Propargyl alcohol as a corrosion inhibitor for AISI 304L stainless steel in hydrochloric acid

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Abstract— Hydrochloric acid solutions (at concentrations of 5 to 28%) are used to acidify or acid-stimulate a rock-reservoir, increasing productivity of an oil well and removing calcareous deposits that lodge inside the carbon steel pipes. Typically, AISI 304 L stainless steel is used to manufacture various components, such as valves, adapters, rings, connectors, and rotors of pumps that are used in these acidifications. In order to guarantee the protection of both the carbon steel and the AISI 304 L, propargyl alcohol can be used as a corrosion inhibitor. The results of mass loss (gravimetric) and electrochemical tests (polarization curve) show a good efficiency of propargyl alcohol as a corrosion inhibitor for AISI 304 L stainless steel in concentrations of 5% (by volume) and 10% (by volume) of hydrochloric acid.
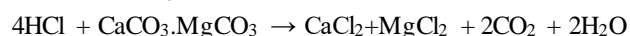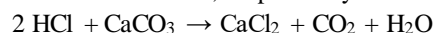
Keywords — AISI 304 L stainless steel, corrosion, corrosion inhibitors, propargyl alcohol, hydrochloric acid.

I. INTRODUCTION

One of the many uses of AISI 304L stainless steel is manufacturing components and equipment for the petroleum industry. Petroleum represents the largest component of the industrial energy matrix and is key in developing the global economy. Corrosion is one of the most harmful challenges encountered in the oil and gas sector. The study of corrosion is therefore fundamental due to its great impact in the oil industry. In fact, corrosion control expenses are estimated to be greater than 3.0% of the gross national product. As a result, new studies that aim to minimize costs of corrosion control expenses are of paramount importance to society [1, 2].

Matrix acidizing is a widely used technique to stimulate the productivity of an oil well that becomes inefficient over time. The main purpose of this process is to remove wellbore formation damage, promoting the dissolution the reservoir rock and consequently increasing the permeability of rock to the passage of oil and gas. Hydrochloric acid (HCl) is the most used in the stimulation operations due to its ease of dissolution of carbonate rocks as limestone ($CaCO_3$) and dolomite

($CaCO_3 . MgCO_3$). The formation of soluble salts ($CaCl_2$ and $MgCl_2$) occurs when HCl penetrates the reservoir rock [3, 4]. The chemical reaction for limestone and dolomite is written, respectively as:

$$2 HCl + CaCO_3 \rightarrow CaCl_2 + CO_2 + H_2O$$

$$4HCl + CaCO_3.MgCO_3 \rightarrow CaCl_2 + MgCl_2 + 2CO_2 + 2H_2O$$

An oil and gas production system made from carbon steel tubing (Figure 1) may include some equipment such as valves, adapters, rings, connections and rotors of special pumps that can made from AISI 304L austenitic stainless steel. Corrosion inhibitors are designed to protect such carbon steel tubing during the HCl stimulation process, without taking into consideration other materials that need anticorrosion protection [5-7].
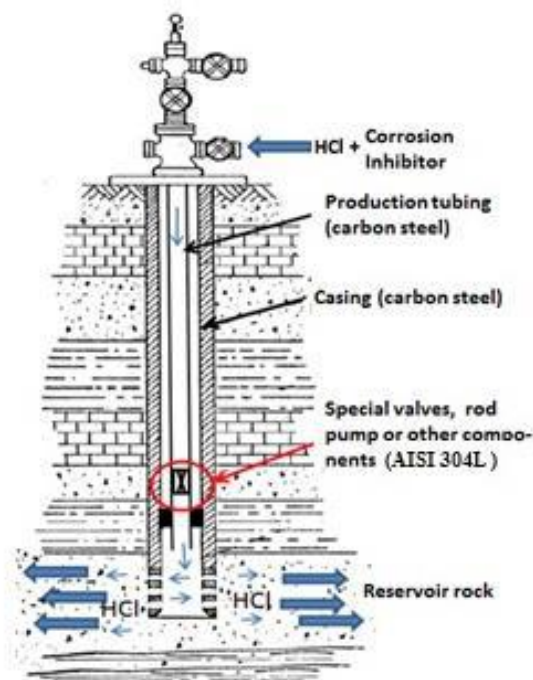

Fig. 1: Acid stimulation of reservoir rock

The application of corrosion inhibitors is commonly employed to combat corrosion damage; these inhibitors have a high efficiency in protecting the material of carbon steel pipes in the oil industry. The oil and gas industry has used the technique of using corrosion inhibitors to prevent the corrosion of carbon steel. Corrosion inhibitors are

defined as chemical substances that add to the corrosive medium to form a barrier on the metal surface (via adsorption or chemisorption), thus preventing or reducing corrosive actions. Corrosion inhibitors made from propargyl alcohol have demonstrated good performance in the protection of carbon steel from HCl solutions [5].

Generally, corrosion inhibitors are built with carbon steel, as carbon steel dominates more than 90% of materials used in the oil industry. Another important point is that the initial cost of stainless steel equipment is 15 to 20 times higher than that made of carbon steel (these costs do not consider manufacture technologies).

Although AISI 304L is classified as stainless steel, it can be corroded, depending on its exposure to certain conditions. Acids such as HCl, sulfuric (H_2SO_4) and hydrofluoric acid (HF) are reducing agents, producing hydrogen (H_2) when reacting with metals or alloys. These acids also can remove the passive oxide layer or passive film that forms on the steel surface. On the other hand, nitric acid (HNO_3) does not damage the passive oxide layer because of its oxidizing properties, thus preventing acid attack. Considering these factors, it is important to protect stainless steel with the addition of corrosion inhibitors [8 -10].

The petroleum industry uses AISI 304L stainless steel in their manufacturing; equipment made with this product is thus susceptible to corrosion via reducing acids. This paper analyses the effectiveness of propargyl alcohol in inhibiting the corrosion of HCl on AISI 304L.

II. MATERIALS AND METHODS

Disks of AISI 304 L stainless steel were made with a 2.5 cm diameter and a 2 mm thickness. The elemental composition of AISI 304 L stainless steel is shown in Table 1. The metal surface was abraded with silicon carbide (SiC) paper ranging from a 100 to 600 grit size, followed by cleaning in deionized water. Subsequently, surfaces of the disks were degreased in ethanol by using ultrasonic cleaning. They were then dried with hot air.

Table 1. The chemical composition of AISI 304L austenitic stainless steel.

C (%)	Mn(%)	Si(%)	Cr(%)	Ni(%)	Fe(%)
0.030	1.80	0.35	18.30	8.60	Balance

The corrosive media used were 5% and 10% volume solutions of high purity HCl. The concentrations of the corrosion inhibitor, propargyl alcohol (2-Propyn-ol-1), were fixed at 0.05 and 0.1 % volume.

Gravimetric assays (measuring weight loss) were performed in 100 mL glass containers. The corrosion coupons were completely immersed in 80 mL of acid solution, leaving the remaining headspace in the container for the evolution of hydrogen (H_2) that resulted from the

acid attack. The jars were maintained at temperatures of 25°C, 40°C and 55°C in a thermostatically controlled bath. The testing times were fixed at one, two, and three hours of exposure. The mass loss tests were conducted in triplicate.

Immediately after completion of the test, coupons were removed from the corrosive medium. Every deposit was rinsed first with deionized water, then with ethanol and subsequently dried quickly with hot air. The deposits were then re-weighed with the same accuracy so that the weight loss could be determined according to ASTM G 31-72 [11].

In the electrochemical tests, specimens were cut to a 0.25 cm² exposed area and encapsulated in polyester resin. The specimens were initially abraded longitudinally with 600-grade emery paper, degreased with acetone, washed in distilled water and dried under air. The electrochemical cell test (Figure 2) consisted of a three-electrode arrangement; a saturated calomel reference electrode, a platinum plate as the counter electrode and the 304L austenitic stainless steel sample as the working electrode. The test was conducted on a Type III Autolab potentiostat by varying the potentials at intervals of 60 mV/min over a range of −300 mV to +300 mV, with respect to an open circuit potential by a desk top computer.
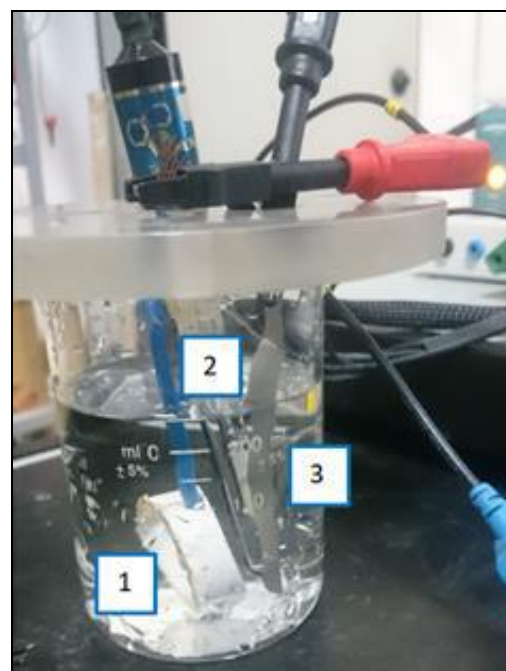

Fig. 2: The polarization cell used in this experiment: (1) the working electrode AISI 304L, (2) the platinum counter electrode, and (3) the saturated calomel reference electrode.

III. RESULTS AND DISCUSSION

The experimental conditions and results of the mass loss tests of AISI 304L stainless steel in the two HCl solutions

in the absence or presence of the two concentrations of propargyl are in Figures 3 and 4. The results show that mass losses are relevant when the corrosion inhibitor is not used, in particular in the three hour experiments. In addition, the mass loss at 10% HCl is the triple that of 5% HCl.
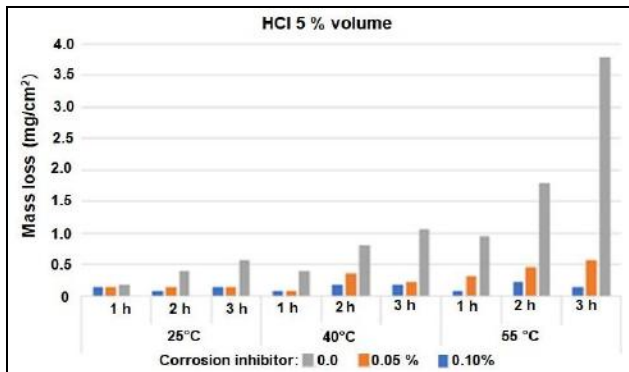

Fig. 3: Results of the mass loss tests of AISI 304L stainless steel in 5% HCl solution with and without corrosion inhibitor.
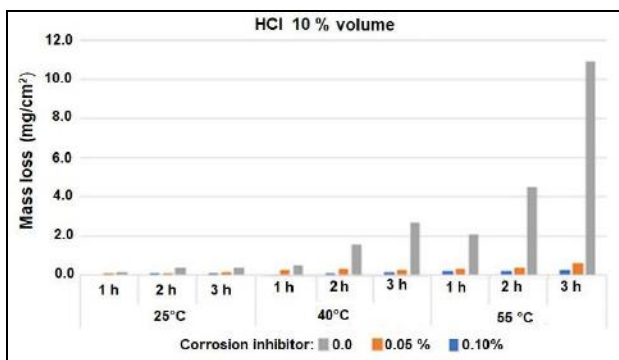

Fig. 4: Results of the mass loss tests of AISI 304L stainless steel in 10% HCl solution with and without corrosion inhibitor.
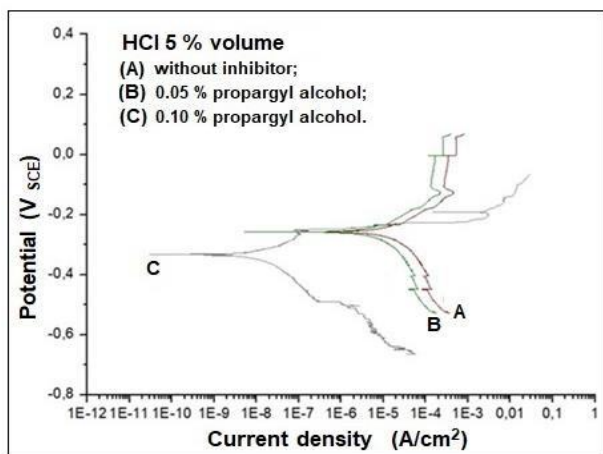

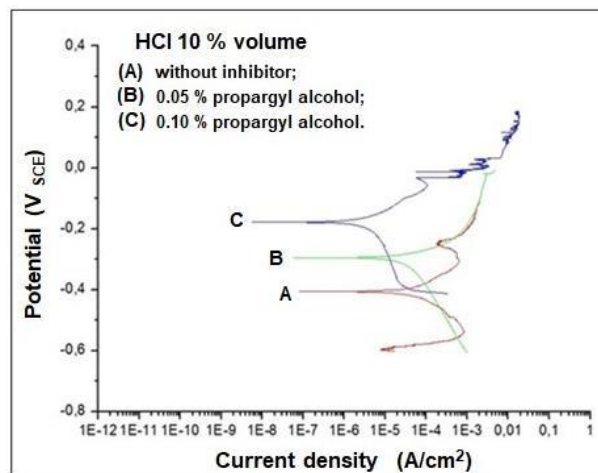*Fig. 5: Polarization test results for 5% HCl at 25°C, with and without inhibitor.*

Fig. 6: Polarization test results for 10% HCl at 25°C, with and without inhibitor.

The polarization resistance (R_p), the current density (I_{cor}) and the corrosion potential (E_{cor}) for each polarization curve with varying concentration and temperature are shown in Tables 2 and 3. The following equations show the efficiency of the corrosion inhibitor under the tested conditions:

Effic. % $= 100$ $(I_o - I_{inhib}/ I_o)$, where

Effic. % $=$ corrosion inhibitor efficiency; $I_o =$ current density without addition of corrosion inhibitor, and $I_{inhib=}$ current density with addition of the corrosion inhibitor.

Table 2. Electrochemical parameters of the polarization curves of AISI 304L steel exposed to a 5% HCl solution with and without the propargyl alcohol corrosion inhibitor.

Inhib. (%)	I_{cor} (A/cm^2)	E_{cor} (V)	R_p (Ω)	Effic. (%)
0	0.9 x10^{-4}	-0.260	2.9 x 10^3	----
0.05	1.5 x10^{-6}	-0.300	3.0 x 10^5	98.33
0.10	9.2 x10^{-7}	-0.350	3.8 x 10^6	98.97

Table 3. Electrochemical parameters of the polarization curves of AISI 304L steel exposed to a 10% HCl solution with and without the propargyl alcohol corrosion inhibitor.

Inhib. (%)	I_{cor} (A/cm^2)	E_{cor} (V)	R_p (Ω)	Effic. (%)
0	8.1 x10^{-4}	-0.410	5.1 x10^2	------
0.05	1.2 x10^{-5}	-0.310	2.6 x10^4	98.51
0.10	1.1 x10^{-6}	-0.290	2.7 x10^5	99.86

The polarization curves and the tables for the electrochemical parameters (Figs. 5-6, Tables 2-3) support the following findings:

- The polarization curves show a significant reduction in current densities (I_{cor}) as the corrosion inhibitor is added to the acid solution.
- The increased polarization resistance (R_p) indicates the protective action of the corrosion inhibitor on the metal surface.
- There is a systematic parallelism between the polarization curves with the displacement of these curves to the right upon greater corrosive attack.
- The current passing through the system is reduced with increasing inhibitor concentration. This phenomenon is because the increase of inhibitor molecules near the surface of the steel forms a resistance barrier to the passage of current, thus reducing the corrosion of stainless steel. The protonation of propargyl alcohol in the acid medium facilitates adsorption on the metal surface [12].
- The increase in the concentration of the inhibitor molecules leads to an increase in the density of inhibitor molecules adsorbed on the metal surface [13].

IV. PROPOSED CORROSION MECHANISM FOR AISI 304 L STEEL IN HYDROCHLORIC ACID IN THE PRESENCE AND ABSENCE OF A CORROSION INHIBITOR

The corrosion of AISI 304L in hydrochloric acid and the protection exerted by corrosion inhibitor (propargyl alcohol) is explained by a proposed model (Figure 7). The corrosion reactions and the competition between the migration of H^+ ions and the adsorption of propargyl alcohol are divided into three steps.
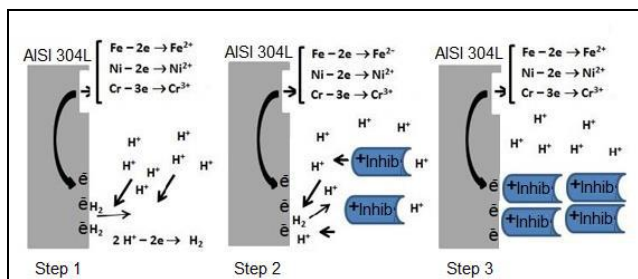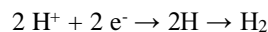

Fig. 7: Proposed mechanism to explain both the corrosion and protection exerted by the corrosion inhibitor in an acidic environment.

In the first step, AISI 304L stainless steel is attacked by hydrochloric acid, destroying the passivated layer and forming the Fe^{2+}, Ni^{2+} and Cr^{3+} ions, which migrate to the acid solution. At the same time, the H^+ ions migrate to the steel surface (cathodic area), forming both atomic (H) and molecular (H_2) hydrogen. These anodic and cathodic reactions are:

Anodic reactions:
$$Fe - 2e^- \rightarrow Fe^{2+}$$
$$Ni - 2e^- \rightarrow Ni^{2+}$$
$$Cr - 3e^- \rightarrow Cr^{3+}$$
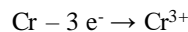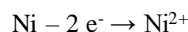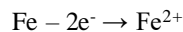
Cathodic reaction:
$$2H^+ + 2e^- \rightarrow 2H \rightarrow H_2$$

In the second step, protonation occurs. With the addition of the corrosion inhibitor to the hydrochloric acid solution, H^+ ions react either totally or partially with the inhibitor molecules. This process causes the positively charged organic molecules to migrate towards the cathodic surface. The protonation of propargyl alcohol in acidic media described in this study is based on the work developed by Bartos and Hackerman [14] and Feng et al. [15].

Finally, in the third step, adsorption of the inhibitor molecules occurs, forming a barrier on the steel surface. This process acts to prevent or delay the approach of H^+ ions, which would then pick up electrons from the metal surface (cathodic area), ultimately inhibiting the development of anodic reactions.

V. CONCLUSIONS

The following conclusions were made based on the experiments conducted in this study:

- The gravimetric tests showed that the loss of mass of AISI 304 L austenitic stainless steel increases with increasing HCl concentration, temperature and immersion time. In the absence of the corrosion inhibitor, with a three hour immersion time and a temperature of 55 °C, the loss of mass of stainless steel at 10% of HCl is three times the loss of mass at 5% HCl.
- The addition of propargyl alcohol to HCl solutions reduced the mass loss of stainless steel under all test conditions, suggesting excellent corrosion protection.
- In the electrochemical tests, the polarization curves showed that the propargyl alcohol increased the corrosion resistance of the AISI 304L steel by creating a barrier of adsorbed molecules that resisted the passage of electric current, thus reducing the corrosion of the metal surface. These results showed that the current density decreases and the polarization resistance increases as the concentration of the corrosion inhibitor rises.

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