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Evaluation of titanium in hydrochloric acid solutions containing corrosion inhibitors

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Abstract: *Currently, the use of titanium alloys components and coating (clad) in petroleum subsea production systems continues to increase. Titanium alloys are lightweight, very flexible; have greater mechanical resistance relationship showing excellent resistance to corrosion and fatigue in ambient seawater and marine environments. The rate of corrosion of titanium alloys are low for hydrochloric acid (3%), however, in the acidification operations from petroleum well is necessary the use of corrosion inhibitors, because the concentration of hydrochloric acid varies from 10 to 28%. A corrosion inhibitor for acidification can be defined as a substance or mixture of substances which are added to the corrosive medium aim inhibit or minimize the action of the corrosive medium. This paper presents the laboratory tests made with titanium coupons subjected to hydrochloric acid solution 10% (weight %), in temperatures of 50° C and 70° C, and additions of phenylamine (aniline), thiocarbamide and β-naphthol as corrosion inhibitors. The results showed that the corrosion protection inhibitors exerted by varies from 50 to 80% depending on the concentration of inhibitors and temperatures used in the tests.*
Keywords: *Corrosion, Corrosion Inhibitor, Titanium, Acidification, Hydrochloric Acid.*

I. INTRODUCTION

Lately, titanium alloys have been used in equipment and other components in the petrochemical industry and in oil exploration and production in deep waters, usually in the form of internal liners (clad) [1, 2].

Titanium alloys posse's coefficients of thermal expansion which are significantly less than ferrous and aluminum alloys providing compatibility with coatings of ceramics and glassy materials.

The innovations and difficulties encountered in the drilling and production of oil in deep water, high temperatures of petroleum reservoirs, the need to meet the conditions prevailing environmental and safety required of projects may justify the use of these alloys costly.

In oil production, as a general rule, the titanium alloys are not attacked and maintain compatibility with most fluids used in petroleum operations, such as completion fluids to base salts such as sodium chloride and potassium chloride, corrosion inhibitors, scale inhibitors, demulsifiers, biocides, paraffin inhibitors, antifreeze agents, among other [3,4].

The injection of acid solutions (stimulation or acidification) in oil or gas wells aims to stimulate or increase your productivity, restoring or increasing the permeability of the petroleum reservoir rock, fracturing or eliminating scaling carbonate ($CaCO_3$) also adhering to the inner wall surfaces of pipes that prevent or restrict the normal flow of oil or gas [5].

Acidification is a stimulation technique in which an acidic solution is injected into the rock formation, to dissolve some of the minerals present in its mineralogical composition or damage present, increasing or restoring the permeability of the formation around the borehole. However, it is important to evaluate critically the performance of operations of acidification when using hydrochloric acid or mixtures of hydrochloric acid (HCl) and hydrofluoric acid (HF), whereas such acids attack a titanium alloy dramatically, especially at concentrations high.

Hence, the need for additions of corrosion inhibitors acidic solutions, whereas the primary functions of the corrosion inhibitor is inhibiting, preventing or minimizing the corrosion process. The main function of the addition of corrosion inhibitors to acid fluids is forming a film or protective barrier on the metal surface preventing or delaying the electrochemical reactions.

The success and importance of this transaction scenario in the oil industry can be assessed by the development of these techniques in operations both onshore and offshore, in the various types of equipment installed on trucks injections or in special vessels adapted and finally the annual consumption of hydrochloric acid for this end. In Brazil, about 10% of the annual production of hydrochloric acid is bound to the oil industry [6].

II. MATERIALS AND METHODS

In this paper we used the titanium alloy, having 99.1% titanium and 0.25% iron. Also noted were the presence of carbon and nitrogen in the chemical composition considered as trace elements. The coupons used in the tests gravimetric (weight loss) were prepared in the dimensions 45 mm x 15 mm x 10 mm, sanded and degreased with acetone and alcohol. They were then weighed to the nearest 0.0001 g.

In laboratory experiments were used as a corrosive medium hydrochloric acid solution 10% (% mass).mass). The basic substances used as corrosion inhibitors were phenylamine (aniline), thiocarbamide and β-naphthol and a mixture of 50% (by weight) of β-naphthol and thiocarbamide at concentrations of 0.001mol/L, 0.01 mol/L and 0.1 mol/L.

Assays gravimetric (weight loss) were performed in glass containers with a capacity of 500 mL. The coupons were completely immersed in 200 mL of acid solution, allowing the remaining capacity of the container for the evolution of hydrogen (H_2) resulting from acid attack.

The jars were kept at temperatures of tests via a thermostatically controlled bath. The temperatures were set at 50 ° C and 70 ° C. The time for testing was fixed at 1 hour of exposure.

Immediately after completion of the test, the coupons were removed from the corrosive medium, rinsed in water, alcohol and quickly dried with hot air, then being weighted with the same accuracy, then the weight loss determined.

The corrosion rate (CR) and the efficiency of corrosion inhibitors (E %) are defined by the following expression:

Corrosion rate = CR = $(W_o - W_i)/ S.t$ (mg/cm^2.h)

Where:

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

S = area (cm^2);

t = exposure time, h.

III. RESULTS AND DISCUSSION

The results of the laboratory tests carried out on the bodies of the test coupon of titanium immersed in hydrochloric acid solutions with additions of phenylamine, thiocarbamide, β-naphthol and a mixture of 50% (% by mass) thiocarbamide and β-naphthol are shown in next, in Table 1 and in graphs presented in Figures 1 to 4.

Table 1 - Results of tests of weight loss titanium coupons with phenylamine, thiocarbamide, β-naphthol and thiocarbamide + β-naphthol in 10% solution of hydrochloric acid at 50 °C and 70 ° C

Inhibitor (mol/L)	Weight loss, mg/cm^2.h							
	Phenylamine		Thiocarbamide		β-naphthol		Thiocarbamide + β-naphthol	
	50 ºC	70 ºC	50 ºC	70 ºC	50 ºC	70 ºC	50 ºC	70 ºC
0.0	0.680	0.780	0.680	0.780	0.680	0.780	0.680	0.780
0.001	0.310	0.363	0.244	0.282	0.382	0.412	0.360	0.402
0.01	0.232	0.250	0.174	0.245	0.245	0.294	0.248	0.292
0.1	0.160	0.200	0.136	0.158	0.187	0.221	0.191	0.220

Generally, a commercial formulation for use in oil wells acidification comprises a mixture of various substances which have among themselves principles of compatibility and have the following characteristics: ability to form a film adsorbed on the metal surface; capacity to disperse or prevent the contact of water with the metal surface; ability to disperse the products formed by the reaction of the acid with the rock; have properties be a solvent or co-solvent to dissolve these substances in acid medium.

The inhibitors adsorptive or film are generally organic substances of high molecular weight that form a monomolecular film on the metal surface preventing the development of electrochemical reactions.

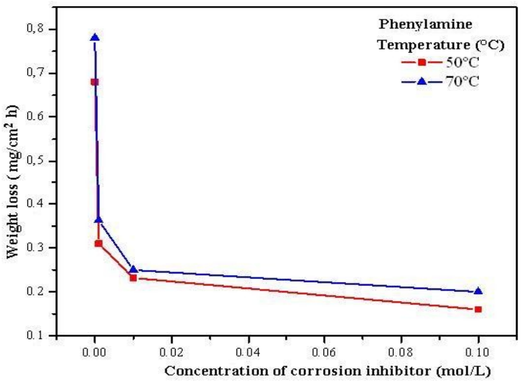

Figure 1 - Rate of corrosion of titanium in hydrochloric acid (10 % mass) with phenylamine

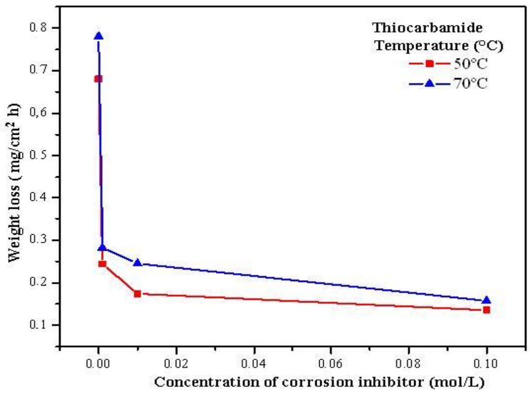

Figure 2 - Rate of corrosion of titanium in hydrochloric acid (10 % mass) with thiocarbamide

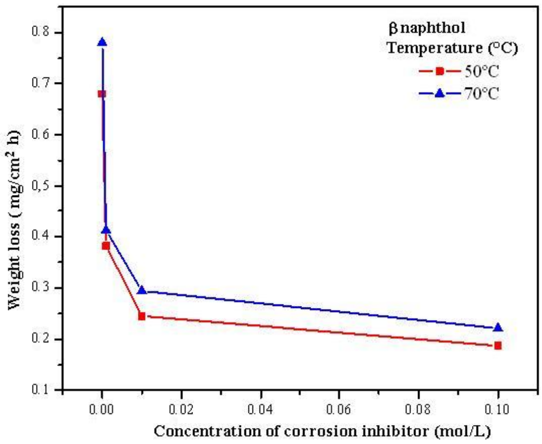

Figure 3 - Rate of corrosion of titanium in hydrochloric acid (10 % mass) with a mixture of 50% (% by mass) thiocarbamide and β-naphthol

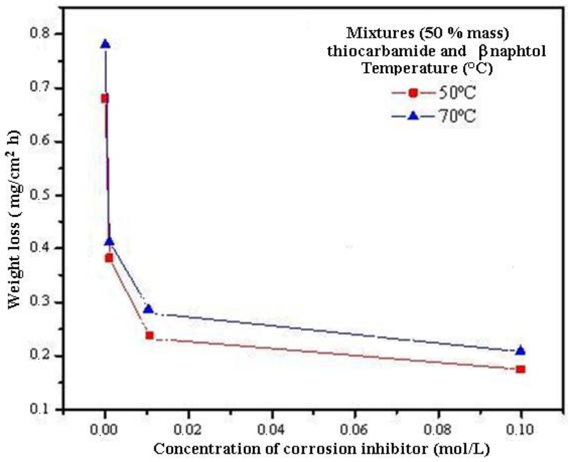

Figure 4 - Rate of corrosion of titanium in hydrochloric acid (10 % mass) with a mixture of 50% (% by mass) thiocarbamide and β-naphthol

The inhibitors adsorptive or film are generally organic substances of high molecular weight that form a monomolecular film on the metal surface preventing the development of electrochemical reactions. To explain the action of acids and non-oxidizing performance of corrosion inhibitors are proposed mechanisms based on the definitions of systems inhibitor-inhibitor acid and acid metal as shown, then the diagram in Figure 5.

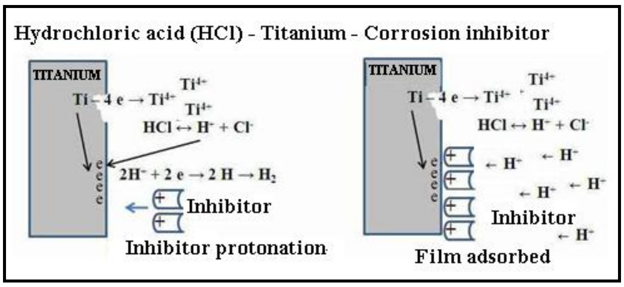

Figure 5 - Scheme of the inhibition corrosion process

The ion Ti^{4+} formed by the attack of acid to titanium leaves the metal (Ti) for the solution and consequently there is a migration of H^+ ions from the acid concentration to the metal surface forming the atomic hydrogen (H) and soon, then molecular hydrogen (H_2) according to the reactions:

$Ti - 4e^{-} \rightarrow Ti^{4+}$ (anodic reaction)

$2\ H^+ \rightarrow 2\ H - 2e^- \rightarrow H_2 - 2e^-$ (cathodic reaction)

The addition of an organic inhibitor type system non-oxidizing acid reaction can lead to partial or total even with the H^+ ions dissociated in acidic solution, having spontaneously captured the positive charges by the inhibitor molecule, a process called protonation [7, 8].

Consequently there is an intense competition between the H^+ ions and protonated inhibitor molecules moving into areas where they accumulate cathode electrons. Although the ion mobility of H^+ ions is much greater (smaller ion) of the molecule inhibitor protonated there is an adsorption stable inhibitor on the metallic surface, forming a barrier that prevents migration of H^+ ions to capture the electrons, thus preventing, the formation of atomic hydrogen (H) and detachment of molecular hydrogen (H_2).

The barrier formation of the molecule of the inhibitor on the metal surface will be a function of the concentration of non-oxidizing acid, the concentration of the inhibitor, the temperature and the adsorption capacity molecule inhibitor.

The loss of passivity in non-oxidizing acids such as b hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and hydrofluoric (HF) entails a very heavy attack, due to the increasing acid concentration and temperature.

Research laboratories developed by Clarke et al. [9] and Nishimura et al. [10] warn about the possibility of fractures induced embrittlement by hydrogen (H) in titanium alloys as the presence of non-oxidizing acids, mainly in the immersion in hydrochloric acid and sulfuric acid.

The tests showed weight loss based on tables (1 and 2) and graphs (1 to 4) show that:

- The corrosion rates for the coupons titanium hydrochloric acid reached 10% (% mass) mean values of the order of 0.680 mg/cm^2.h a temperature of 50 °C and 0.680 mg/cm^2.h to 70 °C and additions of inhibitors reduce these rates;
- The increase of temperature favors the increase of the corrosion rate;
- The corrosion inhibitor based on thiocarbamide hydrochloric acid solutions showed better corrosion performance than phenylamine and β-naphthol;
- The adsorption of thiocarbamide was more effective on the metal surface minimizing the cathodic reactions.

Research carried out by Mogoda et al. [11] has shown that additions of inorganic compounds such as iodates (IO_3^-) metavanadates (VO_3^-) and molybdates (MoO_4^{2-}) has shown a good surface passivation of titanium alloys when in solutions hydrochloric acid and sulfuric acid probably additions of oxidizing agents may promote the formation of passivation and thereby increase the level of protection exerted by corrosion inhibitors.

IV. CONCLUSIONS

Based on the study the following conclusions are made:

- additions thiocarbamide, phenylamine and β-naphthol in solutions of hydrochloric acid (10% by mass) in the test temperatures (50 and 70°C) produce a relative corrosion protection;
- the use of titanium and/or its alloys in the processes of acidification with non-oxidizing acids requires, therefore, the use of corrosion inhibitors.

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