a case study using a green corrosion inhibitor (GCI) prepared from the oil of Ceratonia siliqua L. seeds.

Keywords: corrosion inhibitor, volatile corrosion inhibitors, Ceratonia siliqua L., polarization and impedance measurements

1. Introduction

Corrosion is an unstoppable phenomenon, in order to avoid or reduce the corrosion of metallic materials; the corrosion inhibitor is one of the most effective and flexible means of corrosion prevention and mitigation [1].

2. Generalities about the corrosion inhibitors

2.1 Definition and functions necessary in the corrosion inhibitor

According to ISO 8044, the corrosion inhibitor is a chemical substance added to the corrosion system at a concentration chosen for its effectiveness; this causes a decrease in the corrosion rate of the metal without significantly modifying the concentration of any corrosive agent contained in the aggressive medium [2]. In addition, this role can be assured by other ways such as modification of the pH and incorporation of some metals like zinc in the chemical composition of the materials. In fact, such a definition cannot be perfect; however, it avoids to consider inhibitors as additives.

From this definition, a corrosion inhibitor must therefore verify some fundamental properties:

- Decreasing the corrosion rate of the metal while retaining the physicochemical characteristics of the latter
Corrosion

- Stable in the presence of other constituents, in particular with respect to certain biocides
- Stable in the temperature range used
- Effective at low concentrations
- Inexpensive compared to the savings it allows to achieve
- Compatible with the current standards of nontoxicity and environmental protection

2.2 Utilization conditions

A corrosion inhibitor can be used as method of protection:

- As a permanent protection, the inhibitor allows the use of metallic materials (non-alloyed ferrous example) under satisfactory conditions of resistance to corrosion [3].

- As a temporary protection during a period when the piece or installation is particularly susceptible to corrosion (storage, stripping, cleaning) [4]. In this case, the control of the system is a priori simpler, and the prediction of the behavior of the inhibitor over the time being is easier to carry out.

- As a supplementary protection to improve the resistance against the corrosion, in the case of the surface coating [5].

3. Classification of the corrosion inhibitors

Various authors have classified the corrosion inhibitors differently. Some authors prefer to group the inhibitors by their chemical functionality (organic or inorganic), others by their electrochemical reaction. Figure 1 presents the classification of the corrosion inhibitors.

Figure 1. Corrosion inhibitor classification.
3.1 Liquid phase

The corrosion inhibitors can be classified in the liquid phase as a cathodic, anodic, or mixed.

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the cathodic surface and limit the diffusion of aggressive species to these areas, which means a shift of the corrosion potential to a more negative potential (more than 85 mV) and a decrease in the cathodic current density. Cathodic inhibitors can provide inhibition by two different mechanisms: as cathodic poisons and as cathodic precipitates. Some cathodic inhibitors, such as arsenic and antimony compounds, work by making the combination and discharge of hydrogen more difficult. Other cathodic inhibitors, such as calcium ions, zinc ions, or magnesium ions, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite (Na$_2$SO$_3$) [6] (Figure 2).

Anodic (or passivating) inhibitors cause a large anodic shift of the corrosion potential to a more positive potential (more than 85 mV), forcing the metallic surface into the passivation range (slow the anodic reaction). There are two types of passivating inhibitors: oxidizing anions, such as chromate and nitrate, which can passivate steel in the absence of oxygen and the nonoxidizing ions, such as phosphate, tungstate, and molybdate, which require the presence of oxygen to passivate steel [7].

Anodic inhibitors can actually cause pitting and accelerate corrosion when concentrations fall below minimum limits. This kind of problem is not encountered in the case of cathodic inhibitors (Figure 3).

Figure 2. Effect of addition of the cathodic inhibitor.

Figure 3. Effect of addition of the anodic inhibitor.
Mixed inhibitors can decrease the cathodic and anodic reaction rates at the same time because they affect the oxidation and reduction reaction, with little change in the corrosion potential (less than 85 mV around the corrosion potential) [6] (Figure 4).

3.1.1 Action mode of the corrosion inhibitors in liquid phase

Each type of inhibitor is characterized by its action mode: adsorption, barrier, reinforcing of the oxide layer, passivation, and formed insoluble complex.

In the case of the interposition of a barrier between the metal and the corrosive medium, which is essential in acidic backgrounds, the role of adsorption of the compounds on the surface is essential.

The reinforcement of a pre-existing barrier, in general the oxide or hydroxide layer formed naturally in a neutral or alkaline medium, may consist of an extension of the oxide to the surface or of the precipitation of salts with weak places of the oxide, these salts being corrosive agents.

The formation of the barrier by interaction between the inhibitor and one or more species of the corrosive medium is a type of mechanism which is also specific for neutral or alkaline media.

Obviously, taking into these general notions, the mechanism of action of an inhibitor can be considered under two aspects: a mechanistic aspect (intervention in the fundamental corrosion processes) and a morphological aspect (intervention of the inhibitory molecule in the interfacial structure). It is also clear that the mechanism of action will differentiate strongly depending on the pH characteristics of the medium.

3.2 Gas phase: volatile corrosion inhibitors

Volatile corrosion inhibitor is referred to as gas molecules used as a corrosion inhibitor; they are intended for the temporary protection of metallic materials placed in the atmosphere, essentially in storage or transport condition. Their use is made either in the form of wrapping papers impregnated with product or in the form of powder or by spraying with a solution (volatile solvent) [8] (Figure 5).

Vapor phase inhibitors (VPI) or volatile corrosion inhibitors (VCI) are low nitrogen base salts (cyclohexylamine, dicyclohexylamine, guanidine), and weak acids (nitrous acid, carbonic acid, benzoic acid). The organic part ensures volatility and a certain protective power, and the inorganic part adjusts the volatility, which must correspond to vapor pressures between $10^{-4}$ and $10^{-2}$ mmHg at room temperature, and ensures the supply of groups of protectors (Ph-COO−...).
The inhibitor molecules act by different ways; they are transported or dissociated on the metal surface to ensure an excellent protection by:

- pH effect
- Adsorption leading to hydrophobization of the surface
- Effect on electrochemical processes, essentially on the anodic process: blocking of sites or passivation

The adsorption is more of a chemical type, and the molecule is difficult to remove afterwards. Despite this, the protective action is only maintained if the source of the inhibitor is itself maintained in the immediate environment of the metal surface.

4. Particular inhibitor

The molecule inhibitors have three areas of application which are in particular important for the use of these products: the petroleum industry, water treatment, and pickling/cleaning of metals. Other applications exist for inhibitors, which involve then more specific formulations, which will be described in the following.

4.1 Inhibitors for coating

These are essentially the inhibitors added to the paints.

The incorporation of a pigment having inhibitory properties in the coating primer provides most of the corrosion resistance provided by the coating. There are two types of pigments: the active inhibitor pigment and the inactive inhibitor pigment.

The *active inhibitor pigments*, partially soluble in water, exist on the surface metal under the coating, providing active protection of the metal [9].
At the same time, it helps maintain an optimal ratio between the pigment volume concentration and the critical pigment volume concentration that means the film is not too compact to avoid blistering nor too loose to prevent the penetration of aggressive ions (Cl\(^-\)).

- **Main inhibitors used**
  - Zinc-based formulations include:
    - Zinc powder, which provides cathodic protection of the steel coated, provided that the dry extract is greater than 92% of the mass paint.
    - Zinc chromate, used because of its solubility in water; very effective in paints on aluminum, as well as strontium chromate.
  - Lead-based formulations include:
    - Lead powder, whose mode of action is complex and passing probably by modifying the pH of the aqueous medium on contact paint (alkalization) and metal and reverse polarity between iron and lead, explaining cathodic protection of the ferrous material.
    - Lead oxide Pb\(_3\)O\(_4\), many mechanisms of action are proposed: formation of mixed protective layers of PbO oxide corrosion products, formation of soaps with constituents of paint, etc.

  The inactive inhibitor pigments are essentially iron oxides, natural or synthetic, whose role is only to adjust the pigment volume concentration around the critical concentration.

### 5. Inhibitors for industrial section

Although their use could theoretically be envisaged in most cases of corrosion (with, as main limitations, too large volume of the corrosive medium or the possible impossibility of incorporating additives therein), inhibitors have several traditional application fields [10]:

- **Water treatment** (sanitary water, industrial process water, boiler water, etc.).

- **Petroleum industry**: drilling, extraction, refining, storage, and transport; at all stages of this industry, the use of corrosion inhibitors is essential for the safeguarding of installations.

- **Temporary protection of metals**, whether during acid pickling and cleaning of installations or storage in the atmosphere (volatile inhibitors, incorporation into oils and greases for temporary protection) or for the treatment of cutting oils.

- **Paint industry** on metals where the inhibitors are additives ensuring the anticorrosion protection of metals.
6. Green corrosion inhibitors (GCI)

GCI is the molecule extract from plants; it has a double effect because it has a good ability to protect the metals and no negative effect on the environment at the same time.

In the last few years, the researcher community had oriented to inhibitors extracted from plants such as essential and vegetable oil, flavonoids, coumarins, steroids, terpenoids, and condensed tannins. These substances are excellent inhibitors because they contain heteroatoms such as N, O, P, and S. The free electrons on the heteroatoms form bonds with the electrons on the metal surface. Some atoms in water ionize to release a proton; thus, the now negatively charged heteroatom helps to free an electron on the heteroatom and forms a stronger bond with the metallic electrons. These properties confer them good inhibition properties.

The following table summarized some green inhibitors used for corrosion inhibition of steels, steel alloys, aluminums, aluminum alloys, and other metals and alloys (Table 1).

<table>
<thead>
<tr>
<th>Metal</th>
<th>Inhibitor source</th>
<th>Active ingredient</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel</td>
<td>Tamarind</td>
<td></td>
<td>[11]</td>
</tr>
<tr>
<td>Steel</td>
<td>Tea leaves</td>
<td></td>
<td>[12]</td>
</tr>
<tr>
<td>C-steel, Ni, Zn</td>
<td>Eucalyptus oil</td>
<td>Monomtrene 1,8-cineole</td>
<td>[13]</td>
</tr>
<tr>
<td>C-steel, Ni, Zn</td>
<td>Lawsonia extract (henna)</td>
<td>Lawsone (2-hydroxy-1,4-napthoquinone resin and tannin, coumarine, Gallic, acid, and sterol)</td>
<td>[14]</td>
</tr>
<tr>
<td>Mild steel</td>
<td>Gum exudate</td>
<td>Hexuronic acid, neutral sugar residues, volatile monoterpenes, canaric and related triterpene acids, reducing and nonreducing sugars</td>
<td>[15]</td>
</tr>
<tr>
<td>Mild steel</td>
<td>Garcinia kola seed</td>
<td>Primary and secondary amines</td>
<td>[16]</td>
</tr>
<tr>
<td>Steel</td>
<td>Aloe leaves</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Steel</td>
<td>Mango/orange peels</td>
<td></td>
<td>[18]</td>
</tr>
<tr>
<td>Steel</td>
<td>Hibiscus sabdariffa (Calyx extract) in 1 M H$_2$SO$_4$ and 2 M HCl solutions, stock 10–50%</td>
<td>Molecular protonated organic species in the extract. Ascorbic acid, amino acids, flavonoids, Pigments and carotene</td>
<td>[19]</td>
</tr>
<tr>
<td>Al-Mg alloy</td>
<td>Aqueous extract of Rosmarinus officinalis—neutral phenol subfraction of the aqueous extract</td>
<td>Catechin</td>
<td>[20]</td>
</tr>
<tr>
<td>Al</td>
<td>Opuntia (modified stems cladodes)</td>
<td>Polysaccharide (mucilage and pectin)</td>
<td>[21]</td>
</tr>
<tr>
<td>Zn</td>
<td>Metal chelates of citric acid</td>
<td></td>
<td>[22]</td>
</tr>
<tr>
<td>Zn</td>
<td>Onion juice</td>
<td>S-containing acids (glutamy peptide) and S-(1-propenyl) L-cysteine sulfoxide, and S-2-carboxypropyl glutathione</td>
<td>[23]</td>
</tr>
<tr>
<td>Sn</td>
<td>Natural honey (acacia chestnut)</td>
<td></td>
<td>[24]</td>
</tr>
<tr>
<td>Sn</td>
<td>Black radish</td>
<td></td>
<td>[25]</td>
</tr>
</tbody>
</table>

Table 1. Green inhibitors used for corrosion inhibition of steel, steel alloys, aluminum, aluminum alloys, and other metals and alloys.
7. Green corrosion inhibitor study

In this part, we will present a study of a green corrosion inhibitor using a formulation prepared based on the *Ceratonia siliqua* L. seed oil noted FCSL in simulated acid rain solution with pH equal to 3.6. This medium is simulated to acid rain in urban zone [26].

The inhibition effect was evaluated using the electrochemical measurement such as polarization curves and spectroscopy impedance. The electrode surface was characterized by SEM/EDS.

7.1 Open circuit potential

The results of the open circuit potential (OCP) variation of the iron substrate in acidic solution in the presence and in the absence of FCSL are reported in Figure 6.

The results show that in the absence of FCSL, the potential tends to stabilize at −0.51 V, after 20 min.

The addition of the FCSL formulation leads to a shift in the corrosion potential to a positive direction. This important shift of corrosion potential may indicate an important anodic inhibiting effect of FCSL.

7.2 Potentiodynamic curves

The polarization studies of iron were carried out in acid rain solution both in the absence and in the presence of the FCSL formulation.

All of these curves were obtained after 30 min of immersion time of the electrode in electrolytic solution after performing the automatic ohmic drop compensation (ZIR).

The cathodic and anodic polarization curves of iron in simulated acid rain solution with and without various inhibition concentrations are reported in Figure 7.

![Figure 6. Variation of the open circuit potential (OCP) of the iron substrate in acidic solution with and without the FCSL formulation.](image-url)
7.2.1 The cathodic polarization

In absence of the inhibitor (Figure 7a), the corrosion current increases rapidly with the cathodic overvoltage until the potential value of $-0.8$ V/SCE; for more negative potential values, a pseudo-plateau appears in $0.4\text{ mA cm}^{-2}$, which can be attributed to the oxygen diffusion process, so the cathodic reaction can be expressed in the following equation:

$$2\text{H}_2\text{O} + \text{O}_2 + 4e^- \rightarrow 4\text{OH}^- \quad (1)$$

In the cathodic process, the important factor that must be considered is the mass transport [24].

The adding of the formulation to the corrosive solution is accompanied by both a shift of corrosion potential $E_{corr}$ toward a more positive potential and a decrease of the current density $I_{corr}$, with the disappearance of the diffusion plateau, obtained in the case of the blank solution, in the presence of the FCSL formulation. We observe the formation of the film on the area, which hinders the diffusion of dissolved oxygen toward the electrode surface.

7.2.2 The anodic polarization

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (2)$$

This behavior is associated with the presence of chloride in solution. The anodic reaction can be expressed by the following equation:

According to Figure 7b in the presence of the FCSL formulation, the current density decreases significantly with the presence of the inhibitor. Furthermore, the corrosion potential displayed more positive values, and also the value of the corrosion current density $I_{corr}$ reduced from $74.9\text{ mA cm}^{-2}$ in the absence of the inhibitor to $1.0\text{ mA cm}^{-2}$ in the presence of the inhibitor. So in less than 75 times, then we observe the appearance of a current plateau in a wide potential range.

The inhibition efficiency (% IE) was calculated using the following relation and its value of 98.6%:

$$E(\%) = \frac{i_{0}^{corr} - i_{inh}^{corr}}{i_{0}^{corr}} \times 100 \quad (3)$$
The corresponding current plateau value is in the order of 0.03 mA cm$^{-2}$ in the case of the FSCL formulation. This may indicate that the iron surface is protected by the inhibitor; this protection may be attributed to a passivity of iron substrate resulting from the formation of inhibitor film on the iron electrode surface. Thus results were observed by other authors [27].

From this result, we can conclude that the FSCL formulation is a mixed-type inhibitor that acts by decreasing the current density in both the cathodic and the anodic domains and making the corrosion potential become more anodic.

This good inhibiting effect of the FSCL formulation may be related to the adsorption on the electrode surface by the establishment of a barrier film.

### 7.3 Electrochemical impedance spectroscopy

The impedance diagrams in Nyquist and Bode plots in the absence and in the presence of the FCCL at 293 K are represented in Figure 8.

In the case of the blank solution, as shown in Figure 8, we noted the two capacity loops in the high frequencies and the inductive loop at low frequencies. This inductive effect may be due to the desorption of the H$^+$ ions and salt ions present in the solution or to the redissolution of the passivity surface [26]. In effect, this inductive loop disappeared with the addition of the inhibitor. The same behavior has been observed by other authors [27].

As shown in Figure 8, in the presence of the FCCL formulation, the size of the loops are bigger than in the case of the blank. Indeed, the polarization resistances pass from 380 Ω cm$^2$ in the case of blank to 14,080 Ω cm$^2$ in the presence of inhibitor.

The inhibition efficiency (% IE) was calculated using the following relation and its value of 97.3%:

![Figure 8. Nyquist and Bode impedance plots of the iron electrode in acidic solution with and without the FCCL.](image URL)
Green Inhibitors to Reduce the Corrosion Damage
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\[ E(\%) = \frac{R_{P_{corr}} - R_{P_{Inh}}}{R_{P_{corr}}} \times 100 \] (4)

We noted also a decrease in the electrolyte resistance which may be explicated by the presence of the ionized substances in the formulation.

We can be ascribed to the following contributions. The high-frequency contribution \((C_f, R_f)\) can be attributed to the dielectric character due to the formation of the film on the iron surface in presence of the inhibitor. The low-frequency contribution can be attributed to the double-layer capacitance \((C_{dl})\) at the electrolyte/iron interface at the bottom of the pores coupled with the charge transfer resistance \((R_t)\) [10].

7.4 Surface analysis

The aim of the surface analysis by SEM coupled with the EDX used in this study is firstly to check the hypothesis of the formation of the inhibitor on the electrode surface and secondly to verify its protective qualities against iron corrosion.

Figures 9 and 10 show the area of the substrate of iron with and without the FCSL formulation after 24 h of immersion time in the acidic solution.

In the absence of the FSCL formulation (Figure 9), the SEM examination provides that the metallic surface be heavily attacked by the corrosive ions. The EDX spectrum reported in Figure 9 showed the characteristic peaks of the specimen and marked the presence of oxygen atoms.

Also in the case of the presence the FSCL formulation (Figure 10), in the addition of the optimal concentration of the FSCL formulation into the corrosion

![Figure 9](image1.png)

Figure 9. SEM micrograph and EDS spectrum of the iron substrate in corrosive solution after 24 h of immersion time in the absence of the FCSL formulation.

![Figure 10](image2.png)

Figure 10. SEM micrograph and EDX spectrum of the iron substrate in corrosive solution after 24 h of immersion time in the presence of the FCSL formulation.
solution, a smooth surface noted could explain the good protection effect of the inhibitor by a formation of the film. As confirmed by the EDX spectrum, a very low content of oxygen species is revealed.

8. Conclusion

Corrosion is one of the most destructive phenomena that can affect metallic pieces. Through this work, we present one of the most used method to protect the metals: the corrosion inhibitor. In addition, we present a case study using a green corrosion inhibitor prepared from the oil of *Ceratonia siliqua* L. seeds.

Declaration of competing interest

The authors have declared that no conflict of interest exists.

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