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Internal Corrosion Solution for Gathering Production Gas Pipelines Involving Palm Oil Amide Based Corrosion Inhibitors

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A problem of uncontrolled internal corrosion of over 20 mpy was root cause analyzed within a system of pipelines connecting a set of oil wells onshore central Gulf of Mexico coastline. The root cause analysis was focused on a detailed characterization of the gas, mostly methane, and liquid phases, mostly genic waters as well as CO_2, H_2S, chlorides and MIC bacteria. The metallurgy of the corrosion damage over the steel pipeline involving both zone of uniform corrosion as well as special points of localized corrosion. In the past these pipelines received unsuccessful chemical treatments. Both the inhibitor and the dosage were not available. A trial of a new palm oil based corrosion inhibitor was performed. The corrosion inhibitor passed successful testing in the laboratory employing electrochemical testing by linear polarization resistance as well as harmonic analysis. The corrosion inhibitor formulation was furthermore adapted for massive fabrication involving a set of parallel variables from pipeline engineering such as foam formation elimination, not gel formation and other. The program was conducted producing improvements from the onset. Corrosion inhibitor injection was immediately and a program of pipeline cleaning was launched. In the first four months of the new corrosion inhibitor solution the results produced the desired target of overall compliance to the internal pipeline corrosion control specification below 2 mpy.

Keywords: internal corrosion, CO_2 corrosion, localized attack, palm oil-based inhibitor

1. INTRODUCTION

The oil industry transport and distribution of hydrocarbons is carried out by means of carbon steel pipelines, which are one of the most efficient, safe and economic methods [1-3]. However metallic pipes are prone to failure under conditions of poor maintenance. However, although progress has been made in the corrosion control procedures, today it should further research to develop more and better methods to mitigate the effects of corrosion. In oil production plants, many cases of oil/gas leakage has occurred due to the extensive corrosion in production tubing, valves, and in flow lines from the wellhead to the processing equipment. The reason for this is that oil and gas from the well contain varying amounts of water, which can be precipitated as a separate phase in contact with the material surface. This water contains gases such as CO_2 and possibly H_2S, as well as salts [4-5].

The oil industry in Mexico has a pipeline network around 40,000 kilometers, and in the last six years there have been more than 50 major accidents. This has caused the spill of nearly 42,000 barrels of hydrocarbons, which have caused significant environmental damage, in addition to economic losses.

Due to the acidity of the aqueous phase, one of the main risks in the operation of pipelines for the transport of hydrocarbons is the internal corrosion. To control internal corrosion, one of the main strategies is to inject corrosion inhibitors. The presence of an aqueous phase is almost unavoidable, since during the production of crude oil the formation water or injected water is also transported in a multiphase flow. Furthermore, corrosion control systems are compromised because during the transport of this multiphase flow high shear forces are developed causing its emulsification and increasing tremendously the contact area of the oil and water phase. Due to the corrosion inhibitors show a great affinity for the oil/water interface, this fact may decrease the effectiveness of inhibition [6-7].

This work reports a study about a problem of internal corrosion in a pipelines system. In the past the pipelines received an unsuccessful chemical treatments. An analysis was conducted in order to characterize the material, gas, water, dissolved solutes and the presence of microorganisms. A new palm oil based corrosion inhibitor was developed in order to solve the uncontrolled internal corrosion.

2. ANALYSIS METHODOLOGY

2.1. Source of the problem

During maintenance works performed on a gas pipeline (4 inches in diameter) in the oil fields of southern Mexico a gas leak was detected. Even though these pipelines received chemical treatments, a preliminary analysis indicated a problem of uncontrolled internal corrosion ($\approx$ 20 mpy), however, both the inhibitor and the dosage were not available. As a result, it was necessary to perform a failure analysis in order to determine the root cause of the gas leak. The studies consisted of metallographic analysis of metallic pipelines, the determination of H_2O content, analysis of dissolved gases (CO_2, H_2S and O_2), pH, conductivity, dissolved solids, content of sodium, carbonates, bicarbonates, barium, sulfur, chlorides, iron and manganese, alkalinity, presence of APB (acid producing bacteria) and SRB (sulfate-reducing bacteria), and sediment. Table 1 summarizes the used methods.

Table 1. Analytical methods.

Parameter	Method
CO_2 dissolved	APHA Standard Methods, 19th ed., p. 4-17, method 4500-CO_2 C (1995). ASTM D 513-82.
H_2S dissolved	EPA Methods for Chemical Analysis of Water and Wastes, method 376.2 (1979). APHA Standard Methods, 19th ed, p. 4-124, method 4500-S2- D (1995).
O_2 dissolved	Indigo Carmine -ASTM D 888-87, Colorimetric Indigo Carmine, Test Method A. ASTM D 5543-94, Standard Test Methods for Low Level Dissolved Oxygen in Water.
pH	Standard Test Methods for pH of Water. ASTM D 1356
Chlorides	APHA Standard Methods, 19th ed., p. 4-50, method 4500-Cl- C (1995)
Iron	ASTM D1068-05e1 Standard Test Methods for Iron in Water ASTM-D0596-01
Sulphates	APHA Standard Methods, 19th ed., p. 4-136, method 4500-S042-E (1995). EPA Methods for the Chemical Analysis of Water Wastes, Method 375.4 (1983). ASTM D 516-90

The presence of microorganisms was determined according to the recommendations of API-RP38 Recomended Practice and the standard test method NACE TM194-2004. The sediments were analyzed by X-ray diffraction. The metal samples were prepared metallographically and attacked with 2% Nital for 1 minute, after that, the samples were analyzed by scanning electron microscopy (SEM). The corrosion rate in the pipelines system was determined by installing metallic coupons (SAE 1018 carbon steel) with measures of 2.875*0.875*0.125 inch (Figure 1). After the test, the metallic coupons were removed and cleaned to calculate the mass lost and determine the corrosion rate.

Figure 1. Coupons to determine the corrosion rate in the pipelines system.

2.2. Proposed solution

In order to control the problem of internal corrosion (≈ 20 mpy) a new palm oil-based amide as corrosion inhibitor was used. The inhibitor was prepared trough the direct amidation of palm oil and hydroxyethyl ethylendiamine for 2.5 hours at 140 °C. Figure 2 shows the IR spectrum of the palm oil-based amide obtained. The inhibitor exhibit the 6 characteristic bands (3304 cm^{-1}, 1637.5 cm^{-1}, 1556.5 cm^{-1}, 1464 cm^{-1}, 1375 cm^{-1}, and 719 cm^{-1}), which are known as amide bands, on the other hand, the methyl and methylene groups around 2920 cm^{-1} and 2852 cm^{-1} for C-H stretch and around 1460 cm^{-1} for CH2 deformation.

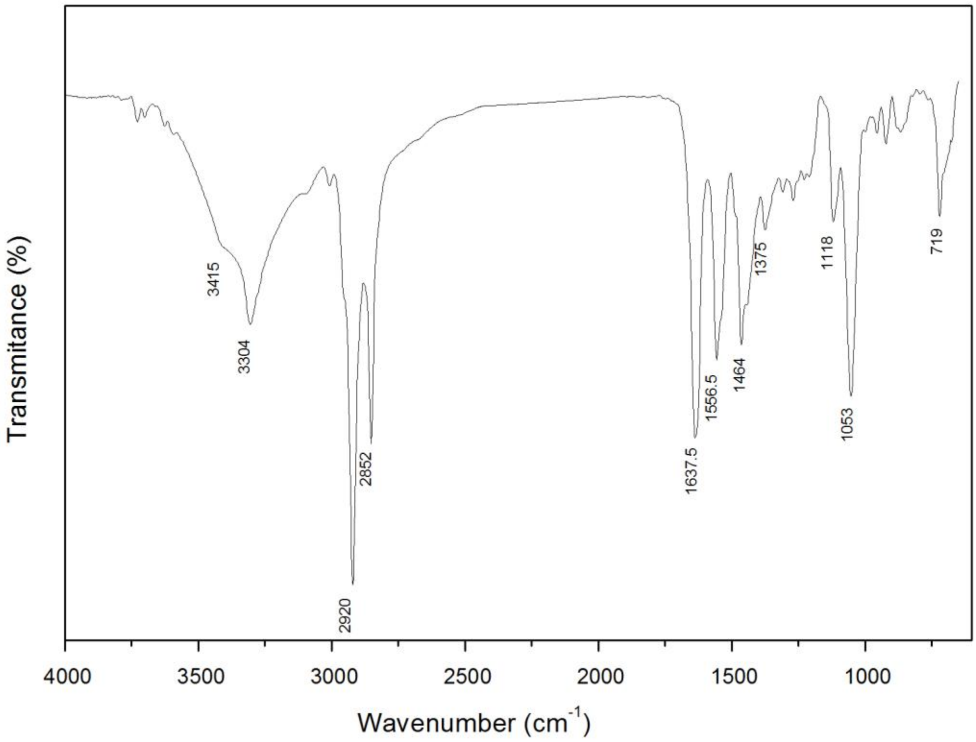

Figure 2. IR spectra of the palm oil-based amide.

In order to determine the performance of the corrosion inhibitor, a multi-technique electrochemical system (SmartCET) was utilized. SmartCET system is based in a combination of measurements of linear polarization resistance (LPR), electrochemical noise (EN), and harmonic distortion analysis (HDA) [8-9]. The electrochemical system uses an arrangement with three identical electrodes. For the corrosion tests, 1018 carbon steel cylinders were used. The metal cylinders were abraded to 600 grit emery paper and then cleaned with distilled water and acetone. The inhibition efficiency was evaluated in an emulsion 90:10 (v/v) of 3% NaCl solution and diesel, respectively. The emulsion was continuously saturated with CO_2 (2 h before testing and during testing). The test temperature was 50°C, and the emulsion was stirred continuously. The metal cylinders (working electrodes) were pre-corroded in the emulsion for 1 h before the inhibitor was added. The concentrations of the palm oil-based amide inhibitor were 5, 10, 25, 50 and 100 ppm.

2.3. Inhibitor injection

The palm oil-based amide formulation was adapted for its massive fabrication considering a set of variables from pipeline engineering such as foam formation elimination, not gel formation and other. A program of corrosion inhibitor injection was conducted producing improvements from the onset.

3. RESULTS AND DISCUSSION

3.1. Physicochemical analysis

From the physicochemical analysis it was observed that the gas flowing in the pipeline also carries a condensed phase, which consisted of a mixture of water with hydrocarbons, and a solid residue. The condensed phase had a pH of 6.5, and a conductivity greater than 20mS/cm. The values of the pH and the conductivities were due to the high concentrations of chlorides (>10,000 ppm) and other salts, which was characterized as a highly corrosive fluid [10]. Concentrations of CO_2 dissolved were in the range of 70-160 ppm, while those of Fe between 20-80 ppm. It is known that the dissolved CO_2 favors a series of chemical reactions leading to the formation of carbonic acid (H_2CO_3), reducing the pH of the electrolyte due to an increase in the concentration of H^+, and thus increasing the corrosion rate [11]. Furthermore, the presence of dissolved CO_2 can form either carbonates (CO_3^{2-}) or bicarbonates (HCO_3) favoring the formation of calcium or magnesium based incrustations [12]. Furthermore, microbiological analysis indicated the presence of sulfate-reducing bacteria (100,000 BCT/ml) and acid producing bacteria (100,000 BCT/ml), which indicates a high probability of developing corrosion influenced by microorganisms, which can cause damage to the production pipelines.

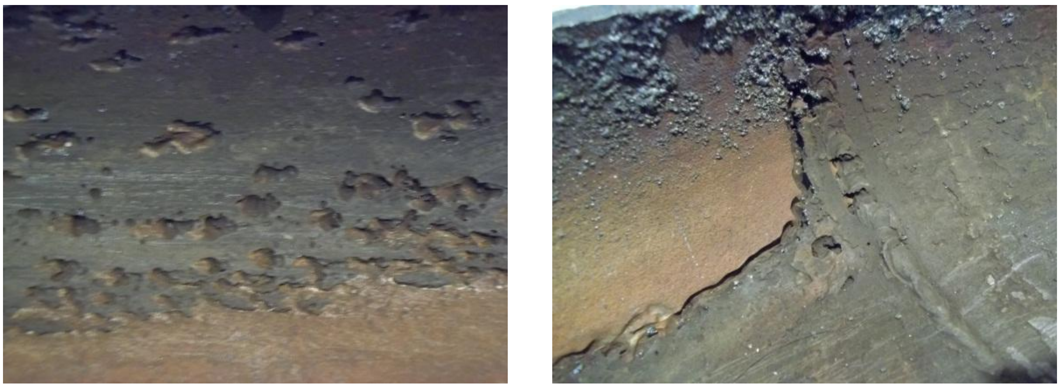

Figure 3. Aspect of the internal corrosion of the pipeline.

Because in the presence of dissolved CO_2 the corrosion rates are high, the addition of corrosion inhibitors is needed in order to counteract it. [13-16]. The carbonic acid (HCO_3) can reacts with the carbon steel, and a layer of reaction products ($FeCO_3$) is formed on the steel surface. The formed deposit is cathodic relative to the carbon steel, and when small defects occur in the layer, localized attack can be developed. This condition may be corrosive in the production pipeline, which carries the hydrocarbons (oil/gas) from the well. Figure 3 shows the presence of localized attack detected on the inner walls of analyzed pipeline (Figure 3).

Figure 4 shows the X-ray diffraction analysis performed on the collected sediment. According to the diffractograms the presence of a large amount of SiO_2 and $FeCO_3$ was found, plus Fe_2O_3 and Fe_3O_4 in a lesser extent. Analysis by scanning electron microscopy showed that the sediments were composed of particles of different sizes with a high Fe content (Figure 5).

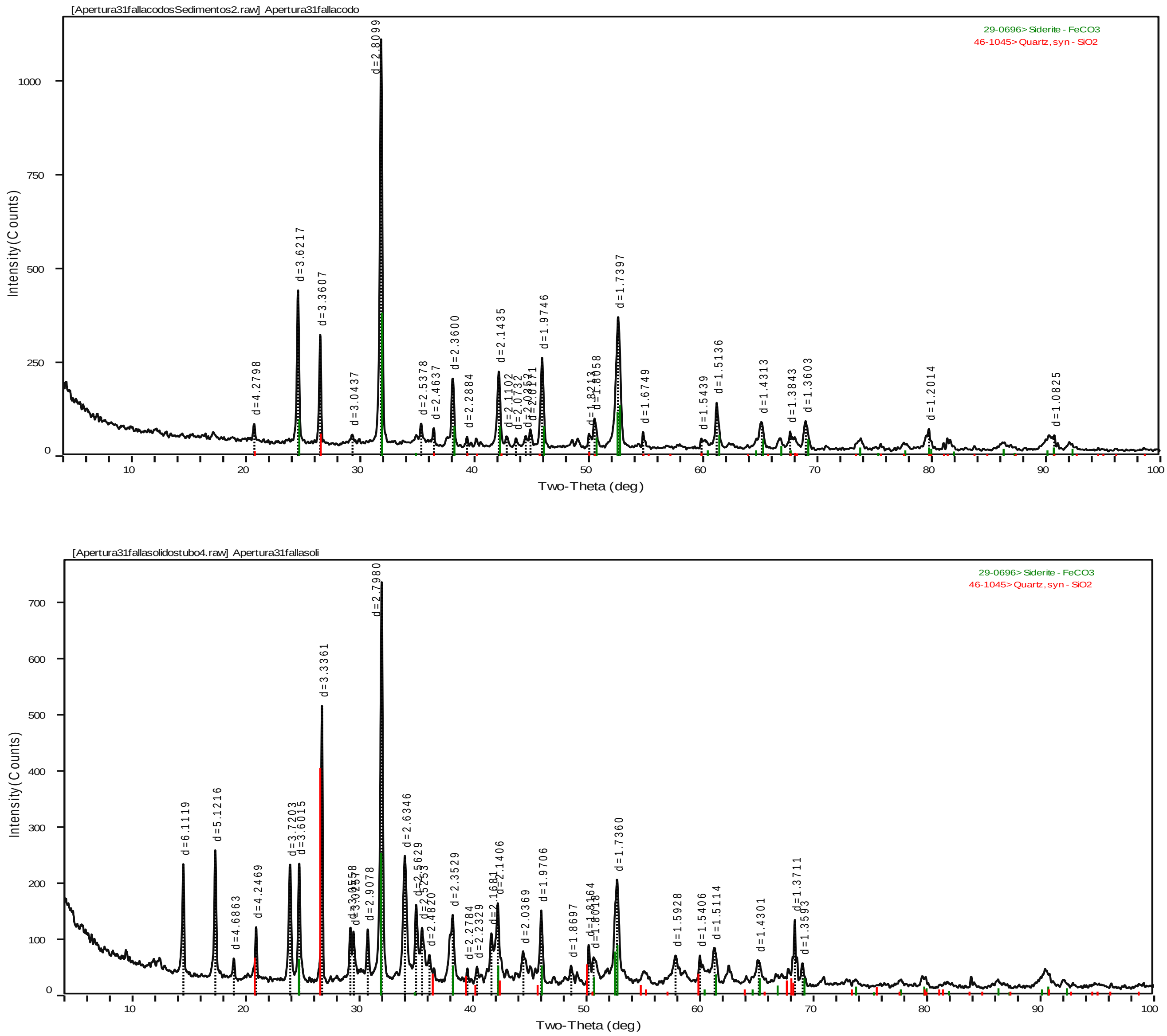

Figure 4. X-ray diffractograms of sediment collected in different areas.

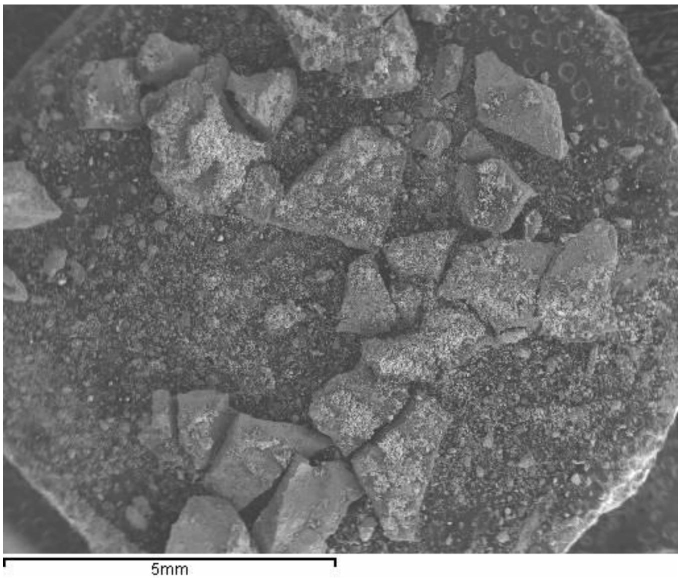

Figure 5. Morphological appearance of the sediment particles.

The microstructural characteristics of the steel pipeline are shown in Figure 6. It is observed that the carbon steel shows a microstructure composed of ferrite and pearlite, with the presence of inclusions primarily of S and Mn.

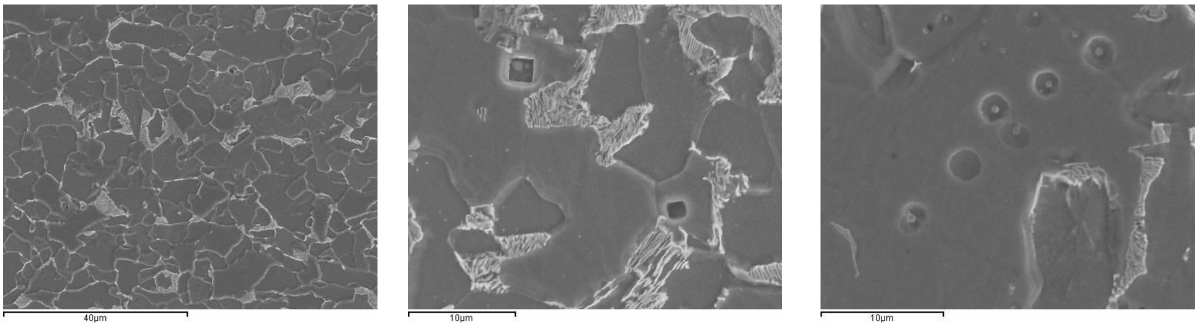

Figure 6. Microstructural characteristics of the steel pipeline.

These results demonstrate that high corrosion rates are due to the poor performance of the added inhibitor. Furthermore, the high concentrations of dissolved CO_2 in the condensed phase caused the observed localized attack. It is known that the corrosion enhanced by CO_2 is one of the main problems of the industry of production and transportation of gas, and the type of damage of the materials can come from uniform corrosion to localized attack. In order to mitigate this type of damage, several studies have been made from different approach: the development of new alloys, the development of new inhibitors and control of flows and temperatures. From the above observations, it was proposed a change of inhibitor, the new inhibitor was a palm oil-based amide which according to our laboratory studies shows a high performance in CO_2-saturated brines.

3.2. Corrosion performance of palm oil based inhibitor

CO_2 corrosion problems have led to the development of different methods of corrosion control, where the use of corrosion inhibitors has proven to be a practical and economic method. Nitrogen-based organic inhibitors, such as imidazolines, amides and its derivatives are typically composed of two main parts, a polar part (electron-rich) that is capable of adhering onto the metallic surface through coordination bonds, and a hydrophobic part which creates a barrier that prevents the active ions in the corrosion reactions to get to the surface that can repel efficiently contaminants of the electrolyte [15-18]. For this reason and in order to control the problem of internal corrosion (≈ 20 mpy) a new palm oil based corrosion inhibitor was synthesized in our laboratories. In particular, this inhibitor was characterized as an amide based on palm oil.

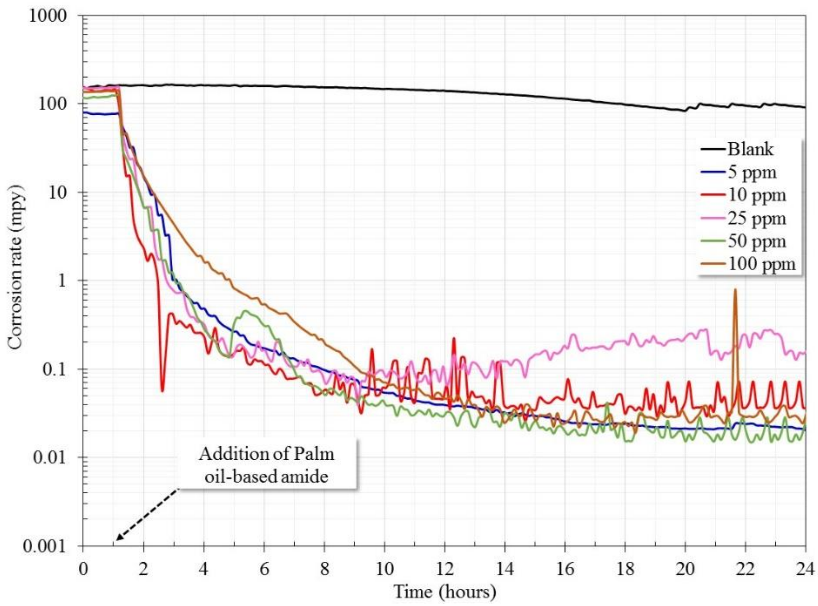

Figure 7. Corrosion rate as determined by LPR measurements for 1018 carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50 °C, with palm oil-based amide.

Figure 7 shows the variations of corrosion rate determined by LPR measurements versus time for carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50 °C, with the palm oil-based amide added at different concentrations. The palm oil-based amide was added after 1.0 h of pre-corrosion of the carbon steel, and the monitoring was carried out for 24 hours. With respect the behavior of carbon steel (without inhibitor added), the corrosion rate increases until 4.0 hours (from 149 mpy to 164 mpy), and then tends to slowly decrease to 91 mpy at the end of the test. The initial increase in corrosion rate can be associated with the early stages of corrosion process, and the subsequent decrease is due to the formation of a passivating layer of iron carbonate. However, the protective layer capacity is compromised by the presence of either pores or cracks through which the electrolyte can reach the metal surface layer [19]. It is known that the CO_2 corrosion is an electrochemical process, which involves the anodic dissolution of iron and the cathodic evolution of hydrogen. Where the hydration of CO_2 to become in H_2CO_3 (carbonic acid) favors the dominant cathodic reactions (reduction of H^+ ions, carbonic acid dissociation, and water reduction), and the anodic reaction (Fe ionization), and at the same time, a corrosion scale of $FeCO_3$ (iron carbonate) is formed onto carbon steel surface [18]. From figure 7, it can be observed that when the palm oil-based amide is added, the corrosion rates fall up to four orders of magnitude until the final of test. The inhibition efficiency is dependent on the concentration of the added inhibitor. However, it can be observed that the corrosion rate falls faster with 10 ppm of inhibitor. This reduction in the corrosion rate is due to the inhibitor film adhered onto the steel surface.

Figure 8 shows the variation in the corrosion inhibition efficiency of the palm oil-based amide versus time (from LPR measurements of Figure 7). The corrosion inhibition efficiencies were calculated from corrosion rate (CR) values (figure 7) based on the following relation:

$$E(\%) = \frac{CR_b - CR_i}{CR_b} * 100$$

where CR_b is the corrosion rate value without inhibitor and CR_i is the corrosion rate value with inhibitor. From the figure, it can be observed that the corrosion inhibition efficiencies are greater than 99% after 5 hours at all concentrations, and with 10 ppm the maximum efficiency is achieved in the shortest time. These results indicate that the palm oil-based amide has a high affinity for the carbon steel surface, since its adsorption rate was relatively fast, being evident the formation of a protective film with excellent barrier properties.

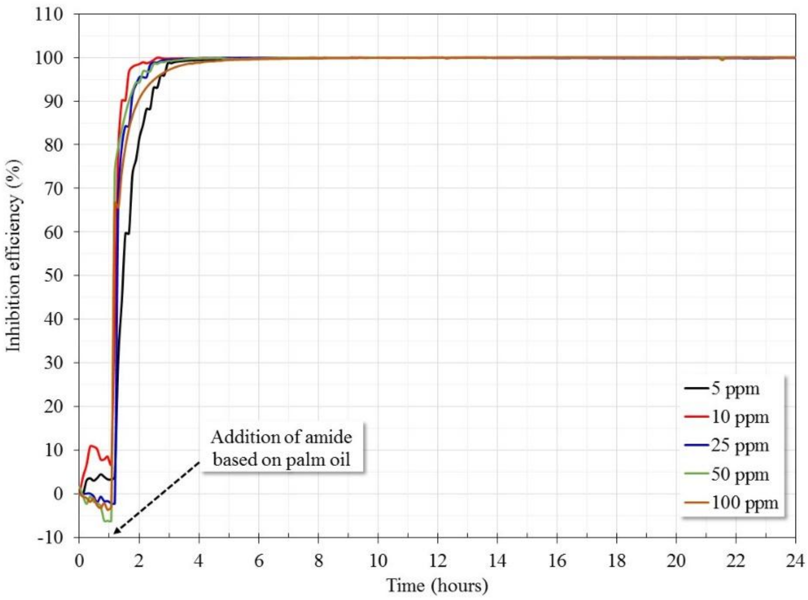

Figure 8. Variations of inhibition efficiency as determined by LPR measurements.

Figure 9 shows the variations of corrosion rate as determined by HDA measurements in time for carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50 °C, with the palm oil-based amide at different concentrations. Notwithstanding the observed disturbances the average data of corrosion rate estimated from HDA measurements are practically the same as those obtained by LPR measurements (figure 5). However the corrosion rates decrease to nearly four orders of magnitude. Again, the inhibition efficiency is dependent on the concentration of the added inhibitor, and the corrosion rate decreases faster with 10 ppm of inhibitor. In this case the disturbances can be interpreted as adsorption-desorption processes of the inhibitor molecules.

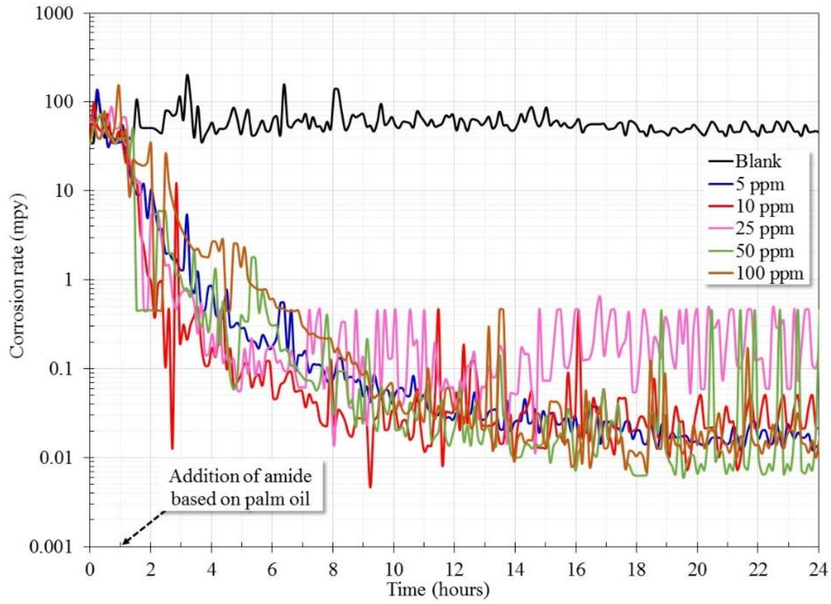

Figure 9. Corrosion rate as determined by HDA measurements for carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50 °C, with palm oil-based amide.

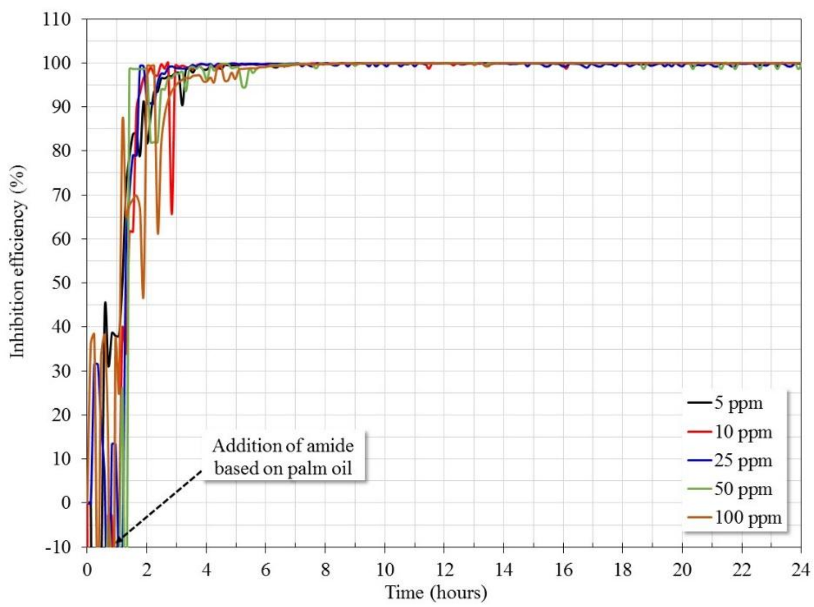

Figure 10. Variations of inhibition efficiency as determined by HDA measurements.

Similarly, in Figure 10 is shown the variation of the efficiency of the palm oil-based amide versus time, from HDA measurements (Figure 9). Efficiency curves show transitories, which can be interpreted as a measure of the adsorption stability of the inhibitor onto the carbon steel surface. The required time to reach an apparent steady state was 5 hours, and from this time the effectiveness of the palm oil-based amide is greater than 99%. Again, the best performance is observed with 10 ppm.

Figure 11 shows the pitting factor variations in time from EN and HDA data for carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50°C, with the different concentrations of palm oil-based amide. The interpretation of the value of pitting factor (PF) is as follow; PF < 0.01, general corrosion; PF from 0.01 to 0.1, general corrosion with presence of pitting attack, and PF > 0.1, represents localized corrosion [8-9]. According to the plot, PF values for carbon steel without inhibitor are lower than 0.01 and show a tendency to decrease in time, and these values indicate a general corrosion mechanism. However, when the inhibitor was added, the PF values showed an abrupt increment to values higher than 0.01. Some authors [20] have found inconsistencies with the PF values, indicating that high PF values and the absence of evidence of localized corrosion is because the HDA measurements are quite noisy, and the corrosion currents are too low. Therefore, special care should be taken when applying this parameter in a corroding system with addition of inhibitors.

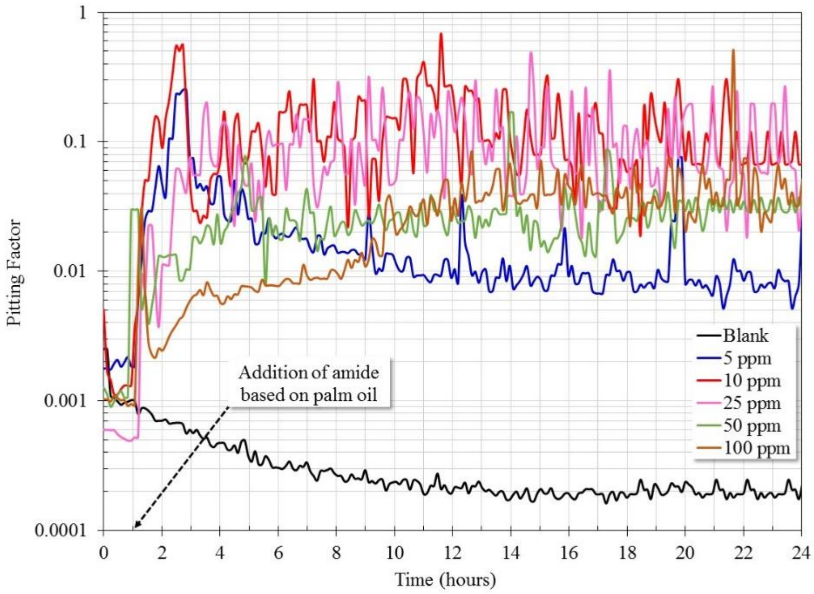

Figure 11. Variations of pitting factor data with time for carbon steel exposed to CO_2-saturated (3% NaCl + diesel) emulsion at 50 °C, with palm oil-based amide.

From previous studies [16], it has been demonstrated that the fatty-amides can be adsorbed on the metal surface by a flat-adsorption process, reducing the presence of active sites and blocking the corrosion process. The amide group resides onto the metallic surface and the alkyl chain stretching out upward into the electrolyte forming a hydrophobic barrier repelling to the aggressive ions from the bulk solution.

Based on this experimental evidence, the palm oil-based amide formulation was adapted for its massive fabrication and a program of corrosion inhibitor injection was conducted.

3.3. Corrosion inhibitor injection program

After verifying the effectiveness of the palm oil-based amide as corrosion inhibitor, a program of inhibitor injection was conducted. Figure 12 shows the injection site of the corrosion inhibitor. The operating conditions of the gas transmission pipeline were; operating pressure of 18.28 kg/cm^2, temperature 28 °C, and a flow rate 150*10^3 m^3/day. Figure 13 shows the altitude of the pipeline above mean sea level (AMSL) from the corrosion inhibitor injection location, to the position where the inhibition efficiency was monitored.

Figure 12. Corrosion inhibitor injection point in the pipeline.

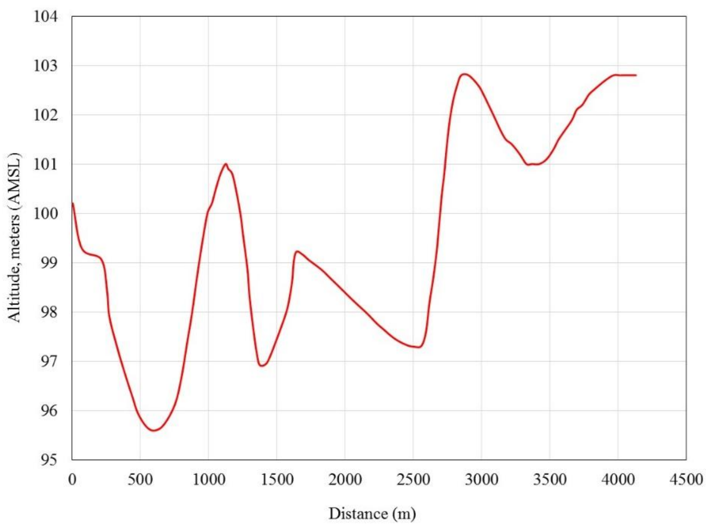

Figure 13. Altitude (AMSL) of the pipeline from the corrosion inhibitor injection location (0 meters) to the position where the inhibition efficiency was monitored (4000 meters).

Figure 14 shows the evolution of the corrosion rate 4000 m upstream of the injection location of the palm oil-based amide inhibitor. The aim of this research project was to reduce the corrosion rate to values lower than 2 mpy. The results indicate that the corrosion rate significantly decreased to values close to 2 mpy after the first two months of injection of the new inhibitor. Subsequently the corrosion rate tended to decrease slowly and the goal was achieved around 4 months of implemented the injection program. A subsequent monitoring indicated that the corrosion rate decreased to values close to 1 mpy after 6 months that the program of inhibitor injection was launched.

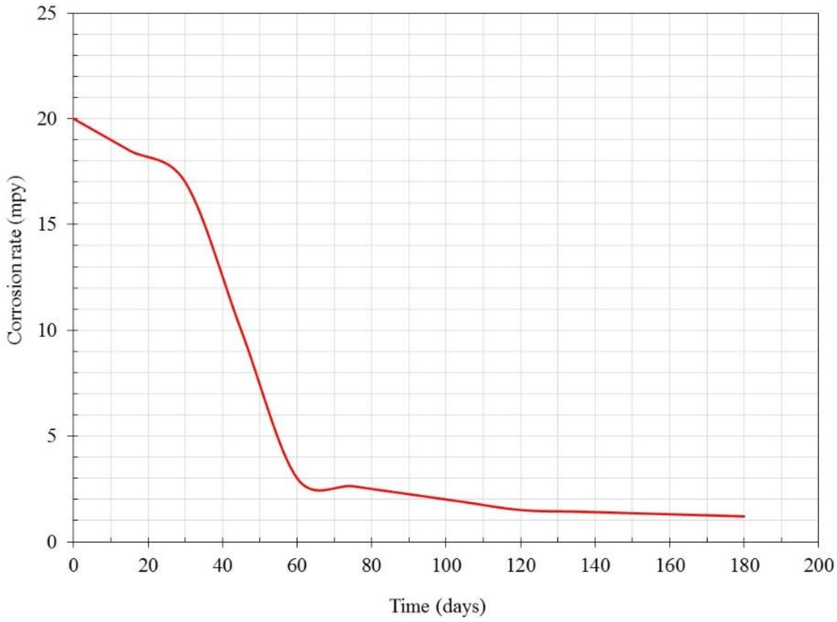

Figure 14. Corrosion rate versus time of the pipeline after the corrosion inhibitor injection.

This study showed that the use of carbon steel for transportation of wet corrosive gas offers potential savings over the more expensive alternatives (use of corrosion resistant alloys or gas drying), but with a higher risk, because the produced fluids may contain significant levels of CO_2 and H_2S, which in combination with free water and dissolved salts make the pipeline environment potentially corrosive. However, establishing a monitoring pipeline integrity program and choosing an inhibitor able to counteract the corrosive effects of water, the risk of pipeline failures can be minimized.

4. CONCLUSIONS

An internal corrosion problem (> 20 mpy) of a connecting pipelines system to the oil wells in the central Gulf of Mexico coastline was analyzed. The pipelines system was analyzed, founding the presence of a condensed phase, which consisted of a mixture of water and hydrocarbons, and a solid residue, in addition to high contents of chloride and dissolved CO_2, which resulted in the presence of localized attack. Due to such results a new palm oil-based amide inhibitor was synthetized and adapted for its massive fabrication. Corrosion tests in laboratory showed that when the palm oil-based amide is added, the corrosion rates decrease up to four orders of magnitude, and the corrosion inhibition efficiency is greater than 99% when 10 ppm of inhibitor is added. This corrosion rate reduction was due to the inhibitor film adhered onto the steel surface. A program of corrosion inhibitor injection was implemented and the new inhibitor was able to reduce the corrosion rate below 2 mpy.

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CONFLICT OF INTEREST
The authors declare that there is no conflict of interests regarding the publication of this article

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