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Evaluation of Propargyl Alcohol as a Corrosion Inhibitor for Duplex Stainless Steel in Hydrochloric Acid

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Abstract: ASTM A182 F51 duplex stainless steel with a 50:50 ratio of austenite to ferrite microstructure is a material used in mechanical engineering. Its uses include the manufacturing of equipment and components subject to acidification or acid stimulation for oil and gas industries. During acid stimulation or acidification, hydrochloric acid (HCl) solution with concentrations ranging from 5% to 28% (by volume) is injected into the limestone ($CaCO_3$) and dolomite ($CaCO_3 \cdot MgCO_3$) reservoir rock to restore permeability and consequently increase oil well productivity. Therefore, it is important to use a corrosion inhibitor, such as propargyl alcohol, to prevent or inhibit the aggressive attack of HCl on duplex stainless steel. The present study evaluates the corrosion resistance of ASTM A182 F51 stainless steel using gravimetric (mass loss) and electrochemical (polarization) tests. Studies were completed with and without the addition of 500 and 1,000 mg/L propargyl alcohol in HCl solutions with concentrations of 10% and 15% (by volume) at temperatures of 25, 40 and 55 °C. The good protection by propargyl alcohol of duplex steel immersed in HCl is observed.

Key words: Duplex stainless steel, corrosion inhibitor, propargyl alcohol, hydrochloric acid, acid stimulation.

1. Introduction

The ASTM A182 F51 denoted duplex is constituted with a 50:50 ratio of austenite and ferrite microstructure. This duplex combines a ferritic alloy with good resistance to stress corrosion cracking (SCC) and the high mechanical resistance of an austenitic alloy with good resistance to corrosion from mainly chlorides (Cl^-). Besides these favorable characteristics, it is also an easily fabricated material. The typical chemical composition (by weight) of this material consists of a high chromium content (21-23%), along with nickel (4.5-6.5%), molybdenum (2.5-3.5%), nitrogen (0.08-0.2%) and a maximum of 0.03% carbon [1, 2].

The corrosion properties of these stainless steels result from the formation of an oxide film on the metal surface. Known as passivation, this process generates a chemical barrier inhibiting or preventing the development of corrosion reactions. Under oxidizing conditions, such a barrier prevents corrosion. However, in the presence of reducing-type acids, such as hydrochloric acid (HCl), hydrofluoric (HF) and sulfuric acid (H_2SO_4), this passivated layer can be destroyed, initiating an intense corrosive process [3].

Recently, there was a significant increase in the use of new alloys, special coatings and new formulations of corrosion inhibitors in oil and gas production. In the field of new alloys, duplex stainless steel has stood out in the manufacture of special valves, fittings, flanges and other components, thereby replacing traditional carbon steel. Based on these uses, duplex stainless steels can be said to be critical in this technological area.

To justify the evaluation of duplex stainless steel in HCl solutions, it is important to show that as oil well production decreases over time, a further re-evaluation of productivity is essential. For example, this re-evaluation could be based on acid stimulation or acidification. This oil operation injects HCl into the reservoir rock to solubilize some minerals present in the mineralogical composition.

The improved solubility increases or recovers the rock formation permeability and consequently the

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productivity of the well [4.6]. Another important point is the occurrence of mineralized scale, which is the layer of calcium carbonate ($CaCO_3$) inside pipes, valves and connections made of carbon steel. These scales are generally hard and fairly adherent with removal usually achieved by HCl containing the addition of a corrosion inhibitor [7, 8].

The present study aims to evaluate the corrosion resistance of duplex stainless steel ASTM A182 F51 in solutions of HCl with and without addition of propargyl alcohol as a corrosion inhibitor.

2. Material and Methods

2.1 Mass Loss Measurement

The ASTM A182 F51 duplex steel coupons used in the gravimetric tests were made in the following dimensions: 6.0 mm × 8.0 mm × 16.0 mm. The chemical composition of ASTM A182 F51 duplex steel is presented in Table 1.

The coupon surfaces were polished with 100 to 600 grade sandpaper, cleaned with acetone, washed with bidistilled water and dried with hot air. The test coupons were weighed using a digital electronic balance.

The corrosive media used were 10% and 15% (by volume) HCl solutions of high purity. The concentrations of the corrosion inhibitor, propargyl alcohol (2-Propyn-ol-1), were fixed at 500 and 1,000 mg/L. The corrosion inhibitor choice and its concentrations are based on the authors' acidification experiments with HCl to ensure the integrity of materials such as carbon steel and special steels [8, 9].

The mass loss tests were carried out by immersing the coupons in polyethylene bottles containing HCl solution kept in thermostatically controlled baths at temperatures of 25, 40 and 55 °C. The testing times were fixed at 1, 2 and 3 hours of exposure. Upon completion of the experiments, the coupons were removed from the corrosive medium, washed with bidistilled water and ethanol and then quickly dried with hot air. Finally the coupons were weighed based on the ASTM G 31-72 standard [10].

The Mass Loss (*ML*) of each solution was defined by $ML = (W_i - W_f)/S$, where W_i is the initial mass (g) of the coupon and W_f is the final mass and S is the area (cm^2).

Inhibition efficiency ($E\%$) is calculated as follows: $E\% = 100\ [(W_{cor} - W_{corr(inhib)})/W_{cor}]$, where W_{cor} and $W_{corr(inhib)}$ are the corrosion rates of coupon in the absence and presence of corrosion inhibitor, respectively.

2.2 Potentiodynamic Polarization Measurements

Samples of the ASTM A182 F51 duplex stainless steel used for the polarization measurements were cut to obtain an electrode surface of 0.25 cm^2. The metal surface was then embedded in a polyester resin and polished with 400, 600, 800 and 1,200 grade emery paper. It was then washed in acetone, washed in bidistilled water and put into the cell with a volume of 400 mL.

A three-electrode cell consisting of a duplex 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 condition without stirring. The HCl solution data at 25 °C were discarded after the gravimetric test (mass loss) revealed that it was insignificant. The temperature maintained in the cell was 40 and 55 °C using a thermostatically controlled bath.

The polarization curves were recorded using a Type III Autolab potentiostat by varying the potentials in steps of 60 mV/min over a range of -300 to +300 mV with respect to an open circuit potential.

Table 1 Chemical composition (wt.%) of ASTM A182F51 duplex stainless steel.

C%	Mn%	N%	Cr%	Ni%	Mo%	Fe%
0.025	1.34	0.13	22.60	4.80	3.20	Bal.

The corrosive medium used was a solution of 10% and 15% (by volume) of high purity HCl while the concentration of the corrosion inhibitor, propargyl alcohol (2-Propyn-ol-1), was fixed to 500 and 1,000 mg/L. 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.

3. Results and Discussions

3.1 Results of Mass Loss Measurement

Results of the mass loss in HCl immersions, 10% and 15% (by volume), with and without addition of propargyl alcohol (500 and 100 mg/L) at 40 and 50 °C are presented below in Figs. 1-4. The assay conducted with 10% and 15% HCl at 25 °C in the absence and presence of the corrosion inhibitor was discarded because the mass losses were insignificant.

In order to visualize the significant differences, the results are presented in the logarithmic scale.

The mass loss growth rate as the HCl concentration and the test temperature were increased in the absence of the corrosion inhibitor was also noted.

Based on the results for the greater immersion time (3 hours), it was possible to determine the efficiency of the corrosion inhibitor as presented in Tables 2 and 3. The propargyl alcohol had protection efficiency in all the experimental conditions studied.

3.2 Results of Potentiodynamic Polarization Measurements

Polarization curves for ASTM A182 F51 duplex stainless steel in 10 and 15% (by volume) HCl solutions in the absence and presence of propargyl alcohol (500 and 1,000 mg/L) at 40 and 55 °C are shown in Figs. 5 and 6.

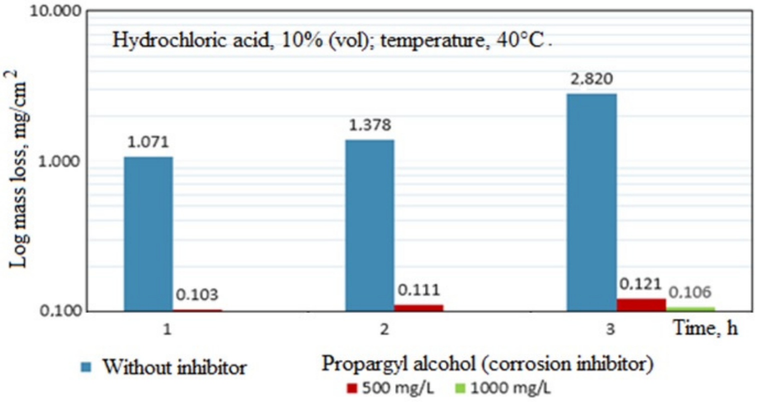

Fig. 1 Results of duplex stainless steel mass loss with HCl at 10% (by volume) and 40 °C.

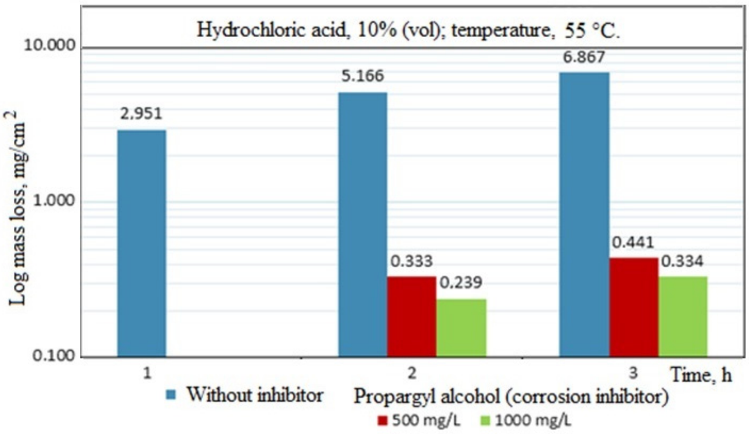

Fig. 2 Results of duplex stainless steel mass loss with HCl at 10% (by volume) and 55 °C.

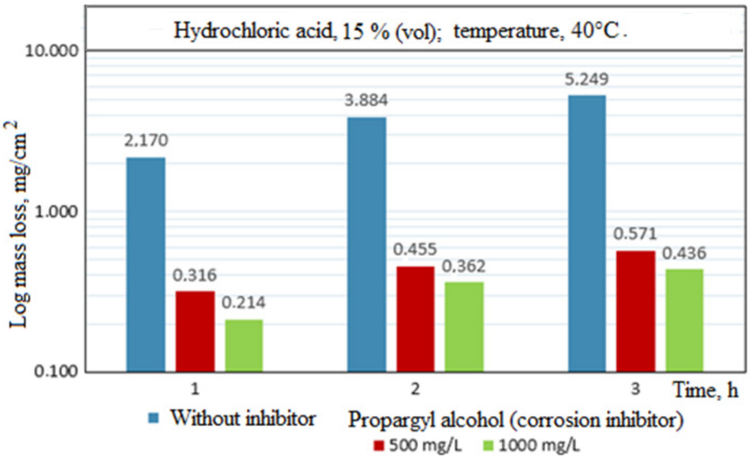

Fig. 3 Results of duplex stainless steel mass loss with HCl at 15% (by volume) and 40 °C.

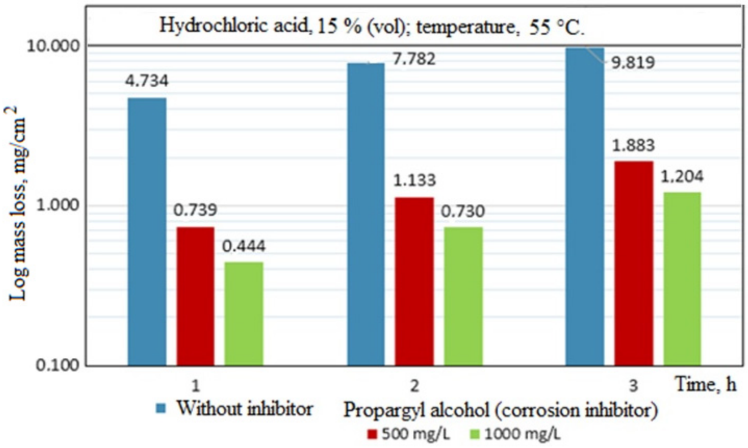

Fig. 4 Results of duplex stainless steel mass loss with HCl at 15% (by volume) and 55 °C.

Table 2 Corrosion inhibitor (propargyl alcohol) efficiency at 40 °C with HCl at 10 and 15% (by volume) for 3 hours of immersion.

Corrosion inhibitor, mg/L	Inhibition efficiency (%) at 40 °C	
	Hydrochloric acid, %	
	10	15
500	95.70	89.12
1,000	96.24	91.70

Table 3 Corrosion inhibitor (propargyl alcohol) efficiency at 55 °C with HCl at 10 and 15% (by volume) for 3 hours of immersion.

Corrosion inhibitor, mg/L	Inhibition efficiency (%) at 55 °C	
	Hydrochloric acid, %	
	10	15
500	93.60	80.82
1,000	95.13	86.15

These polarization curves (anodic and cathodic branches) demonstrate that addition of propargyl alcohol to the HCl solution causes these curves to shift towards lower currents. To a similar extent, the shift may be the consequence of a barrier effect or the absorption of a propargyl alcohol film formed on the metal surface. The polarization curves show a clear reduction in both the anodic and cathodic currents in the presence of propargyl alcohol compared to the values for HCl solution without a corrosion inhibitor.

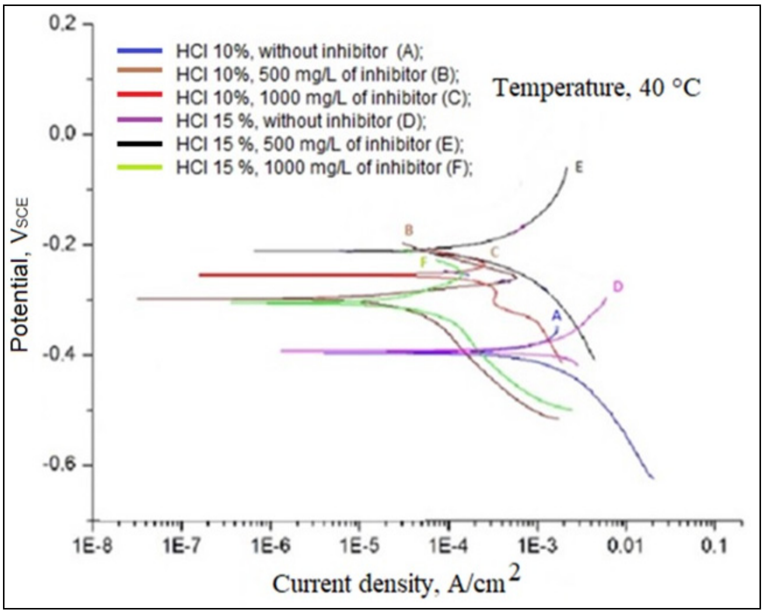

Fig. 5 Duplex stainless steel polarization for 10 and 15% (by volume) HCl at 40 °C.

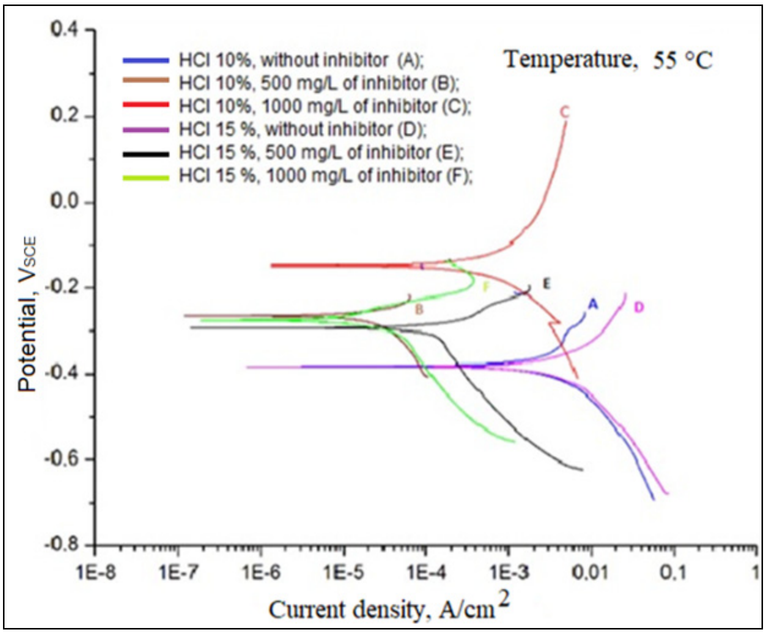

Fig. 6 Duplex stainless steel polarization for 10 and 15% (by volume) HCl at 55 °C.

Table 4 Polarization resistance (R_p), potential (E_{corr}) and corrosion current density (I_{corr}) for the 10 and 15% (by volume) HCl solution at 40 °C.

Inhibitor mg/L	HCl %	I_{corr} A/cm^2	E_{corr} V	R_p $\Omega\cdot$cm^2
0		6.7×10^{-4}	-0.39	58
500	10	1.5×10^{-4}	-0.22	1,470
1,000		4.86×10^{-5}	-0.26	5,300
0		2.79×10^{-3}	-0.37	308
500	15	1.92×10^{-3}	-0.14	729
1,000		7.84×10^{-5}	-0.27	3,444

Table 5 Polarization resistance (R_p), potential (E_{corr}) and corrosion current density (I_{corr}) for the 10 and 15% (by volume) HCl solution at 55 °C.

Inhibitor mg/L	HCl %	I_{corr} A/cm^2	E_{corr} V	R_p Ω·cm^2
0		4.88×10^{-4}	-0.39	80
500	10	4.76×10^{-4}	-0.12	250
1,000		5.25×10^{-5}	-0.26	5,000
0		7.88×10^{-4}	-0.39	501
500	15	3.75×10^{-4}	-0.29	773
1,000		1.10×10^{-4}	-0.29	2,636

Values for the polarization resistance (R_p), potential (E_{corr}) and the corrosion current density (I_{corr}) were obtained by extrapolating the Tafel lines of the polarization curves for 5 and 10% HCl solutions at different temperatures. These results are presented in Tables 4 and 5.

Researchers previously presented good results regarding the use of propargyl alcohol in protecting carbon steel in HCl solutions [11-14]. However, considering the same conditions, the experiment also shows good protection for ASTM A182 F51 duplex stainless steel. Therefore, one can suggest that the adsorption capacity of propargyl alcohol ($HC{\equiv}C{-}CH_2{-}OH$) on metallic surfaces is due to the π-electron cloud from the triple bond interacting with the metallic surfaces.

4. Conclusions

Based on the referenced literature and laboratory tests carried out, conclusions can be summarized, as follows:

In the gravimetric tests, there was a significant increase in mass loss at temperatures of 40 and 55 °C as the immersion time and the HCl concentration increased. At 25 °C the mass loss was negligible.

The addition of propargyl alcohol at concentrations of 500 and 1,000 mg/L to the HCl solutions reduced the loss of duplex steel. The efficiency of propargyl alcohol was greater than 80% even under the most aggressive conditions.

The polarization curves presented a higher current density as the temperature increased. The presence of propargyl alcohol in the assays for each analysed temperature always generated a reduction in the current density results.

ASTM A182 F51 duplex stainless steel is susceptible to corrosion when used in environments with non-oxidizing acids. Therefore, based on the results presented here propargyl alcohol effectively reduces corrosion.

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