

# Evaluation of the Inhibitory Properties of the Imidazole Compound ((1-[(2-Chlorophenyl)-Diphenylmethyl]Imidazole)) as an Alternative to the Protection of Corrosion in Metallic Structures Mimicking Offshore Environments

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## Abstract

With the growing oil demand, the need to obtain efficient processes during its extraction and processing has become increasingly important worldwide. When drilling on the high seas began, it was noted that there were some factors that could cause equipment wear. One such wear is seawater, a uniform saline solution consisting of sodium chloride and magnesium dissolved in water. For the oil industry, corrosion in steel is a serious problem, especially in aqueous medium. With that in mind, one of the main methods adopted by the industry is to avoid or decrease the development of corrosion reactions. These inhibitors are usually adsorbed, making a very thin and persistent film, which leads to a decrease in the corrosion rate, due to the slowing down of anodic, cathodic, or both reactions.

## Keywords

Corrosion, Inhibitors, Offshore Environment

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## 1. Introduction

Corrosion consists of a procedure of materials deterioration, that produces chemical alternations leading them to lose mass and, as a consequence, essential properties in their use, such mechanical resistance, elasticity, ductility, aesthetic, and others [1].

In the control of corrosion, we must consider the reagents (metal and corrosive environment), the mechanism in which the corrosion occurs [2] and its velocity.

The knowledge of the mechanism helps to control the reactions involving the corrosion procedure, the main mechanisms are chemical and electrochemical [3].

The industries that suffer more from these corrosive agent attacks are the petrochemical industry, which causes damage to the production chain, from its extraction until the refinery. The study of these procedures involving corrosion has grown, especially in the oil industry, which is seriously affected by this phenomenon. It is estimated that half of these materials' flaws have been the reason for the corrosion suffered. Knowledge about this phenomenon and ways to avoid it is shown as a challenge in the engineering field.

The establishment of one or more ways of protection against steel corrosion must take into account the technical and economic aspects. Among the technical aspects, the environment of the exposition is a huge important parameter. In respect of this parameter, the use of inhibitors of aggressive agents ( $\text{SO}_2$ ,  $\text{H}^+$ ,  $\text{Cl}^-$ ) is impractical in cases in which is required to protect certain metals against atmospheric corrosion.

The objective of this study is to evaluate the protective effect of a pseudo inhibitor like imidazoles in situations of corrosion, mimicking structures of steel in salt waters (offshore environment) and analyzing their respective corrosion rates.

## 2. Materials and Methods

### 2.1. Samples

#### 2.1.1. Steel Plates

The plates used (a total of 16 samples) comprehended Steel SAE 1020 with a superficial area of  $62.5 \text{ cm}^2$ , acquired commercially. All of the samples were subjected to sanding with abrasive wool steel for the removal of oxide layers, degreasing with the use of neutral surfactant for laboratory cleaning, and complete drying for the removal of potential contaminants.

#### 2.1.2. Reagents and Environment

The solutions were comprehended in salt water (AS), obtained in the city of Guarujá SP, with a conductivity approximately of  $53,000 \mu\text{S}/\text{cm}$ , and distilled water (AD) with a conductivity of  $15 \mu\text{S}/\text{cm}$ . In addition, it was introduced  $\text{Na}_2\text{CO}_3$  5% m/m of the Kitano brand was to the AS for the simulation of the presence of  $\text{CO}_2$  forming a new environment named ASB. Temperature variations have a significant impact on the performance of imidazoles as corrosion inhibitors, influencing both the stability of their adsorption onto metallic surfaces and the overall corrosion rate. Nevertheless, in the present study, all experiments were carried out under ambient temperature conditions, without simulating the thermal fluctuations typically encountered in offshore environments. This limitation highlights an opportunity for future research to investigate the thermal stability and efficacy of the inhibitor under more realistic operational conditions.

#### 2.1.3. Inhibitor

As a potential inhibitor (IP) it was used an imidazole antifungal drug of a lipo-

philic character granted by the structure (1-[(2-chlorophenyl)-diphenylmethyl]imidazole). Imidazoles are plane organic compounds, heterocyclic, aromatics with 5 members, with 2 nitrogens in their structure being one of the nitrogens pyrrole type and the other pyridine type [4]. The imidazole presents amphoteric behavior: it shows acid in the N-H bond like the pyrrole and a close basicity to the pyridine. Both molecules (imidazole and pyridine) have nitrogen as a pair of free electrons. Since it is not necessary to use these electrons to complete the system  $\pi$ , they can receive a proton composing an aromatic cation in an acid environment [5]. The IP was in pharmaceutical form assisting in its emulsifying process with the aqueous solution of action.

The selection of the compound was primarily based on the chemical characteristics of the imidazole ring, which features two nitrogen atoms within the aromatic system (one exhibiting pyridine-like behavior and the other pyrrole-like), both possessing lone pairs of electrons. These electron pairs are capable of forming coordinate covalent bonds with the metallic surface, thereby promoting the adsorption of the compound and creating a protective barrier against corrosive agents. The coordinate bonding between the nitrogen atoms of the imidazole and the vacant d-orbitals of the metal plays a critical role in preventing surface oxidation.

The chosen compound, an antifungal agent commonly known as clotrimazole, possesses a highly lipophilic structure (favoring interaction with hydrophobic, oxidized metal surfaces), stability in aqueous media, and additional aromatic groups (phenyl and chlorophenyl) that enhance its adsorption affinity. Its good solubility in aqueous and lipophilic environments facilitates homogeneous dispersion in the testing media. The compound was utilized in its pharmaceutical cream form, which facilitated emulsification in the aqueous solutions employed during the experiments.

Corrosion protection mainly occurs through the adsorption of imidazole molecules onto the metal surface, forming a stable barrier. This adsorption involves coordinate covalent bonding between the lone electron pairs on the nitrogen atoms of the imidazole ring and the vacant d-orbitals of iron atoms. Imidazole acts as a nucleophile and iron as an electrophile, resulting in a strong bond that prevents contact between the metal and corrosive agents such as  $O_2$ ,  $H_2O$ ,  $Cl^-$ ,  $CO_2$ , and  $H_2S$ . The effectiveness increases under low temperatures, on partially charged surfaces, and in the presence of aromatic groups, which enhance the adsorption area and lead to a denser protective layer [6].

## 2.2. Methodology

The analytic process consisted of the mass assistance in the oxide formation in the subjected samples to different aggressive aqueous environments for the verification of the influence of outside factors (like salinity) which were evaluated through the evolution of corrosion rates. It used the IP in order to notice its possible protective and or inhibitory action on the process. Saltwater with high electrical conductivity ( $\sim 53,000 \mu S/cm$ ) was used, close to the typical salinity of marine environments. The presence of  $CO_2$  was simulated by adding sodium bicarbonate, which represents one

of the common corrosive agents in offshore oil environments. The study incorporated control samples without the addition of the inhibitor for each testing condition. These control samples established the baseline corrosion rates, enabling a systematic comparison and quantification of the imidazole's inhibitory effectiveness. The results demonstrated substantial reductions in corrosion rates, thereby validating the inhibitor's protective performance.

### 2.3. Preparation of Samples

After the samples were properly sanded, degreased, and dried, they were weighed in an analytical balance and completely immersed, in duplicates, in solution (with and without inhibitor), and remained under rest for the seasonal assistance of corrosion rate. For each measurement, it was realized that a sanding and superficial cleaning of the sample was performed, removing the oxide layer, and it obtained information about the mass of each piece.

Each duplicate was held in a glass jar hermetically closed previously cleaned and dried, removing impurities presented, with the exception of the AR sample, which was exposed to air during the period. The samples that contained liquid were held closed during the procedure, while the samples that didn't contain liquid as a corrosive agent were held open during the process. **Table 1** shows the organization of the samples.

**Table 1.** Organization and experimental codification (Subtitle: \*\*contain; - not contain). Source: The author.

Sample	Code	Corrosive Environments				
		IP	Ar	AS	AD	ASB
1	ARIP	**	**	-	-	-
2	ARn	-	**	-	-	-
3	ASIP	**	-	**	-	-
4	ASn	-	-	**	-	-
5	ADIP	**	-	-	**	-
6	ADn	-	-	-	**	-
7	ASBIP	**	-	-	-	**
8	ASBn	-	-	-	-	**

### 2.4. Corrosion Rate

The corrosion rate expresses the speed of abrasion verified on the steel surface. The correct evaluation of the corrosion rate is, in a general way, of great importance for the determination of the lifespan of the equipment and industrial installations [7].

The corrosion rate can be calculated following the rule ASTM G31-72, through the following Equation:

$$mpy = \frac{834 \times \Delta m}{s \times t \times \rho}$$

Where:

$mpy$  = Is the loss of thickness, (thousandth of an inch per year);

$\Delta m$  = Lost of mass (mg);

$s$  = Exposed area, (in<sup>2</sup>);

$t$  = Time of exposure (h);

$\rho$  = Density of material (g/cm<sup>3</sup>).

The ASTM G31-72 standard was selected due to its status as an internationally recognized guideline for: conducting immersion corrosion tests of metals and alloys in aqueous solutions; determining corrosion rates based on mass loss (gravimetric method); and establishing standardized conditions for sample preparation, testing procedures, and result calculation to ensure comparability. The present study aimed to evaluate corrosion behavior in simulated offshore environments using static exposure, aqueous solutions, and monitoring over a period of 46 days. These experimental conditions align closely with the scope for which ASTM G31-72 was designed, namely, controlled laboratory immersion corrosion testing. Furthermore, employing this standard legitimizes the methodology used to assess the efficiency of imidazole as a corrosion inhibitor, providing a widely accepted framework for evaluating improvements in corrosion resistance.

### 3. Results and Discussions

Imidazole has these inhibitor properties as a result of the pair of free electrons in the nitrogen atom. Consequently, the compounds can adsorb themselves in a metal surface through a coordinated covalent bond which occurs among these free electrons of the nitrogen and the empty “d” orbitals of the metal. Therefore, the metal acts as an electrophile, receiving a pair of electrons and working as a Lewis acid while the molecule

acts as a nucleophile, providing a pair of electrons and consequently acting as a Lewis base [8]. Once the molecule is absorbed on the metal surface, it occurs the formation of a film that acts as a barrier against corrosive agents. This barrier can be the result of physical or chemical adsorbing. The profile of the adsorbing is influenced by the chemical structure of the inhibitor, the type of electrolyte, and the nature, and charge of the metal [9]. The strength of the covalent bond depends on the electronic and polarizability of the donator atom of the functional group [10].

Considering the mass variations suffered by the samples during a long period of time in a cumulative way, **Table 2** shows the results obtained in the duplicates.

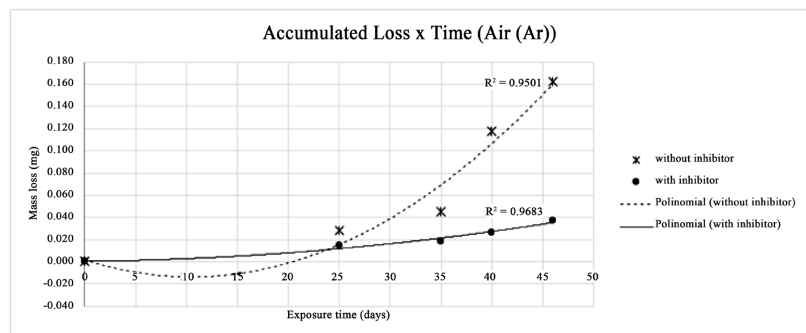
**Table 2.** Results of mass loss (in g) accumulated in relation to time. Source: The author.

Time	ARn (days)	ARIP	ASn	ASIP	ADn	ADIP	ASBn	ASBIP
0	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
25	0.028	0.015	0.055	0.040	0.083	0.085	0.039	0.015
35	0.045	0.018	0.127	0.066	0.133	0.094	0.040	0.021
40	0.118	0.026	0.156	0.086	0.171	0.115	0.048	0.028

It is possible to observe the presence of the IP in a reactionary environment has

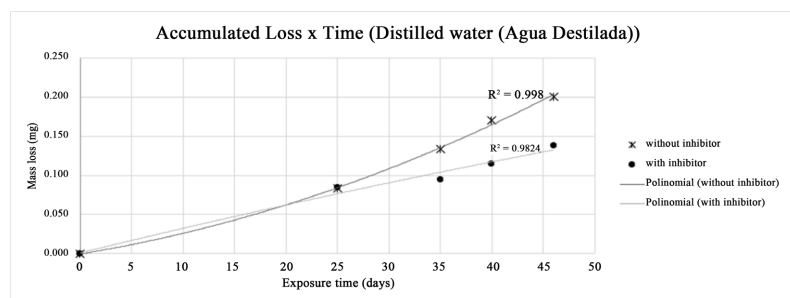
significantly decreased to the steel corrosion. This fact can be observed through the visual inspection of the sample parts at the end of the testing. The superficies of the inserted samples in the solutions containing the IP were less worn down than the immersive samples that didn't have the IP. In these cases, the brightness of the surfaces in the sample parts was noticed. The steel samples that contained bicarbonate even with the behavior of the cathodic protection provided by the salt and noticed at the head of other conditions (characterized according to Lazaris (2001) around 400 mV) obtained good results in their inhibition process in the IP addition [11].

AS specimen had a performance smaller than expected in relation to the AD, probably because of the low concentration of  $O_2$  dissolved in the reactional environment, although the  $O_2(g)$  dissolved in the air can be considered constant, its solubility in water is too low ( $0.0014 \text{ mol}\cdot\text{L}^{-1} \text{ H}_2\text{O}$  at  $20^\circ\text{C}$ ), being this one consumed rapidly on the steel surface. The  $O_2(g)$  generally is replaced naturally, but this should pass through a layer of rust even thicker to reach an exposed area even smaller, reducing the corrosion speed during a time; as the bottles were hermetically closed there was a consumption of the  $O_2$  present in the environment affecting the oxide performance in these specimens above. **Figure 1** shows a correlation of the specimens' performance submitted to air. It is noticed that the specimen with inhibitor showed a behavior almost linear in relation to its inhibitory efficiency, reducing 77.1% the corrosion in the specimens measured in the end.

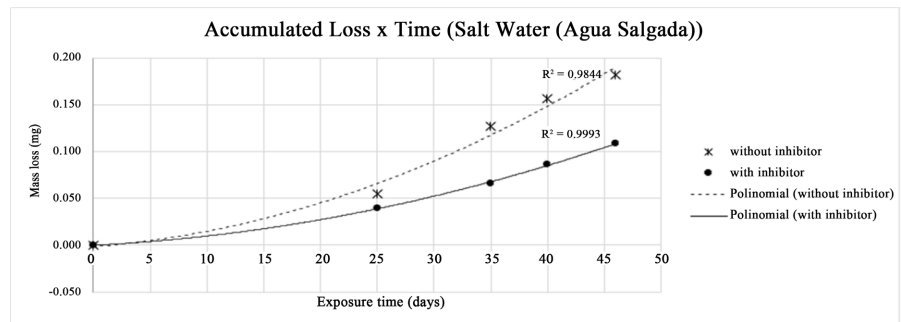


**Figure 1.** Relation between the accumulated loss (perda acumulada) in relation to the time (tempo) for the samples submitted to air.

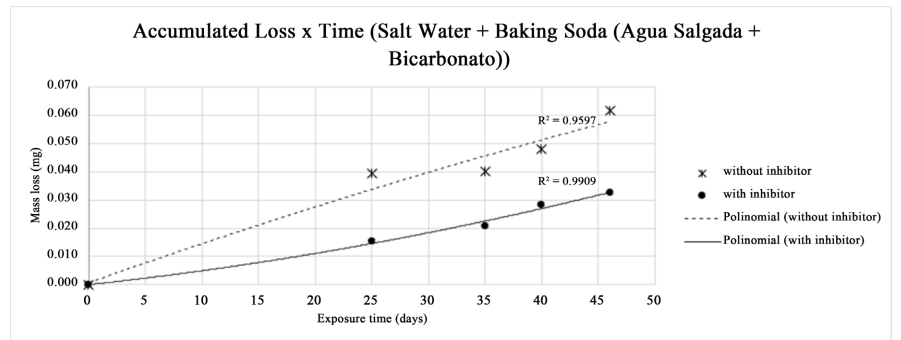
In relation to the submersed specimens all of them showed a similar behavior (**Figure 2**).



(a)



(b)



(c)

**Figure 2.** Relation between the accumulated loss in relation to the samples AD (a), AS (b) and ASB (c).

Comparing the efficiency of the inhibitor taking of the last mass result, it was noticed an inhibitory efficiency in the corrosion formation was approximately 40.5% in the AS specimen, 31.3% in the AD specimen, and 47.2% in the ASB specimen; According to Luz (2020) the density of the Steel SAE 1020 is equal to  $7.87 \text{ g/cm}^3$ , therefore it was calculated in relation to the corrosion rates shown in the specimens for the 46 days, whose results were shown in **Table 3** [12]. Pmach (2020) established that [13]:

- Low corrosion rates or equal to 5 mpy are classified as good resistance and appropriate for critical parts of the equipment;
- Higher corrosion rates than 5 mpy and lower than 50 mpy are classified as medium resistance and used in cases in which high corrosion rate is tolerated;
- Corrosion rates above than 50 mpy are classified as low resistance and the
- materials in use aren't recommended.

**Table 3.** Resistance of metals in relation of corrosion. Source: Adjusted from Pmach (2020) [13].

Sample	Corrosion rate (mpy)	Resistance of corrosion
ARIP	1.181	Good
AR	5.118	Medium
ASIP	3.425	Good
AS	5.787	Medium
ADIP	4.370	Good

**Continued**

AD	6.299	Medium
ASBIP	1.063	Good
ASB	1.929	Good

All the specimens containing the inhibitor improved the corrosion resistance in exposed conditions.

#### 4. Final Consideration

Is it important to highlight that the regime of the equipment operations has a direct influence on the corrosion. The operation, when occurs in an uneven way, performing a temperature alternation in highs and lows, increases the incidents of corrosion than when the temperature is maintained in a constant way, since this variation increases the possibility the occurrence of electrochemical corrosion due to the higher probability of the presence in water and low temperatures. The experiments mentioned, apart from the corrosion rate, were necessary for the understanding of the corrosion phenomenon in carbon steel in air, distilled water, salt water, and NaHCO<sub>3</sub>, and also to establish similarity with the experiments presented by Vaz (2011) in the reliability of the proposed results [14].

In consideration of the data presented, it was concluded that the specimens coated with the inhibitor obtained a lower corrosion rate than the specimens which weren't coated with the inhibitor, which proves its efficiency. From the deeper studies, it can be said that these methods can be used in the petroleum industries with the main to solving problems related to corrosion, as fractures and parts rupture, avoiding so, unwanted accidents. The maintenance of these materials extends the lifespan of the equipment and guarantees the safety of all individuals involved in the process, in order to reach the main objective.

#### Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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