CORROSION INHIBITION EFFECT OF THIOUREA ON MILD STEEL IN HYDROCHLORIC ACID CONTAMINATED WITH CHLORINE

Fernando B. Mainier[1,2],Alan Eduardo R. de Freitas[1,3],Marcus V. Santoro Gonçalves[1,4]
[1]Universidade Federal Fluminense, Escola de Engenharia, Niterói, RJ, Brazil
[2]fmainier@uol.com.br ; [3]alfreitas@hotmail.com ; [4]marcus.santoro@hotmail.com

ABSTRACT

Inexpensive industrial hydrochloric acid, containing chlorine (Cl2) and other chlorinated organic compound *contaminants, generally comes from the recovery of chlorinated organic compounds. The objective of this work is to evaluate, based on laboratory tests, the performance of the corrosion inhibitor (thiourea) in protecting carbon steel when immersed in hydrochloric acid contaminated with chlorine. In this evaluation, mass loss tests and electrochemical polarization tests were conducted under the following conditions: a concentration of hydrochloric acid of 5, 10, and 15% (by mass); chlorine (Cl2) was added to the acid in quantities of 50 - 5000 mg/L; the concentrations of thiourea were 250, 500, and 1000 mg/L; and the temperature was maintained at 25°C. Gravimetric and polarization tests carried out using mild steel coupons show a significant loss of thiourea inhibitory protection because there is an increase in the concentration of hydrochloric acid associated with an increase in chlorine content.*

KEYWORDS: *Corrosion inhibitors, Thiourea, Chlorine, Hydrochloric Acid, Acidification*

I. INTRODUCTION

In the last 30 years there has been a great expansion in the global production of chlorinated organic compounds [1, 2] used in several industrial segments, such as plastics (polyvinyl chloride and derivatives) and solvents. In addition, other chemical intermediates chemicals have also been produced that accelerate the production of new plastics, synthetic rubber, solvents, paints, insecticides, additives, etc. Consequently, the production of these chlorinated organic compounds has generated, directly or indirectly, hydrogen chloride – HCl(g) – and other chlorinated organic compounds as a by-product as shown in the following reaction, where RH is the organic compound, Cl_2 the chlorine, and RCl the chlorinated organic compound:

$$RH + Cl_2\,(g) \rightarrow HCl\,(g) + RCl$$

Based on the cost of the final product, technical specifications, recovery projects, and the qualifications and guidelines of environmental agencies, produced hydrogen chloride has two main industrial routes [2-6]:

- Hydrogen chloride gas is separated from the main contaminants and is then absorbed in water, producing a hydrochloric acid of 20 to 28% by mass.
- Hydrogen chloride undergoes thermal decomposition in special reactors with or without catalysts; at temperatures above 1200ºC it is transformed into chlorine and steam according to the reaction:

$$2\,HCl + \tfrac{1}{2}\,O_2 \rightarrow Cl_2 + H_2O\ (\text{steam})$$

Therefore, considering the low cost of hydrochloric acid sold on the market, it is acceptable to assume that this product comes from the direct recovery of the production of chlorinated organic compounds;

consequently, it contains chlorine contamination and chlorinated compounds. The higher the chlorine content, the lower its cost.
To minimize the attack of HCl on carbon steel, thiourea was chosen as a corrosion inhibitor: that is, an organosulfur compound whose formula is $SC[NH_2]_2$. Because the thiourea molecule contains sulfur (S) and two nitrogen (N) atoms, it can act as a good corrosion inhibitor. This type of corrosion inhibitor acts as a protective film; the strength of its adsorption bond depends on the density of the electron, the donor atom of the functional group, and also the polarization of the group [7-12].

It is important to highlight that the literature specialized in the evaluation of corrosion inhibitors develops their research based on the high purity of hydrochloric acid and the various formulations of corrosion inhibitors.

Given this fact, the objective of this laboratory work is to determine the deleterious action that hydrochloric acid containing a contaminant such as chlorine can exert on the corrosion inhibitor whose action is to protect the surface of carbon steel during acidification.

II. MATERIALS AND METHODS

2.1 Gravimetric Test

The AISI 1020 carbon steel coupons used in the gravimetric tests were made in the following dimensions: 3.17 cm (outside diameter), 0.76 cm (internal diameter), and 0.19 cm (thickness). The chemical composition of the carbon steel is presented in Table 1.

Table 1: Chemical composition (wt.%) of AISI 1020 carbon steel

C%	Mn%	Si%	S%	P%
0.22	0.56	0.040	0.030	0.006

The metal surfaces were prepared with sandpaper that ranged from grade 100 to grade 600. The surfaces were cleaned with acetone and ethanol and dried with hot air. The weights of the test coupons were recorded up to four decimal places using a digital electronic balance.

The corrosive media used were solutions of 5, 10, 15% (% mass) hydrochloric acid (HCl) of high purity and deaerated with a continuous flow of nitrogen. To these standardized solutions were added 50, 100, 500, 1000, 2000, 3000, 4000, and 5000 mg/L of chlorine (Cl_2) in the form of calcium hypochlorite to represent a commercial hydrochloric acid contaminated with chlorine. The concentrations in the experiment are referred to as chlorine (Cl_2).

The corrosion inhibitor used was thiourea which is an organosulfur compound with the formula $SC[NH_2]_2$. The concentrations in these experiments were 250, 500, and 1000 mg/L [13].

Mass loss tests were carried out by immersing the coupons in glass containers with a capacity of 500 mL containing HCl solution kept in thermostatically controlled baths at temperatures of 25°C. The coupons were completely immersed in 400 mL of acid solution, leaving the remaining capacity of the container free for the evolution of hydrogen (H_2) resulting from the acid attack. The testing times were fixed at 1 and 3 h of exposure.

Upon completion of the experiments, the coupons were removed from the corrosive medium, washed with bidistilled water and alcohol, and then quickly dried with hot air. Finally, the coupons were weighed based on the ASTM G 31-72 standard [14].

Four coupons were used to check the reproducibility of the results. The corrosion rate (CR) was defined by the following expressions [14-16]:

$$\text{Corrosion rate} = CR = (W_o - W_i)/S \ (\text{mg/cm}^2)$$

Where:

W_o and W_i are the loss weight in the absence and presence of the inhibitor;

S = area of the coupon (cm^2).

2.2 Potentiodynamic polarization measurements

Samples of carbon steel AISI 1020 were cut for the polarization measurements so as to obtain an electrode surface of 0.20 cm^2. The surface metal was then embedded in a polyester resin and polished with 400, 600, 800, and 1200 grade emery paper. It was then washed in acetone, washed in bidistilled water, and put into a cell with a volume of 400 mL.

A three-electrode cell consisting of a carbon steel working electrode (WE), a platinum counter electrode (CE), and a saturated calomel electrode (SCE) as a reference electrode was used for measurements. All experiments were performed under atmospheric conditions without stirring. A temperature of 25°C was maintained in the cell using a thermostatically controlled bath.

The polarization curves were recorded using a Type III Autolab potentiostat, by varying the potentials at a rate of 60 mV/min, carried out over a potential range of −250mV to +250mV with respect to open circuit potential.

The corrosive medium was used a solution of 10% (% mass) hydrochloric acid of high purity and deaerated with a continuous flow of nitrogen and with additions of corrosion inhibitor (thiourea in concentrations of 250, 500, and 1000 mg/L). To these standardized solutions was added chlorine (concentrations of 50, 500, and 1000 mg/L) in the form of calcium hypochlorite. Before each experiment, the electrode was allowed to corrode freely and its open circuit potential (OCP) was recorded as a function of time up to 1 h [13].

From this technique, various corrosion kinetic parameters such as I_{corr} (corrosion current densities), R_p (polarization resistance), and E_{corr} (corrosion potential) were predicted at temperatures of 25°C.

III. RESULTS AND DISCUSSION

3.1 Weight Loss Measurements

Figure 1 shows the loss of mass of coupons (average of four coupons) of carbon steel immersed in hydrochloric acid with additions of thiourea as a corrosion inhibitor. An increase in mass loss is observed with an increase in time and concentration.

The test results of mass loss of carbon steel coupons in hydrochloric acid with additions of corrosion inhibitor (thiourea) and additions of chlorine (Cl_2) and corrosion inhibitor are presented in Figures 2–7, which refer to the average of the four coupons.

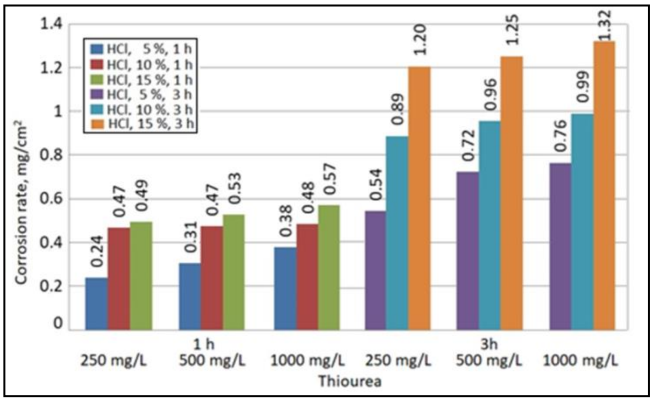

Figure 1 - Mass of carbon steel in hydrochloric acid solution with additions of thiourea at a temperature of 25°C

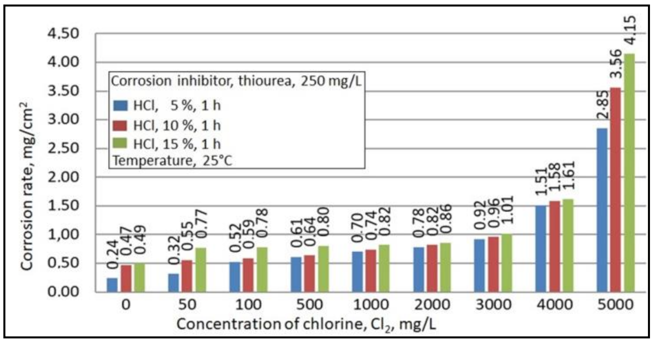

Figure 2 - Mass loss of carbon steel in hydrochloric acid solution with additions of 250 mg/L of thiourea

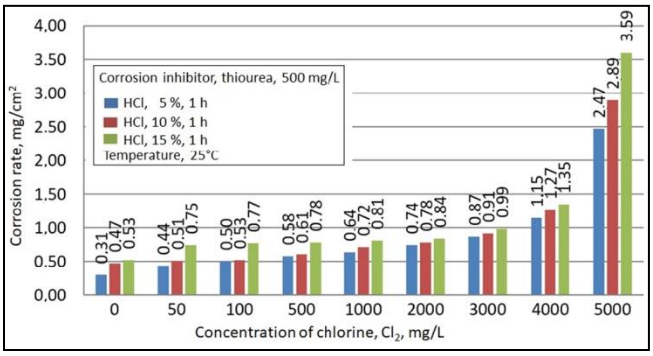

Figure 3 - Mass loss of carbon steel in hydrochloric acid solution with additions of 500 mg/L of thiourea

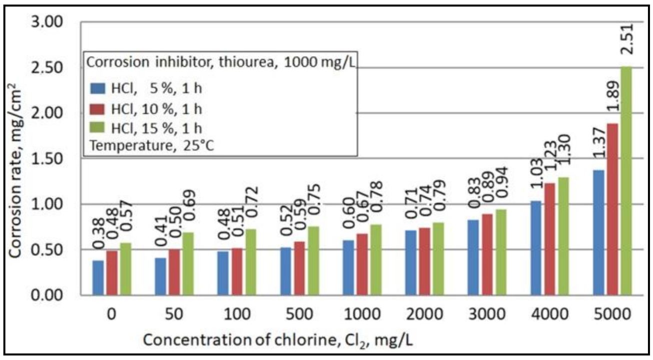

Figure 4 - Mass loss of carbon steel in hydrochloric acid solution with additions of 1000 mg/L of thiourea

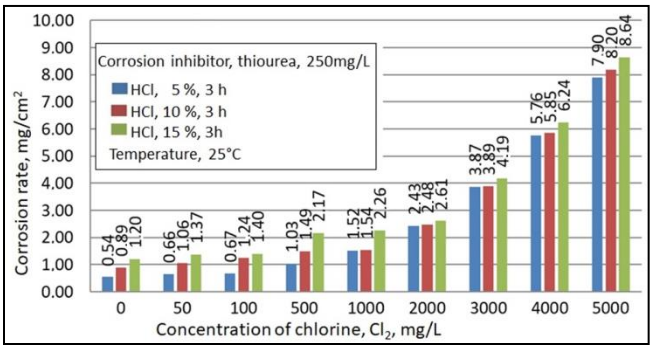

Figure 5 - Mass loss of carbon steel in hydrochloric acid solution with additions of 250 mg/L of thiourea

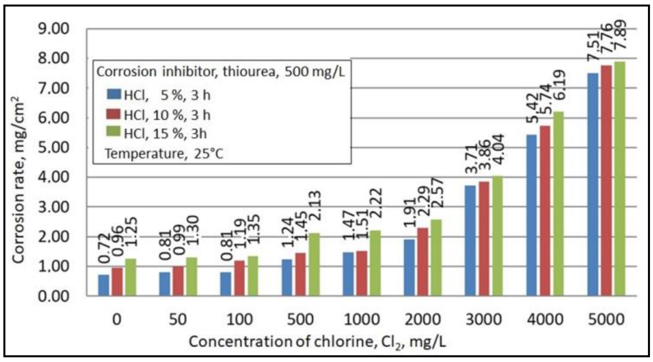

Figure 6 - Mass loss of carbon steel in hydrochloric acid solution with additions of 500 mg/L of thiourea

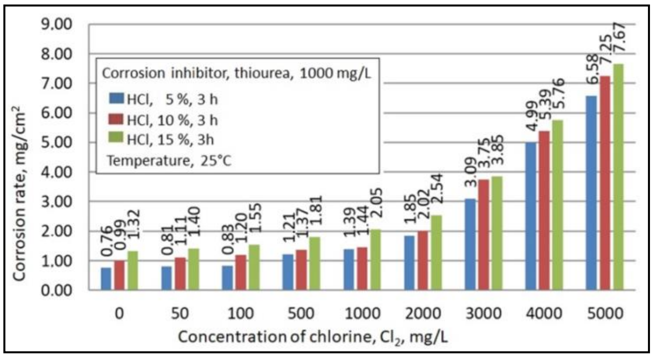

Figure 7 - Mass loss of carbon steel in hydrochloric acid solution with additions of 1000 mg/L of thiourea

The mass loss tests verify that in the concentrations of 50 and 100 mg/L of chlorine there is little influence on the performance of thiourea as a corrosion inhibitor; however, at concentrations of 500 to 5000 mg/L of chlorine, there is a significant increase in the rate of corrosion, indicating a loss of protection of the thiourea.

It can also be determined that an increase in the concentration of HCl and the time of immersion in the laboratory test intensifies the attack of chlorine and reduces the protective capacity exercised by the corrosion inhibitor.

Considering that the protection mechanism of thiourea is exercised by its adsorption [7,8] to carbon steel, it is reasonable to conclude that chlorine promotes competition on the metallic surface, consequently reducing the adsorption capacity of thiourea.

3.2 Potentiodynamic polarization measurements

The anodic and cathodic Tafel polarization curves for carbon steel in a solution of 10% (by mass) of hydrochloric acid in the presence in concentrations of thiourea (250, 500, 1000 mg/L) and chlorine (Cl_2; 50, 500, 1000 mg/L) at 25°C are shown in Figures 8 to 10.

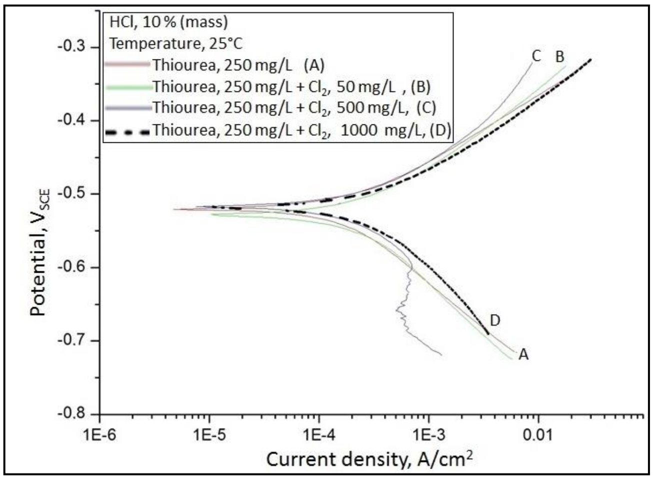

Figure 8 - Polarization curves of carbon steel in HCl 10 % (by mass) with additions of thiourea and chlorine

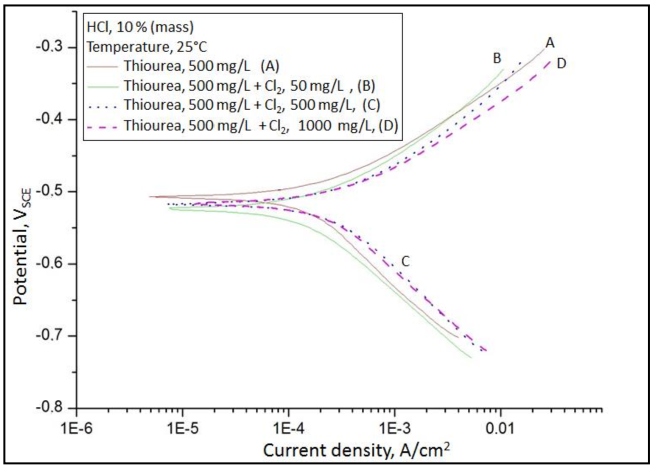

Figure 9 – Polarization curves of carbon steel in HCl 10 % (by mass) with additions of thiourea and chlorine

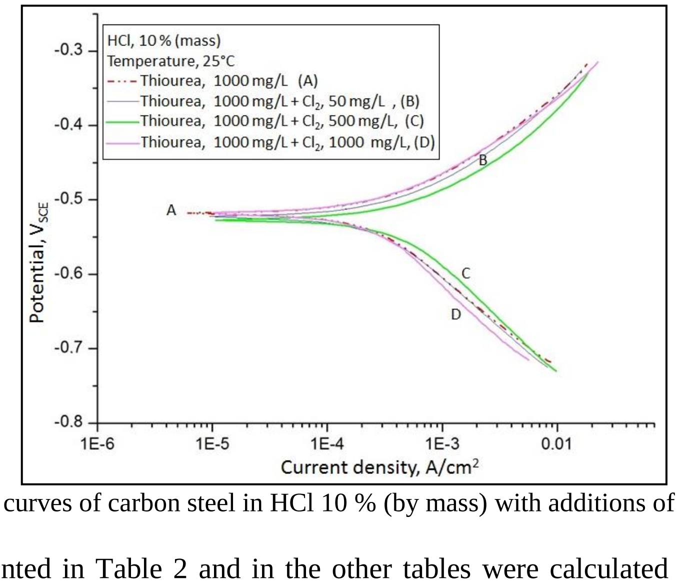

Figure 10- Polarization curves of carbon steel in HCl 10 % (by mass) with additions of thiourea and chlorine

The parameters presented in Table 2 and in the other tables were calculated from the experimental data by means of graphical data analyses using Origin Pro 8.0 software.

Table 2 - Corrosion current density (I_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) for the HCl 10 % (by mass) solution at 25°C with additions of 250 mg/L of thiourea and chorine

Chlorine (Cl_2), mg/L	I_{corr}, A/cm^2	E_{corr},V	R_p, Ω.cm^2
0	1.65 x 10^{-4}	-0.526	1132.5
50	2.37 X 10^{-4}	-0.482	600.6
500	2.36 x 10^{-4}	-0.491	595.8
1000	2.38 x 10^{-4}	-0.486	594.5

Table 3 - Corrosion current density (I_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) for the HCl 10 % (by mass) solution at 25°C with additions of 500 mg/L of thiourea and chorine

Chlorine (Cl_2), mg/L	I_{corr}, A/cm^2	E_{corr}, V	R_p, Ω.cm^2
0	1.40 X 10^{-4}	-0.509	960.2
50	1.62 X 10^{-4}	-0.516	627.7
500	2.24 x 10^{-4}	-0.518	610.3
1000	3.95 x 10^{-4}	-0.527	602.1

Table 4 - Corrosion current density (I_{corr}), corrosion potential (E_{corr}), polarization resistance (R_p) for the HCl 10 % (by mass) solution at 25°C with additions of 1000 mg/L of thiourea and chorine

Chlorine (Cl_2),mg/L	I_{corr},A/cm^2	E_{corr}, V	R_p,Ω.cm^2
0	2.16 x 10^{-4}	-0.522	895.7
50	2.57 X 10^{-4}	-0.527	542.6
500	2.46 x 10^{-4}	-0.526	504.5
1000	2.85 x 10^{-4}	-0.526	497.5

It can be verified that the polarization curves presented in Figures 8–10 have the same profile and are very close to each other, indicating that the addition of chlorine does not substantially modify the protection mechanism exerted by the thiourea molecule on the metallic surface.

The polarization resistances (Rp) obtained using Origin Pro 8.0 software decrease as chlorine is added to the acid solution containing thiourea. This result corroborates the mass loss tests in which the addition of chlorine increases the corrosion rate; that is, it reduces the efficiency of the corrosion inhibitor.

IV. CONCLUSIONS

It is important to highlight that the chlorine contained in hydrochloric acid as an industrial impurity is derived, directly or indirectly, largely from the recovery process of the production of chlorinated organic products. Such impurities can cause problems in several industrial segments.

The laboratory tests carried out show that an increase in the concentration of hydrochloric acid and chlorine significantly affects the protective effect exerted by thiourea as a corrosion inhibitor on the surface of carbon steel.

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AUTHORS

Fernando B. Mainier, Chemical Engineer, has 52 years of experience in the Academic Area (Military Institute of Engineering and Fluminense Federal University, Brazil) and actively acts in the activities of research & development in corrosion, corrosion inhibitor, materials, coatings and industrial contamination. He holds a PhD in Education, Full Professor and currently advises master's and doctoral students and teaches the disciplines of Corrosion and Environmental Control in the Graduate Courses (Fluminense Federal University) of Chemical, Civil, Assembly and Management Engineering.

Alan Eduardo R. de Freitas, Chemical Engineer, he holds a Master's degree in Chemical Engineering with an emphasis on corrosion and corrosion protection, held at the Fluminense Federal University, Brazil. He currently works in a water treatment company for industrial purposes.

Marcus Vinicius Santoro Gonçalves, Mechanical Engineer has more than 20 years of experience in materials and equipment for oil production, industrial control and industrial safety. He is part-time studying in the master's degree in materials with an emphasis on stainless steels at the Fluminense Federal University, Brazil.