Reduction of the Protective Action of Corrosion Inhibitors for Carbon Steel in Acidification by Using Hydrochloric Acid Contaminated with Chlorine

Fernando Benedicto Mainier*, Alan Eduardo R. de Freitas, Anne Aparecida M. Figueiredo and Thiago Teobaldo Silva

Engineering School, Federal Fluminense University (UFF), Niterói, Rio de Janeiro 24220-261, Brazil

Abstract: The commercial hydrochloric acid obtained by synthetic processes or from chlorinated products of recoveries shows in its final chemical composition contaminants such as chlorine and organochlorides. In acid stimulation of oil wells, hydrochloric acid is used to increase the productivity of the well by dissolving calcareous rock. However, there is increasing concern about the action of these contaminants as they can cause damage to the reservoir rock or corrosion inhibitors act on reducing its performance in corrosion protection of carbon steel pipes through which the hydrochloric acid is injected into the rock. In order to evaluate the performance of propargyl alcohol as a corrosion inhibitor, laboratory tests were carried out with hydrochloric acid solutions at concentrations of 10% (mass%) and chlorine in quantities of 50 to 5,000 mg/L. Gravimetric and electrochemical techniques showed that carbon steel coupons showed a significant reduction in the ability of corrosion inhibitors when the acid concentration and the chlorine concentration were increased. It was also verified that increasing temperature increased the corrosion rate of the system, regardless of the concentration of the corrosion inhibitor. The results showed that propargyl alcohol is efficient as a corrosion inhibitor for mild steel in hydrochloric acid solution.

Key words: Corrosion inhibitor, acid stimulation, chlorine, hydrochloric acid, carbon steel, petroleum.

1. Introduction

In industrial production of hydrochloric acid diverse processes occur that, directly or indirectly, produce an acid with a quality that depends on the raw materials and operating procedures. The hydrochloric acid produced industrially and used for pickling carbon steel artefacts comes from three main processes: the salt acid process, the synthetic process and the process of recovery of hydrochloric acid from chlorination and/or chlorine-fluoridation of organic products, represented by the reactions and simplified process shown in the flow chart below (Fig. 1).

The basic differences between the industrial processes relate to raw materials, to the reactions involved and to some operational procedures, since

the water absorption of hydrogen chloride (HCl), in gaseous form, generated in reactions in the formation of hydrochloric acid is a unitary operation identical to all processes in getting end of acid [1]. This means that the industrial routes and the raw materials used in a sense define the type and level of contaminants that constitute the final quality of the product.

Aiming to identify and quantify contaminants that may be present in commercial hydrochloric acid solutions, the following criteria are proposed. They set out the possibilities of occurrence of industrial contaminants, as well as their levels, in different industries. Tables 1 and 2 present the probability of contamination and the concentration levels which may present in chlorinated acids usually found on the international market.

Considering that currently more than 80% of hydrochloric acid produced is derived from synthetic

*Corresponding author: Fernando B. Mainier, Ph.D., professor, research fields: corrosion, corrosion protection, materials and environment.

Fig. 1 Hydrochloric acid production processes.

Table 1 Possibility of contamination of hydrochloric acid.

Possibility of contamination	Index
Probable	P
Slightly probabl	SP
Improbable	I

Table 2 Level of contamination of hydrochloric acid.

Level of contaminants (mg/L)	Index
0-1	A
1-10	B
10-100	C
100-500	D
500-1000	E
<1000	F

Table 3 Level of contamination of hydrochloric acid.

Contaminants	Contamination possibility/Contaminant level		
	Industrial process		
	Salt-acid	Synthetic	Organic chlorination
Ferrous (Fe^{2+})	L/C, D	SP/A, B	SP/A, B
Ferric (Fe^{3+})	L/C, D	SP/A, B	SP/A, B
Chlorine (Cl_2)	I	SP/A	P/F
Fluoride (F^-)	SP/A, B	I	SP/C
Sulfate (SO_4^{2-})	P/D, E	I	I
Phosphate (PO_4^{3-})	P/D, E	I	I
Nitrate (NO_3^-)	P/C, D	I	I
Sodium (Na^+)	P/B, C	I	I
Organo-chlorine (R-Cl)	I	I	P/F
Organo-fluorides (R-F)	I	I	SP/C

processes and recovery of chlorinated products it is possible to establish levels of contaminants, especially those that can affect the effectiveness of corrosion

inhibitors during the pickling of carbon steel or oil well stimulation in petroleum production.

Table 3 below provides an overview of the main contaminants that may be present in chlorinated acids on sale in international markets.

1.1 Action of Chlorine and Chlorinated Products in Acid Stimulation of Oil Wells

Acid stimulation, also called acidification, comprises the injection of hydrochloric acid into the petroleum reservoir rock to increase productivity through increasing the veins or grooves in such a way as to facilitate and increase the extraction of oil from the rock as shown in the diagram in Fig. 2. Another important point that justifies emphasis is the incrustations or deposits that occur during the production and reduce the flow of oil as shown in Fig. 3. This material consists of calcium carbonate (CaCO_3) adhering to the inner surface of the tubing and it is removed easily by injecting hydrochloric acid and adding an inhibitor to protect the inner surface of the tubing. They are usually used for 5% to 28% hydrochloric acid solutions (by mass) [2, 3].

They are usually used for 5% to 28% hydrochloric acid solutions (by mass). This acid solution is injected into the well through carbon steel tubing, standard API-N80 [4], and the addition of a corrosion inhibitor for anti-corrosion protection is essential to increase the lifecycle of this oil.

The success and importance of this operation in the

Reduction of the Protective Action of Corrosion Inhibitors for Carbon Steel in Acidification by Using Hydrochloric Acid Contaminated with Chlorine

Fig. 2 Acidification in oil well.

Fig. 2 Incrustation in tube production.

oil industry is evidenced by the development of such techniques in onshore and offshore operations, in the various types of injection equipment installed in specially adapted trucks or vessels and finally in the annual consumption of hydrochloric acid for this purpose. In Brazil, about 10% of the annual

production of hydrochloric acid is destined for the oil industry.

In acidification held in Brazil are used the standard N-1906 [5] where are presented the characteristics required for the qualification and acceptance of industrial hydrochloric acid to be used in petroleum operations. Contaminants to be determined are presented in Table 4.

As shown in Table 4, the standard does not refer to the chlorine (Cl_2) content that may present as a contaminant in the hydrochloric acid used in oil well stimulation. This fault in the specification with respect to chlorine can be dangerous in the process of acidification because the solubility of chlorine is a function of temperature, pressure and acid concentration. The properties of chlorine can promote oxidation, and the destruction and formation of organic chlorine compounds, affecting the properties of other products that are used in oil production.

2. Materials and Methods

2.1 Gravimetric Tests

The material evaluated in this work was an AISI 1020 carbon steel sheet (0.22% carbon, 0.56% Mn, 0.040% Si, 0.03% S and 0.006% P) used for manufacturing the coupons. The coupons used in the gravimetric tests (weight loss) had the following dimensions: 3.17 cm in outside diameter, 0.76 cm in internal diameter and 0.19 cm in thickness. The metal surface was prepared with grade 100 sandpaper until grade 500. The coupons were cleaned with acetone and ethanol and dried with

Table 4 Contaminants specified in standard Petrobras, Brazil N- 1906 [5].

Level of contaminants	Concentration	
	mass%	ppm (mass)
Sulfite (SO_4^{2-}), max.	0.005	50
Sulfate (SO_4^{2-}), max.	0.005	50
Phosphate (PO_4^{3-}), max.	0.020	200
Total iron, max.	0.002	20
Fluoride (F^-)	0.100	1,000
Organo-chlorine (R-Cl), max.	0.0005	5

hot air. The test coupons were weighed to the fourth decimal place with a digital electronic balance.

The corrosive medium used was a solution 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 artificially represent a commercial hydrochloric acid contaminated with chlorine. The concentrations in the experiment were referred to as chlorine (Cl_2). The concentrations of corrosion inhibitor based on propargyl alcohol (2-Propyn-ol-1) in these experiments were 250, 500 and 1,000 mg/L.

Gravimetric assays (weight loss) were performed in glass containers with a capacity of 500 mL. 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 jars were maintained at the test temperatures via a thermostatically controlled bath. The test temperature was set at either 25 °C. The times for testing were fixed at one and three hours of exposure.

Immediately after completion of the test, the coupons were removed from the corrosive medium, whereas there were no deposits have been rinsed first in water, then alcohol and quickly dried with hot air, then re-weighed with the same accuracy so the weight

loss could be determined. The difference in weight for an exposed period of one hour was taken as the total weight loss. Four coupons were used to check the reproducibility of the results. The corrosion rate (CR) was defined by the following expressions [6-8].

$$\text{Corrosion rate} = CR = \frac{W_o - W_i}{S} \quad (1)$$

where, W_o and W_i are the loss weight (mg) in the absence and presence of the inhibitor, respectively, S is the area of the coupon (cm^2), t is exposure time (h).

2.1 Electrochemical tests

Samples of AISI 1020 carbon steel for the polarization measurements were cut so as to obtain an electrode surface of 0.20 cm^2 . The metal was then embedded in polyester resin and polished with No. 600 emery paper. Next, the samples were degreased with acetone and washed in distilled water before being inserted in a conventional polarization cell as shown in Fig. 3. The polarization curves were recorded with an Autolab potentiostat (type [III]) by varying of the potentials 60 mV/min over a potential range of -250 to +250 mV with respect to open circuit potential. All measurements were carried out at a constant temperature of 25 °C and without agitation. A solution of 10% (mass%) hydrochloric acid of high purity and deaerated with continuous flow of nitrogen was used as corrosive medium, with additions of corrosion inhibitor (propargyl alcohol in concentrations

Fig. 3 Conventional polarization cell.

of 250, 500 and 1,000 mg/L) and chlorine (concentrations of 50, 500 and 1,000 mg/L) in the form of calcium hypochlorite as presented in the gravimetric testing.

With this technique, various corrosion kinetic parameters like I_{corr} , R_p (polarization resistance) and E_{corr} were predicted at temperatures such as 25 °C. From the I_{corr} values, the corrosion rate and inhibitor efficiency were calculated by the expression:

$$\theta = \frac{(I_0 - I_{inh})}{I_0} \quad (2)$$

where, I_0 and I_{inh} are the values of corrosion current of carbon steel in uninhibited and inhibited solutions, respectively.

3. Results and Discussion

3.1 Weight Loss Measurements

The test results of weight loss of carbon steel

coupons in hydrochloric acid with additions of corrosion inhibitor (propargyl alcohol) and joint additions of chlorine (Cl_2) and corrosion inhibitor are presented in Figs. 4-10 for the average of four coupons.

It can be observed that the corrosion rate values decrease with the increase of the propargyl alcohol concentrations. According to the literature [9, 10], the propargyl alcohol may be polymerized on the metal surface to protect against corrosion.

However, the corrosion rate increases in the presence of the contaminant chlorine (Cl_2). The strong oxidizing character of the chlorine molecules in acidic solution can destroy completely or in part the triple bond ($-C \equiv C-$) of the propargyl alcohol, contributing to reducing the anticorrosive capacity protection offered by the corrosion inhibitor. Increase in the concentration of the chlorine and the exposure

Fig. 4 Weight loss of carbon steel in hydrochloric acid solution with additions of propargyl alcohol.

Fig. 5 Weight loss of carbon steel in hydrochloric acid solution with additions of 250 mg/L of propargyl alcohol and chlorine at one hour.

Fig. 6 Weight loss of carbon steel in hydrochloric acid solution with additions of 500 mg/L of propargyl alcohol and chlorine at one hour.

Fig. 7 Weight loss of carbon steel in hydrochloric acid solution with additions of 1,000 mg/L of propargyl alcohol and chlorine at one hour.

Fig. 8 Weight loss of carbon steel in hydrochloric acid solution with additions of 250 mg/L of propargyl alcohol and chlorine at three hours.

time promotes the loss of protection and therefore increases the rate of corrosion [11].

3.2 Potentiodynamic Polarization Measurements

The anodic and cathodic Tafel polarization curves for carbon steel in a solution of 10% (mass) of

hydrochloric acid (HCl) in the absence and presence of concentrations of propargyl alcohol 250, 500 and 1,000 mg/L at 25 °C, are shown in Fig. 11.

Based on the graph in Fig. 11 the polarization parameters are shown in Table 5, such as: corrosion potential (E_{cor}), resistance polarization (R_p) and corrosion

Reduction of the Protective Action of Corrosion Inhibitors for Carbon Steel in Acidification by Using Hydrochloric Acid Contaminated with Chlorine

Fig. 9 Weight loss of carbon steel in hydrochloric acid solution with additions of 500 mg/L of propargyl alcohol and chlorine at three hours.

Fig. 10 Weight loss of carbon steel in hydrochloric acid solution with additions of 1000 mg/L of propargyl alcohol and chlorine at three hours.

Fig. 11 Polarization curves of carbon steel in HCl 10% (mass) with additions of propargyl alcohol.

Table 5 Polarization of carbon steel in hydrochloric acid and additions of propargyl alcohol.

Inhib mg/L	i_{cor} (A)	I_{cor} (A/cm ²)	E_{cor} (V)	E_{cor} Calc, V	R_p (Ω)	Efficiency (%)
0	6.46×10^{-5}	5.93×10^{-4}	-0.476	-0.469	262.2	-
250	6.94×10^{-6}	6.37×10^{-5}	-0.411	-0.409	2,882	89.26
500	1.55×10^{-6}	1.42×10^{-5}	-0.427	-0.422	11,230	97.60
1,000	1.47×10^{-6}	1.35×10^{-5}	-0.433	-0.420	13,150	97.72

Fig. 12 Polarization curves of carbon steel in HCl 10% (mass) with additions of propargyl alcohol and chlorine (Cl₂).

Table 6 Polarization of carbon steel in hydrochloric acid and additions of propargyl alcohol and chlorine.

Inhib + Cl ₂ mg/L	i_{cor} (A)	I_{cor} (A/cm ²)	E_{cor} (V)	E_{cor} Calc, V	R_p (Ω)	Efficiency (%)
0	6.46×10^{-5}	5.93×10^{-4}	-0.476	-0.469	262.2	-
500	1.55×10^{-6}	1.42×10^{-5}	-0.427	-0.422	11,230	97.60
500 + 50 Cl ₂	4.07×10^{-6}	1.70×10^{-5}	-0.450	-0.450	5,684	91.24
500 + 500 Cl ₂	6.50×10^{-6}	4.31×10^{-5}	-0.451	-0.446	8,015	87.12
500 + 1,000 Cl ₂	7.77×10^{-6}	6.01×10^{-5}	-0.443	-0.435	7,196	83.93

current density (I_{cor}), and the calculated efficiency of propargyl alcohol in hydrochloric acid solution (10% mass).

It can be observed in Table 5 that I_{cor} value decreases from 593 to 135 $\mu\text{A}/\text{cm}^2$ and the inhibitor efficiency values increase from 89.26% to 97.72% with the increase of propargyl alcohol concentrations at 25 °C. It can be seen that the E_{cor} value tends to move in the less positive direction and that the inhibitor functions as an anodic inhibitor system at higher concentrations.

With the increase of propargyl alcohol

concentration, both anodic and cathodic currents were inhibited, but the reduction of the anodic currents was more significant than that of the cathodic currents. These results suggest that the addition of propargyl alcohol inhibitor reduces anodic dissolution and also retards the hydrogen evolution reaction.

The electrochemical experiments were carried out in the presence of chlorine and the concentration of the corrosion inhibitor was fixed at 500 mg/L. The results are presented in Fig. 12 and Table 6.

Tables 5 and 6 show that propargyl alcohol in hydrochloric acid solution gives an excellent

performance in terms of protecting carbon steel, confirmed by research works presented in the literature [12-15]. This suggests that the adsorption capacity of propargyl alcohol molecules in metallic surfaces is owed to the π -electrons that interact with the metallic surfaces and consequently is associated with the properties of triple bonds of the propargyl alcohol molecule ($\text{HC}\equiv\text{C}-\text{CH}_2-\text{OH}$).

It can be observed from this Table 6 that I_{corr} value increases from 646 to 777 $\mu\text{A}/\text{cm}^2$ and the inhibitor efficiency values decrease from 97.60% to 83.93% with the increase of additions of chlorine concentrations at 25 °C.

Gravimetric and electrochemical tests carried out show that contamination by chlorine in hydrochloric acid promotes a reduction in the formation of a protective film on the surface of carbon steel. Consequently, it increases the probability of anodic and cathodic reactions on metallic surfaces with hydrogen evolution. Application of the high oxidizing power of chlorine (Cl_2) is valid as it is responsible for the breaking of the triple bond of propargyl alcohol.

5. Conclusions

In the light of the evidence described above it can be concluded that:

- It is important to identify and evaluate the routes of industrial manufacture of hydrochloric acid and the level of contamination that can cause reduced capacity of anticorrosive protection of steel, as is the case of contamination by chlorine] (Cl_2).
- The results obtained by means of electrochemical and gravimetric techniques show that propargyl alcohol is an efficient corrosion inhibitor in HCl solution.
- Carbon steel corrosion rate increases considerably in solutions containing contaminating chlorine (Cl_2), because the chlorine (Cl_2) attacks the triple bond of propargyl alcohol, reducing inhibitor adsorption capacity on the metal surface.
- The presence of contaminant chlorine (Cl_2) can

impede the polymerization of the propargyl alcohol on the metal surface by the destruction of the triple bond of the inhibitor.

- Electrochemical tests prove that the propargyl alcohol acts to inhibit the anodic and cathodic reactions in HCl solutions, and when the inhibitor concentration is increased, the corrosion current (i_{corr}) decreases.

References

- [1] Büchel, K. H., Moretto, H. H. and Werner, D. 2008. "Industrial Inorganic Chemistry." John Wiley & Sons.
- [2] Fink, J. K. 2003. "Oil Fields Chemicals." New York: Gulf Professional Publishing.
- [3] Mainier, F. B., Freitas, A. E. R. and Figueiredo, A. A. M. 2015. "Acid Removal of Mineralized Incrustation in Petroleum Production Pipe." *International Journal of Research and Reviews in Applied Sciences* 23 (1): 65-71.
- [4] API N-80. 2004. Specification 5L, Specification for Line Pipe Steel. American Petroleum Institute, New York.
- [5] Petrobras N-1906. 1988 (in Portuguese). Ácido clorídrico para restauração e estimulação de poços de petróleo (Petrobras Standard N-1906- Hydrochloric Acid for Restoration and Oil Well Stimulation).
- [6] ASTM G 31-72. 1999. American Society for Testing and Materials, Standard practice for Laboratory Immersion Corrosion Testing of Metals.
- [7] Baboian, R. 2005. Corrosion Tests and Standards: Application and Interpretation. v. 20. ASTM International.
- [8] Revie, R. W. and Uhlig, H. H. 2011. Uhlig's Corrosion Handbook. John Wiley & Sons.
- [9] Podobaev, N. I. and Avdeev, Y. G. 2001. "The Effect of Several Anions and Inhibitors Mixed with Propargyl Alcohol on Electrode Reactions and Corrosion of Steel in Sulfuric acid." *Protection of Metals* 37 (1): 13-7.
- [10] Muralidharan, V. S., Uduman Mohideen, A. M. and Arun Mozhi Selvan, R. 1995. "Mechanism of Inhibition of Iron Corrosion in HCl by Acetylenic Alcohols." *Anti-Corrosion Methods and Materials* 42 (5):17-20.
- [11] Mainier, F. B. 1993. "Influência do cloro em inibidores de corrosão para ácido clorídrico (Influence of Chlorine on Corrosion Inhibitors for Hydrochloric Acid)." Anais: 17º Congresso Brasileiro de Corrosão, Associação Brasileira de Corrosão, 3 a 7 de outubro, Rio de Janeiro, 695-704 (in Portuguese).
- [12] Shetty, S. D., Shetty, P. and Nayak, H. S. 2005. "Inhibition of Corrosion of Mild Steel in Hydrochloric Acid by N-cyclohexyl-N-phenyl Thiourea." *Indian*

Journal of Chemical Technology 12 (4): 462-5.

- [13] Pati, B. B., Chatterjee, P., Singh, T. B. and Singh, D. D. N. 1990. "Effect of Propargyl Alcohol on Corrosion and Hydrogenation of Steel in Hydrochloric Acid Solution." *Corrosion* 46 (5): 354-9.
- [14] Spinelli, A. and Gonçalves, R. S. 1990. "Electrochemical Studies of the Adsorption of Propargyl Alcohol on Low

Carbon Steel Electrodes in H₂SO₄ Solutions." *Corrosion Science* 30 (12): 1235-46.

- [15] Feng, Y., Siow, K. S., Teo, W. K. and Hsieh, A. K. 1999. "The Synergistic Effects of Propargyl Alcohol and Potassium Iodide on the Inhibition of Mild Steel in 0.5 M Sulfuric Acid Solution." *Corrosion Science* 41 (5): 829-52.